United States
Environmental Protection
Agency

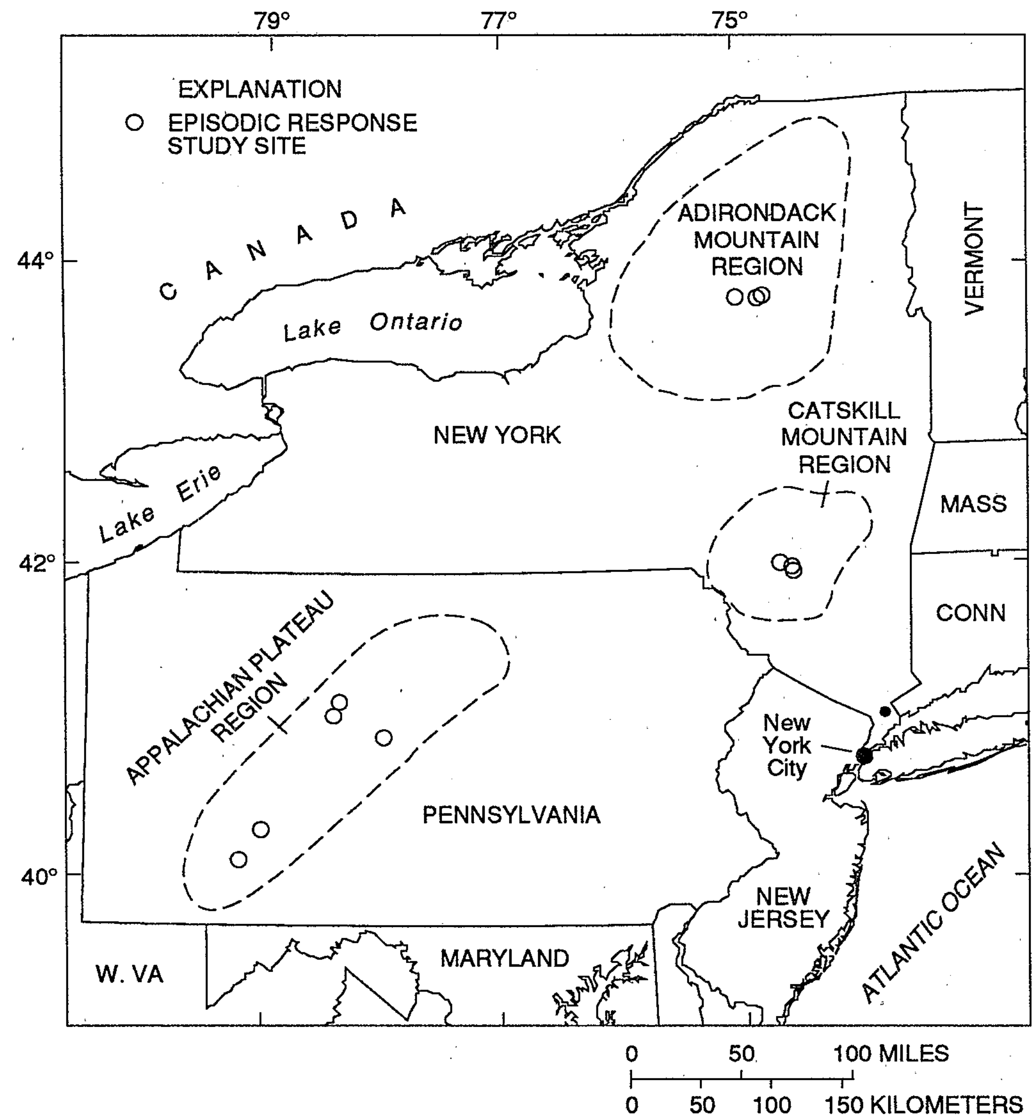
Office of Research and
Development
Washington DC 20460

EPA/600/R-93/190
September 1993

EPA

Episodic Acidification of Streams in the Northeastern United States

Chemical and Biological Results of the Episodic Response Project



ERRATA

Page 92, third paragraph, line 3.

Change "19 to 33 episodes" to "13 to 26 episodes".

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September 1993

EPISODIC ACIDIFICATION OF STREAMS IN THE NORTHEASTERN UNITED STATES: CHEMICAL AND BIOLOGICAL RESULTS OF THE EPISODIC RESPONSE PROJECT

Episodic Response Project Final Report

September 1993

By

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The research described in this report has been funded by the U.S. Environmental Protection Agency. This document has been prepared at the EPA Environmental Research Laboratory in Corvallis, Oregon. It has been subjected to the Agency's peer and administrative review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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TABLE OF CONTENTS

Section **Page**

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENTS

The Episodic Response Project (ERP) was a large, complex project that involved many people over a period of almost six years. We wish to acknowledge and to thank the many people who contributed to the ERP.

Keith Eshleman (formerly with Northrop Services, Inc., and currently with the University of Virginia) led the development of the technical approach for the ERP. His efforts were essential to both the establishment and initiation of the project. He also provided useful comments and insight during the course of the project.

The difficult field and laboratory work for the ERP was accomplished by a large number of graduate students, technicians, and scientists. Although there are too many of these individuals to name, the ERP would not have been possible without them and we are very grateful for their efforts.

Susan Christie (ManTech Environmental Technology, Inc.) served a vital role as technical editor for the report. Her efforts have greatly improved the quality of the document and made production of the draft and final reports possible.

Roger Blair (U.S. EPA) was especially helpful through his support and encouragement during the completion of the ERP report. We appreciate the efforts he made to allow the U.S. EPA authors to continue to work on the completion of the report after the end of project funding.

Charles Gagen (Pennsylvania State University), Barry Baldigo (U.S. Geological Survey), and Dale Bath (Adirondack Lakes Survey Corporation) provided data analysis results and interpretations for inclusion in the report.

As co-principal investigators of the Pennsylvania State University study, Bob Carline (U.S. Fish and Wildlife Service), Bill Sharpe, Brian Dempsey, Ed Corbett (USDA Forest Service), and Jim Lynch made important contributions to ERP research in Pennsylvania.

Other individuals who contributed to various aspects of the ERP include: Ming Hu (ManTech Environmental Technology, Inc.), database management/statistical analyses; Larry Hughes (formerly ManTech Environmental Technology, Inc.), data validation; Rod Slagle (Lockheed

Engineering and Sciences Company), data management/entry design; Gan Satterwhite (Lockheed Engineering and Sciences Company), data verification; Gary Bishop (ManTech Environmental Technology, Inc.), climate data acquisition/GIS; Cindy Burgeson (formerly ManTech Environmental Technology, Inc.), form management; Brenda Huntley (ManTech Environmental Technology, Inc.), graphics; Bill Lanham (Oregon State University), graphics; Carol Roberts (ManTech Environmental Technology, Inc.), word processing; Barb Rosenbaum (ManTech Environmental Technology, Inc.), GIS; and Don Sachs (formerly with Northrop Services, Inc.), modeling.

Dan Heggem's (U.S. EPA) management efforts throughout the project are much appreciated.

Robbins Church (U.S. EPA) made important contributions to the ERP in two ways. He was instrumental in the establishment of episodic acidification research at EPA. He also provided technical review comments on the ERP final report.

Deborah Coffey (ManTech Environmental Technology, Inc.) provided insightful comments on quality assurance throughout the project. She also provided technical review comments on this report.

We are very thankful to Jack Cosby (University of Virginia), Steve Gloss (University of Wyoming), John Gunn (Ontario Ministry of Natural Resources), Gerry Jones (University of Quebec, INRS-Eau), Steve Kahl (University of Maine), Gilles Lacroix (Canadian Department of Fisheries and Oceans), Phil Larsen (U.S. EPA), John Melack (University of California, Santa Barbara), Paul Ringold (U.S. EPA), and John Stoddard (ManTech Environmental Technology, Inc.) for technical review comments on the final report. The insight of all the reviewers has greatly improved the document.

During the course of the ERP, Trevor Davies (University of East Anglia) and Martyn Tranter (University of Bristol) were very helpful by commenting on episodic chemistry data analysis approaches.

Kent Thornton (FTN and Associates, Inc.) and David Marmorek (Environmental and Social Systems Analysts, Ltd.) made important contributions to the ERP through their participation in the development of the ERP research plan. Numerous other scientists contributed to the ERP through their technical reviews of the ERP research plan.

Rick Linthurst (U.S. EPA), Dan McKenzie (U.S. EPA), and Dixon Landers (U.S. EPA), as directors of the Aquatic Effects Research Program, were instrumental in securing funding for the ERP.

Dennis Leaf (U.S. EPA) was flexible and patient while waiting for the completion of the report.

The senior author would like to thank Carol, Chris, and Mandy Wigington for their patience and support during the course of the ERP and the preparation of the final report.

ABBREVIATIONS AND ACRONYMS

AERP — Aquatic Effects Research Program
ANC — acid neutralizing capacity
ASI — acid stress index
cfs — cubic feet per second, unit of streamflow
CMS — continuous monitoring site
DDRP — Direct/Delayed Response Project
DIC — dissolved inorganic carbon
DOC — dissolved organic carbon
DOE — Department of Energy
DQO — data quality objectives
EMSL-LV — U.S. EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada
EPA — Environmental Protection Agency
ERL-C — U.S. EPA Environmental Research Laboratory in Corvallis, Oregon
ERP — Episodic Response Project
ISI — Innovative Sensors, Inc.
LESC — Lockheed Engineering and Sciences Company
LRTAP — Long Range Transboundary Air Pollution (Program)
MAP3S — Multistate Atmospheric Power Production Pollution Study
METI — ManTech Environmental Technology, Inc.
NADP — National Atmospheric Deposition Program
NAPAP — National Acid Precipitation Assessment Program
NOAA — National Oceanic and Atmospheric Administration
NSS — National Stream Survey
NSWS — National Surface Water Survey
NTIS — National Technology Information Service
NYSDEC — New York State Department of Environmental Conservation
OEN — Operational Evaluation Network
PNL — (Batelle's) Pacific Northwest Laboratory
PSU — Pennsylvania State University
QA/QC — quality assurance/quality control
SOP — standard operating procedures
USGS — U.S. Geological Survey
UK — United Kingdom

SYMBOLS

A^-	—	organic anion
AC/DC	—	alternating current/direct current
Al	—	aluminum
Al_{im}	—	inorganic (monomeric) aluminum
Al_{td}	—	total dissolved aluminum
Ca^{2+}	—	calcium ion
C_A	—	sum of strong acid anions
C_B	—	sum of base cations
C_BC_A ANC	—	ANC calculated by $\Sigma C_B - \Sigma C_A$
Cl^-	—	chloride
cm	—	centimeter
D_{ANC}	—	$(\Sigma C_B - \Sigma C_A)$ – Gran ANC
g	—	gram
Gran ANC	—	ANC measured by Gran titration
H^+	—	hydrogen ion
HNO_3	—	nitric acid
ha	—	hectare
K^+	—	potassium ion
km	—	kilometer
m	—	meter
Mg^{2+}	—	magnesium ion
n	—	number
Na^+	—	sodium ion
NH_4^+	—	ammonium ion
NO_3^-	—	nitrate ion
p	—	probability
SO_4^{2-}	—	sulfate ion
VAC	—	volts alternating current
°C	—	degrees Celsius
$<$	—	less than
$\leq$	—	lesser than or equal to
$>$	—	greater than

≥	—	greater than or equal to
μeq/L	—	microequivalents per liter
μg/L	—	micrograms per liter
Σ	—	sum of

GLOSSARY

The following is a list of definitions of selected terms used in the Executive Summary of the report.

Abundance – the number of organisms per unit area or volume.

Acid neutralizing capacity (ANC) – the equivalent capacity of a solution to neutralize strong acids. The components of **ANC** include weak bases (carbonate species, dissociated organic acids, alumino-hydroxides, borates, and silicates) and strong bases (primarily, OH^-). In the ERP, as well as in most other recent studies of acid-base chemistry of surface waters, **ANC** was measured by the Gran titration procedure.

Acidic deposition – transfer of acids and acidifying compounds from the atmosphere to terrestrial and aquatic environments via rain, snow, sleet, hail, cloud droplets, particles, and gas exchange.

Acidic episode – an **episode** in a water body in which **acidification** of surface water to an **ANC** level less than or equal to 0 occurs.

Acidification – the decrease of **ANC** in water or base saturation in soil caused by natural or anthropogenic processes.

ANC depression – the decrease of **ANC** that occurs from the beginning of an **episode** to the minimum **ANC** during the **episode.**

Atmospheric deposition – the transfer of natural and anthropogenic compounds from the atmosphere to terrestrial and aquatic environments via rain, snow, sleet, hail, cloud droplets, particles, and gas exchange.

Automated pumping sampler – a device that collects water samples at predetermined times or stream **stage** levels.

Base cation – an alkali or alkaline earth metal cation (Ca^{2+}, Mg^{2+}, K^+, Na^+).

Base flow – streamflow during periods between **hydrologic events**.

Biomass – the total quantity of organic matter in units of weight or mass.

Chronic acidification – the decrease of **ANC** in a lake or stream on a seasonal or longer time frame.

Data logger – a computerized device that stores data collected by remote sensors or measuring devices.

Dissolved organic carbon (DOC) – organic carbon that is dissolved or unfilterable in a water sample.

Density – the number of individual organisms per unit area. In this report, each study stream was sampled to estimate the average number of brook trout per unit area of stream.

Discharge – the volumetric flow of water. Equivalent to streamflow. Units are volume per unit time.

Electrofishing – capture of fish using an electrical current to stun (but not kill) fish, which are then usually collected using a hand-held net.

Electroshocker – a fish sampling apparatus, which produces an electrical current in water to stun (but not kill) fish. The stunned fish are then usually collected with a hand-held net.

Episodes – a subset of hydrological phenomena known as events. **Episodes,** driven by rainfall or snowmelt, occur when **acidification** takes place during a **hydrologic event.** Changes in other chemical parameters, such as aluminum and calcium, are frequently associated with **episodes.**

Episodic acidification – the short-term decrease of **ANC** from a lake or stream. This process has a time scale of hours to weeks and is usually associated with **hydrological events.**

Gauging station – a stable location on a stream where **stage** and **discharge** are measured. In the ERP, the gauging stations were also the locations of the automated pumping samplers and other instrumentation.

Hydrologic event – an increase in water flow or **discharge** resulting from rainfall or snowmelt.

***In situ* bioassay** – measurement of the response of an organism or group of organisms upon exposure to environmental conditions in place (*in situ*) within the natural setting. In this report, fish were held in small cages in each study stream; we recorded the number (and percentage) of fish dying over time in relation to chemical conditions in the stream, in particular the occurrence and severity of **episodic acidification.**

Inorganic aluminum (Al_{im}) – the sum of free aluminum ions (Al^{3+}) and dissolved aluminum bound to inorganic ligands; operationally defined by labile monomeric aluminum.

Ion – an atom or group of atoms carrying an electric charge.

Major episode – an **episode** with severe episodic chemistry. In this report, the five **episodes** in each stream with the lowest **ANC** levels were identified as the major **episodes.**

Nonreference stream – an ERP study stream that experienced episodic chemistry that was anticipated to have adverse effects on fish. Biological studies in these streams provided data for examining the effects of **episodic acidification** of fish. There were eight **nonreference streams.**

Organic acids (A^-) – acids possessing a carboxyl (–COOH) group or phenolic (C-OH) group; includes fulvic and humic acids.

pH – the negative logarithm of the hydrogen **ion** activity. The **pH** scale runs from 1 (most acidic) to 14 (most alkaline); a difference of one **pH** unit indicates a tenfold change in hydrogen **ion** activity.

Radiotag – a small device that transmits radio signals. Radiotags can be surgically implanted or inserted into a fish's stomach. A remote receiver is used to identify the location of the radiotag and, thus, the location of the fish. Each radiotag is often set at a unique frequency to track the movement of individual fish.

Radiotelemetry – a method for tracking the movement of fish (as well as other animals). A **radiotag,** which transmits radio signals, is surgically implanted or inserted into a fish's stomach. The location of the radiotag (and fish) is determined using a remote receiver set at the appropriate frequency.

Reference stream – an ERP study stream with stream chemistry (relatively stable **pH**, low Al_{im} concentrations) that was anticipated to have little, if any, adverse effects on fish populations. Biological studies in these streams were used as a comparison for biological studies in streams that experienced more severe episodic chemistry (see **nonreference stream**). There were five **reference streams.**

Refugia – areas or zones in aquatic ecosystems in which environmental conditions are relatively nonstressful for biological organisms.

Snowpack – an accumulation of snow from multiple snow storms that lasts for a period of weeks to months.

Snowmelt – the melting of a **snowpack**. The melt may occur in response to warm temperatures or rainfall.

Stage – the height of a stream water surface above a datum (reference point). In the ERP, relationships were developed between stream **stage** and stream discharge. These relationships were used to estimate **discharge** throughout the study.

Sum of base cations (ΣC_B) – refers to the equivalent sum of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}. The term specifically excludes cationic Al^{n+} and Mn^{2+}.

Yearling (fish) – fish between one and two years of age (age 1+).

Young-of-the-year (fish) – fish less than one year old (age 0+).

EXECUTIVE SUMMARY

Episodic acidification is the process by which streams or lakes experience short-term decreases in acid neutralizing capacity (ANC), usually during high streamflow associated with large rainstorms or snowmelt (Figure 1). An episode, then, is any occurrence of a short-term decrease in ANC; in an *acidic* episode, acidification to an ANC level of ≤ 0 μeq/L occurs. If a stream or lake experiences an episode, typically there are accompanying changes in the concentrations of other chemical ions, such as base cations, nitrate (NO_3^-), hydrogen ion (H^+) and inorganic aluminum (Al_{im}). Exposures to low pH and elevated Al can cause significant stress and increased mortality in fish and other aquatic biota.

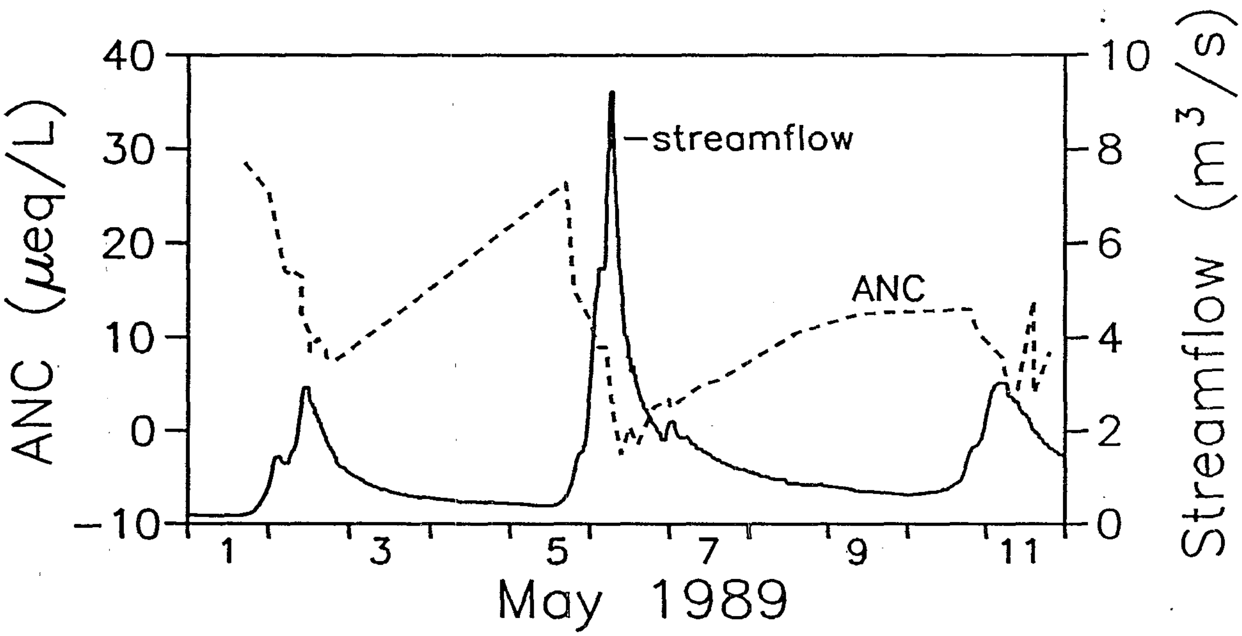

Figure 1. Variation of streamflow and ANC during example episodes in Biscuit Brook, New York.

The Episodic Response Project (ERP) was funded by the U.S. Environmental Protection Agency (EPA) as part of the Aquatic Effects Research Program (AERP), which was established to study the effects of acidic deposition on aquatic ecosystems. Prior to the ERP, EPA research concentrated on chronic acidification, that is, long-term changes in surface water acid-base chemistry and their associated effects on biological communities. The ERP was conducted to address uncertainties about the occurrence, nature, and effects of episodic acidification.

Project Objectives

The objectives of ERP field research were to:

- Determine the magnitude, duration, frequency, and characteristics of episodic chemical changes that accompany hydrological events (rainstorms and snowmelt) in streams.
- Evaluate the effects of episodic acidification on fish populations in streams.
- Define key characteristics of episodes that determine the severity of effects on fish populations.

Episodic acidification occurs in both lakes and streams, but ERP research efforts were conducted only in streams, for three reasons. First, the available evidence suggested that episodes were likely to have more significant impacts on fish populations in streams than in lakes. Episodes in lakes are often accompanied by a high degree of spatial variability that may mitigate the effects on fish and other biota. Second, sampling episodic chemical conditions and biological responses to episodes is much more difficult in lakes than in streams, because of the spatial variability in lakes, as well as the safety problems associated with collecting samples during spring snowmelt on lakes with thin ice covers. Third, episodic responses in streams are more directly linked to watersheds. Therefore, understanding episodic acidification in streams is a necessary precursor to understanding the more complex episodic responses of lakes.

The ERP did not directly address the regional extent of episodic acidification. To aid in decisions regarding acidic deposition controls, we would eventually like to know the number, area, and geographic distribution of waters that experience episodes severe enough to cause significant adverse biological effects. As part of the ERP planning process, however, we decided that (1) not enough information was available to determine what characteristics of episodes were most important in controlling biological effects and, therefore, most important to measure, and (2) regional surveys of episode chemistry, similar to the National Surface Water Survey (NSWS) assessment of chronic acidity, are not logistically feasible because of the transient nature of episodes. For these reasons, the ERP was designed as an intensive study at a relatively small number of selected sites, rather than an extensive regional survey.

A fourth objective of the ERP was to develop and calibrate regional models of episodic chemistry, based on the ERP field data, that link atmospheric deposition to biologically relevant chemistry during episodes. Models provide an alternative to regional surveys for estimating the regional extent of biologically significant episodes. Results from these model development efforts are not included in this report, but will be described in subsequent journal articles.

Study Areas

Episodic acidification is of concern in all regions of the United States susceptible to adverse impacts on aquatic ecosystems because of acidic deposition. The ERP was conducted in three priority areas, the Adirondack Mountains of New York, the Catskill Mountains of New York, and the Northern Appalachian Plateau of Pennsylvania (Figure 2), selected because of the importance of their stream resources, the likely occurrence of acidic episodes, and the high probability that episodes are an important factor affecting the current status of fish populations in these areas.

Four or five study streams were selected in each region based on the following criteria:

- Range of baseflow chemistry, but focusing on streams likely to be adversely affected by episodic acidification, that is, those with ANC between 0 and 100 μeq/L during baseflow.
- Range of expected episode severity, based on existing data or preliminary water chemistry samples collected during site selection.
- Physical suitability for fish survival and reproduction, and similar size and quality fish habitat.
- Indigenous fish populations, of the species of interest, present in at least some part of the stream system at some time of the year.
- At least one reference stream per region, with similar physical and baseflow chemical characteristics as the other streams, but with relatively stable pH during events and no anticipated adverse effects on fish populations in the stream.
- Logistical considerations, because of the intensity of field activities, including ease and availability of access, ease of installing chemical and hydrological monitoring equipment, ease of fish sampling and monitoring, proximity to central research facility or field station, and proximity of sites to each other, to minimize travel times between sites.

The sites selected for the ERP are considered generally representative of other streams in the region with baseflow ANC between 0 and 100 μeq/L. Table 1 summarizes some of the important characteristics of the 13 ERP streams.

Project Organization

The ERP was a cooperative research effort involving scientists from several different institutions and agencies. Field research was conducted by three regional cooperators:

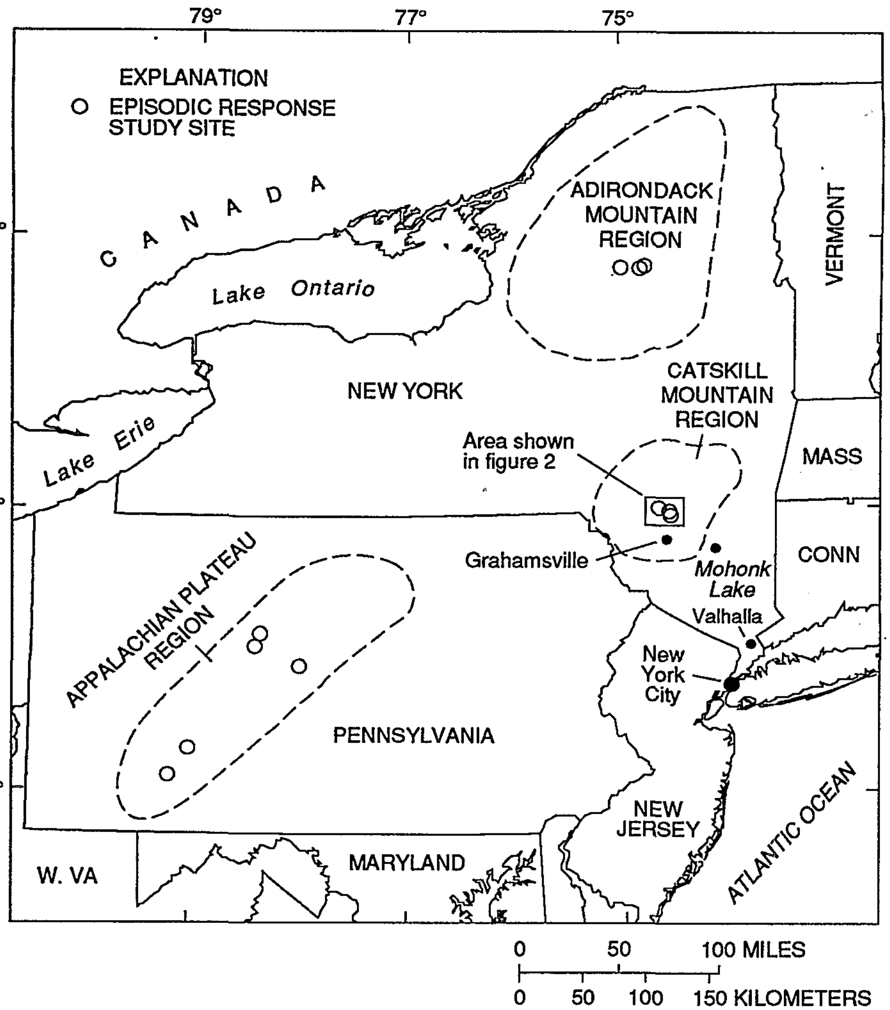

Figure 2. Location of the three Episodic Response Project regions and individual study streams (circles) (adapted from Ranalli et al., 1993).

1. The Adirondack Lakes Survey Corporation (Walter A. Kretser and Howard A. Simonin, principal investigators) in the Adirondack Mountains of New York.

2. The U.S. Geological Survey (Peter S. Murdoch, principal investigator) in the Catskill Mountains of New York.

3. The Environmental Resources Research Institute at Pennsylvania State University (David R. DeWalle, principal investigator) in the Northern Appalachian Plateau of Pennsylvania.

The U.S. EPA Environmental Research Laboratory in Corvallis, Oregon (ERL-C), served as the project lead. The U.S. EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV), developed and guided the ERP quality assurance/quality control (QA/QC) program. EMSL-LV also developed the field-based data management system. ERL-C performed central database management functions. The Pacific Northwest Laboratory designed and coordinated deposition monitoring for the project, working in cooperation with the U.S. EPA Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina.

Table 1. Characteristics of Episodic Response Project Study Streams

Region/Stream	Stream Order	Watershed Area (km^2)	Vegetation	Lake/Pond Present	Wetland Present
Adirondacks					
Bald Mountain Brook	1	1.8	Maple, birch, beech, some conifers	No	Yes
Buck Creek	2	3.1		No	Yes
Fly Pond Outlet	1	0.9		Yes	Yes
Seventh Lake Inlet	2	6.4		Yes	Yes
Catskills					
Biscuit Brook	2	9.8	Maple, birch, beech	No	No
Black Brook	1	3.7		No	No
East Branch Neversink River	3	23.1		No	No
High Falls Brook	2	7.1		No	No
Pennsylvania					
Baldwin Creek	2	5.3	Oak, mixed hardwoods	No	No
Benner Run	2	11.3		No	No
Linn Run	2	10.0		No	No
Roberts Run	2	10.7		No	Yes
Stone Run	2	11.6		No	No

Methods

Each stream was monitored intensively from fall 1988 through spring 1990. A *gauging station* was located on each of the study streams where discharge was measured continuously, using either a pressure transducer connected to a data logger or strip chart, or a water level recorder. An important part of the ERP field effort was to thoroughly characterize rapidly changing chemistry during episodes. For this reason, and the fact that it is very difficult to predict when episodes will occur, automated pumping samplers, located at the discharge gauging stations, were used to collect water samples for chemical analysis during hydrological events. Automated samplers were programmed to collect water samples at fixed time intervals (2-6 hours) or at specified changes of stage levels (i.e., increase or decrease in streamflow discharge). Field crews also collected water samples manually on a weekly basis, as well as, to the degree possible, during episodes when problems occurred with the automated samplers.

Water samples were analyzed for ANC, pH, total dissolved aluminum (Al_{td}), dissolved organic carbon (DOC), sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), calcium, magnesium, potassium, and sodium. In addition, a subset of samples were analyzed for inorganic aluminum (Al_{im}), the fraction of aluminum considered most toxic to fish. Regional cooperators analyzed samples in their own laboratories. Standard procedures and rigorous QA/QC measures were employed for field sampling and chemical analyses to produce high-quality data that were comparable among the three regions.

Assessments of the biological effects of episodes in the study streams involved three major activities:

1. *In situ* bioassays to quantify the toxic effects of episodic acidification on fish.
2. Radiotelemetry and fish traps to track fish movements during episodes and thus determine whether fish can behaviorally avoid exposure to toxic chemical conditions during episodes by moving into areas with higher pH and lower Al_{im} concentrations.
3. Surveys of fish community composition and the density and biomass of brook trout to evaluate fish population status.

In situ bioassays and radiotelemetry studies were conducted each fall and spring (fall 1988, spring 1989, fall 1989, spring 1990). Test periods were selected to coincide with the expected timing of spring snowmelt and fall rainstorms. Experiments in the spring were often delayed, however, by the difficulties caused by high flows and/or ice cover on the streams. Brook trout (*Salvelinus fontinalis*) was selected as the ERP target fish species. Brook trout is the sportfish most widely distributed in the small headwater streams in the Adirondacks, Catskills, and Pennsylvania that are most susceptible to episodic as well as chronic acidification. All 13 of the ERP streams supported at least some brook trout. Bioassays involved young-of-the-year and yearling brook trout; adult trout were used for radiotelemetry tracking of fish movements. *In situ* bioassays were also conducted with at least one forage fish species, in addition to brook trout, in each stream. The forage species varied among regions and streams because of differences in native fish fauna. Blacknose dace (*Rhinichthys atratulus*), a highly acid-sensitive fish species, was used for bioassays in the Adirondacks; slimy sculpin (*Cottus cognatus*) were used in the Catskills; and either slimy sculpin or mottled sculpin (*Cottus bairdi*) were used in Pennsylvania, depending on the stream. All fish used in bioassays and radiotelemetry studies were wild strains, collected by electrofishing from local streams with similar habitats.

Fish communities were surveyed 4-8 times in each stream, using a backpack electroshocker, to quantify the density and biomass of brook trout and occurrence of other fish species. Some streams had distinctly lower fish biomass than others. To ensure that differences among streams were not related to problems with fish access (e.g., natural fish barriers), additional brook trout and forage fish (blacknose dace or sculpin) were transplanted into each study reach to achieve an initial, comparable level of fish density per stream.

Characteristics of Episodes

Episodes were common occurrences in all three regions. We recorded from 19 to 33 episodes in each of the study streams (Figures 3–5). Episode durations ranged from less than 1 day to more than 10 days. Acidic episodes occurred in at least some of the streams in all regions and were common when ANC values were $\leq$ 50 μeq/L immediately before the episode. When acidic episodes occurred, they were accompanied by depressed pH levels and elevated Al_{im} concentrations. The study streams were divided into six ranked classes of chemical severity, based on ANC, pH, and Al_{im} behavior during episodes and low-flow periods.

1. The East Branch of the Neversink River was chronically acidic (median ANC $\leq$ 0) and had strong episodic ANC and pH depressions. It had the longest sustained durations of severe chemical conditions (low pH and ANC and high Al_{im}) among the ERP streams.

2. Stone Run and Roberts Run were also chronically acidic, but pH and Al_{im} levels were not as extreme as in the East Branch of the Neversink River. These streams experienced severe episodes with low pH and high Al_{im}. During summer low-flow periods, ANC levels were positive.

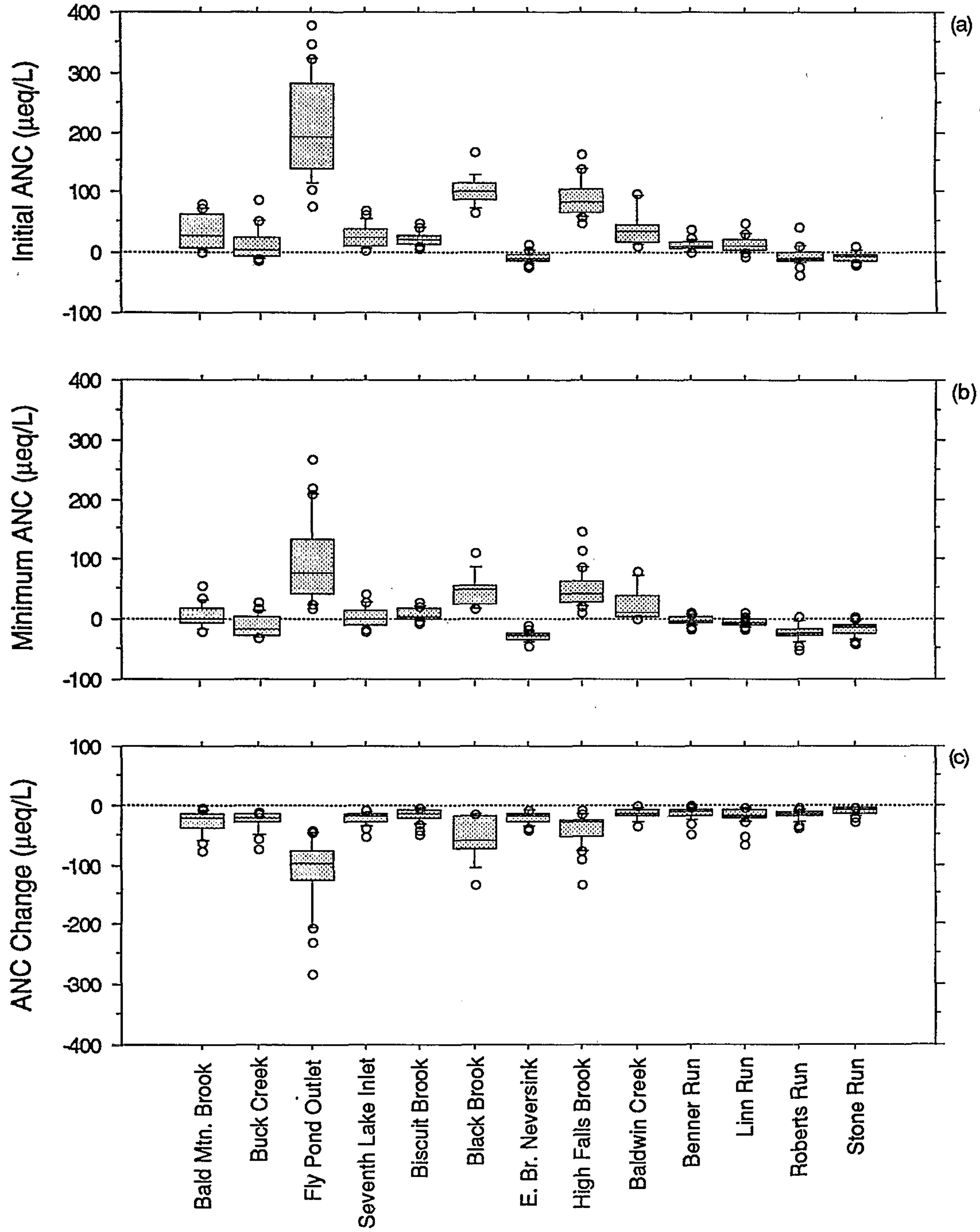

Figure 3. Box plots of (a) initial ANC, (b) minimum ANC, and (c) ANC change, for episodes in ERP streams. Line in box indicates median; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.

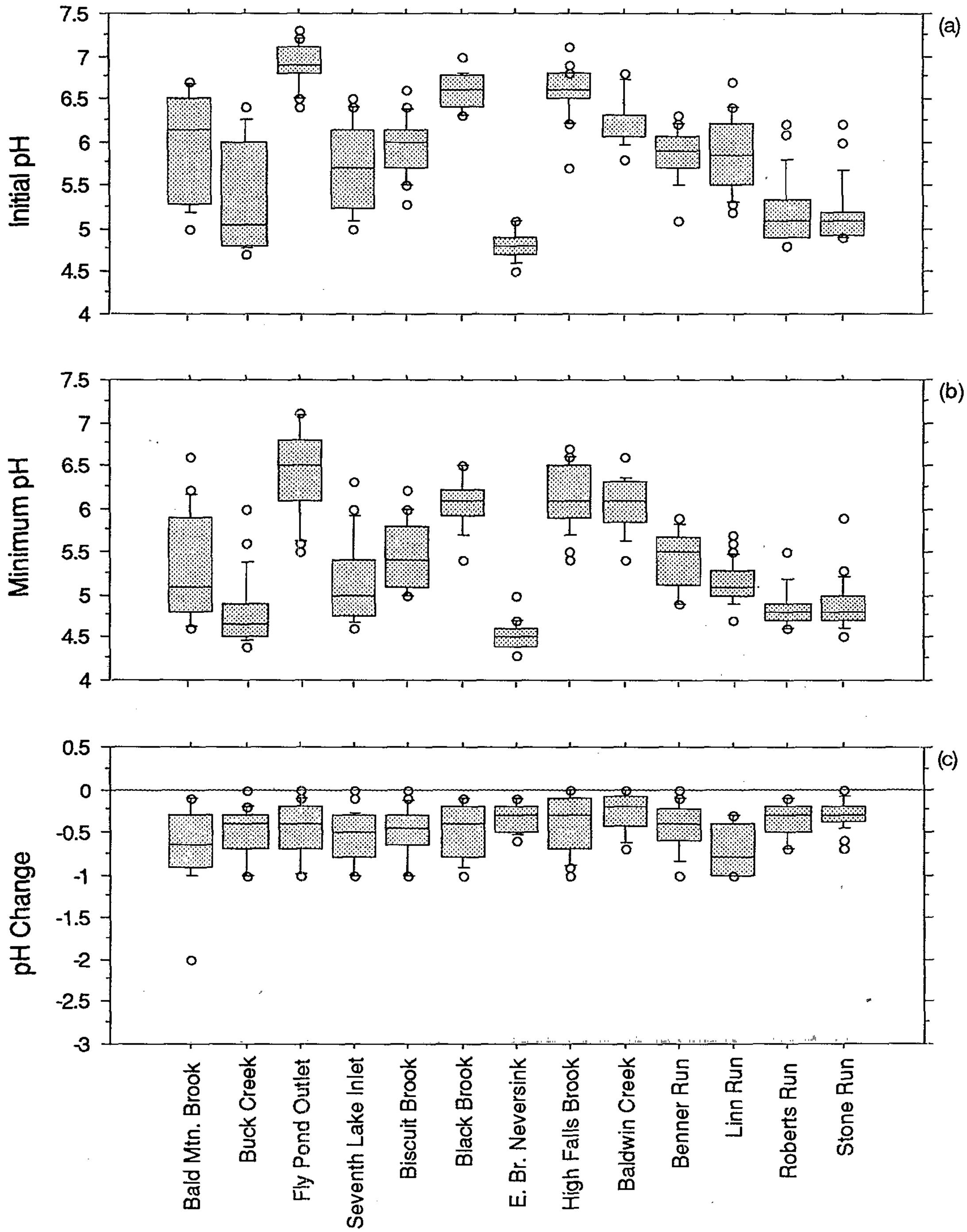

Figure 4. **Box plots of (a) initial pH, (b) minimum pH, and (c) pH change, for episodes in ERP streams. Line in box indicates median; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.**

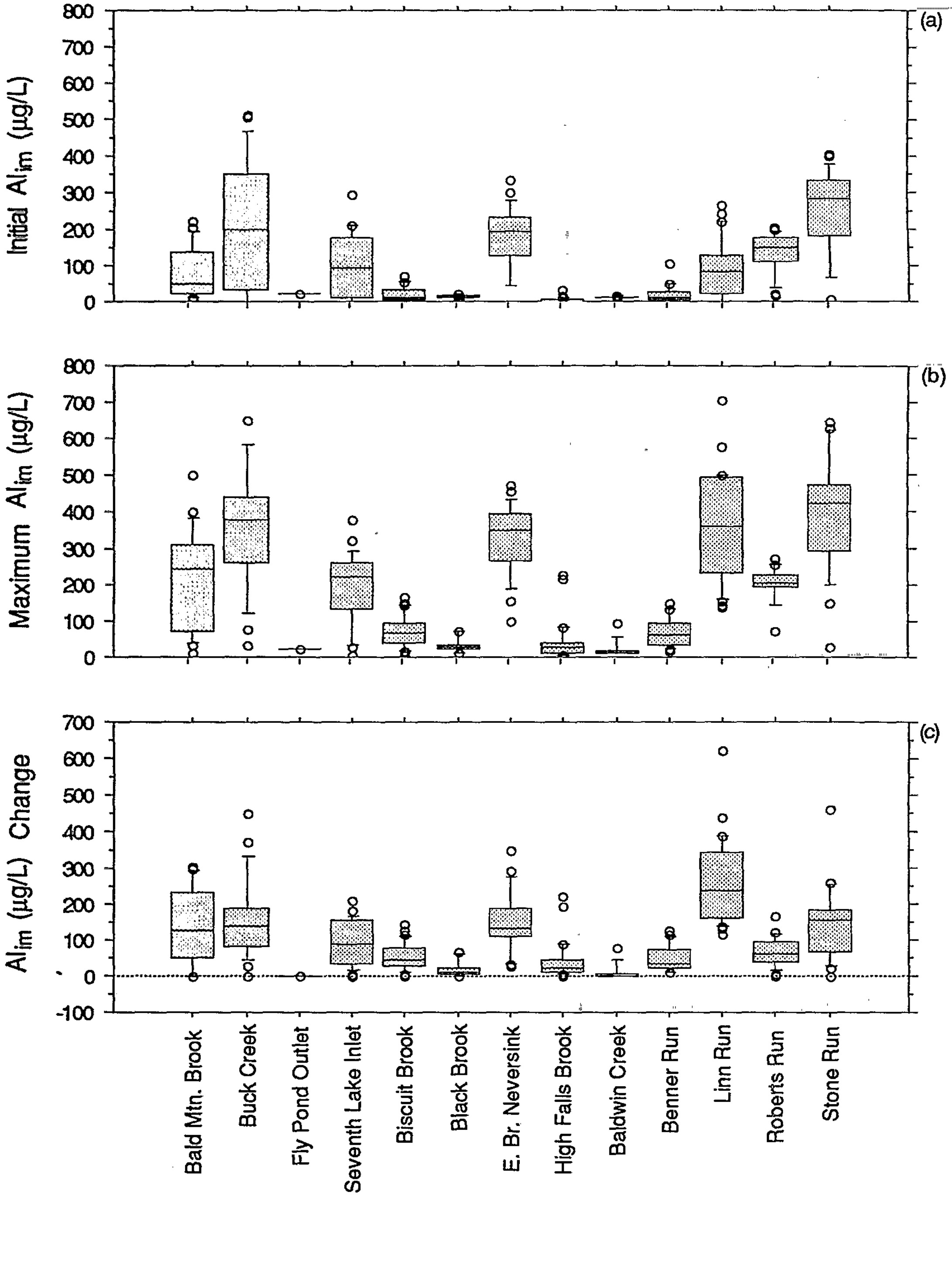

Figure 5. **Box plots of (a) initial estimated Al_{im}, (b) maximum estimated Al_{im}, and (c) estimated Al_{im} change, for episodes in ERP streams. Line in box indicates median; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.**

3. Buck Creek and Linn Run were not chronically acidic but had severe acidic episodes with low pH and ANC and high Al_{im} for long durations.

4. Bald Mountain Brook and Seventh Lake Inlet had episodes of moderate severity (low pH and ANC, but moderate Al_{im} levels) and duration.

5. Biscuit Brook and Benner Run experienced acidic episodes but they were of short duration with moderate pH levels and relatively low Al_{im} concentrations.

6. Fly Pond Outlet, Black Brook, High Falls Brook, and Baldwin Creek were classified as nonacidic (with ANC always > 0, except for one brief excursion below 0 in Baldwin Creek) and had relatively high pH and low Al_{im} throughout the study period.

The ERP was designed to examine the chemical and biological responses of streams to episodic acidification. The study ideally would have been conducted during a period when snowmelt and rainstorms generated hydrologic events with normal or above normal flows. In practice, the hydrologic conditions during the study varied from region to region. In the Adirondacks, winter conditions allowed significant snowpacks to develop during both winters of the ERP. In each case, snowpacks > 50 cm developed, with meltwaters contributing to episodes during late winter and early spring periods. Spring and fall rainstorms also generated hydrologic events. In the Catskills, below normal snowpacks developed during both winters. Most of the episodes were generated by rainstorms. A similar situation developed in Pennsylvania. No significant snowpacks accumulated in either of the winters during the ERP. Because of the small snowpacks in Pennsylvania and the Catskills, episodic conditions in these regions may not have been as severe during the ERP as during years with normal snowpack accumulations. However, large rainstorms during the spring and late winter did produce high streamflows and major episodes.

Ionic Controls on ANC Depressions

Episodic ANC depressions result from complex interactions of multiple ions that are controlled by natural processes and acidic deposition. The importance of major ions in determining the minimum ANC during episodes varies among regions and among streams (Table 2). In the Adirondacks, base cation decreases and organic acid (A^-) increases most consistently contributed to ANC depressions during episodes. Nitrate increases were also very important contributors to episodes in Adirondack streams. In the Catskills, base cation decreases, NO_3^- increases, and A^- increases were all consistently important contributors to episodic ANC depressions. For most of the Catskill streams, base cation decreases were the highest ranked contributors, NO_3^- increases were the second most important contributor, and A^- increases were the third most important ion changes. In the Pennsylvania streams, SO_4^{2-} increases and base cation decreases frequently

Table 2. Number of Episodes for Which Ion Changes Contributed to ANC Depressions and Mean Rank of Ion Change Contributions (1 = most important) to ANC Depressions

Region/Stream	No. Episodes[a]	No. Episodes Ion Changes Contributed to ANC Depressions						Mean Rank of Importance[b] of Ion Changes to ANC Depressions					
		SO_4^{2-}	NO_3^-	Cl^-	A^-[c]	ΣC_B[d]	Al	SO_4^{2-}	NO_3^-	Cl^-	A^-[c]	ΣC_B[d]	Al[e]
Adirondacks													
Bald Mountain Brook	14	10	5	9	12	14	0	2.6	2.4	3.9	2.2	1.4	–
Buck Creek	18	10	15	12	17	17	1	3.1	2.4	4.3	1.9	1.8	3.0
Fly Pond Outlet	21	18	11	8	14	21	4	2.3	2.8	3.6	2.8	1.0	4.0
Seventh Lake Inlet	18	9	13	8	16	17	0	2.3	2.3	3.9	1.8	2.0	–
Catskills													
Biscuit Brook	23	1	20	5	21	18	0	3.0	1.5	3.4	2.3	1.7	–
Black Brook	11	4	9	4	9	11	0	3.2	2.2	3.5	2.6	1.1	–
East Br. Neversink River	20	7	20	9	19	15	0	3.4	2.2	3.4	1.9	1.8	–
High Falls Brook	25	5	13	7	22	23	2	2.0	1.9	3.4	2.4	1.2	3.5
Pennsylvania													
Baldwin Creek	13	8	7	6	5	7	3	1.1	2.4	3.0	2.6	1.3	2.3
Benner Run	21	19	4	3	13	10	2	1.1	3.0	2.0	2.3	1.9	3.0
Linn Run	25	15	12	7	17	24	1	2.3	3.2	3.0	2.8	1.1	2.0
Roberts Run	24	10	10	7	20	21	3	2.1	2.8	3.1	2.2	1.1	3.0
Stone Run	23	20	11	11	19	11	2	1.5	3.3	3.4	2.6	1.5	3.5

[a] With enough ion measurements to perform analysis.

[b] Mean rank for episodes in which ion changes made contributions to ANC depressions.

[c] A^- = organic acids.

[d] ΣC_B = sum of base cations.

[e] – = no episodes measured in which Al ion changes contributed to ANC depressions.

made strong contributions to episodic ANC depressions. Organic acids, on average, were the third most important contributor to ANC depressions in all Pennsylvania streams. Nitrate and Cl^- increases made minor contributions to ANC depressions in the Pennsylvania streams.

From a biological perspective, the greatest concern is about major episodes—those that generate low pH and ANC and high Al_{im} for relatively long periods of time (days to weeks). Ion behavior that controlled ANC depressions during major episodes recorded in each stream was not necessarily the same as the ion changes most important to smaller, more frequent episodes. In the Adirondacks, the only region to have major snowpacks, the most severe episodes generally occurred during spring snowmelt. Nitrate was a more important contributor to ANC depressions during the major snowmelt episodes than during the other episodes recorded. During major Adirondack episodes, base cation decreases were usually the most important contributors to ANC depressions, and A^- and NO_3^- changes contributed to episodes and had similar ranks (2 or 3) of importance to ANC depressions (Table 3). One Adirondack stream experienced a major snowmelt episode in which an increase in NO_3^- was the most important ion change. Three of the four Catskill streams experienced one episode influenced by snowmelt in which NO_3^- pulses were the first ranked contributor and base cation decreases were the second ranked ion change (Table 4).

Within regions, the major episodes generated by rainstorms had more variable ionic controls than did snowmelt episodes. The large rain-induced Adirondack episodes occurred in the spring and fall (Table 3). In these episodes, increases in A^- and decreases in base cations were the most important ion changes to ANC depressions. In major rain-driven spring episodes in the Catskills, decreases in base cations or increases in NO_3^- were typically the first or second ranked ion changes contributing to ANC depressions (Table 4). For the major episodes in Pennsylvania, base cation decreases and SO_4^{2-} increases were usually the most important or second most important ion changes contributing to ANC depressions (Table 5). Two Pennsylvania streams experienced major rain-induced episodes in which A^- increases were the most important ion changes. Nitrate pulses were the second ranked ion change in two major episodes in another Pennsylvania stream.

Acidic deposition, as evidenced by stream water SO_4^{2-} and NO_3^- during episodes, contributed significantly to the occurrence of acidic episodes with low pH and high Al levels in all three study areas. Although base cation decreases were frequently the most important ion change that occurred during episodes, base cation decreases alone cannot create acidic stream water condi-

Table 3. Rank (1 = most important) of Ion Changes Contributing to ANC Depressions During Episodes with Lowest Minimum ANC Values in Adirondack Streams

Stream	Start Date[a]	Hydrologic Stimulus[b]	ANC Minimum (μeq/L)	Rank of Ion Changes Contributing to Episodic ANC Depressions			
				1[c]	2[c]	3[c]	4[d]
Bald Mountain Brook	3/12/90	Snowmelt	-21	ΣC_B	NO_3^-	A^-	—
	3/27/89	Snowmelt	-20	ΣC_B	A^-	$NO3^-$	Cl^-
	5/16/90	Rain	-13	ΣC_B	A^-	—	—
	9/20/89	Rain	-13	ΣC_B	SO_4^{2-}	A^-	—
	11/16/89	Rain	-6	ΣC_B	A^-	Cl^-	—
Buck Creek	11/16/89	Rain	-30	A^-	NO_3^-	ΣC_B	Cl^-
	3/12/90	Snowmelt	-29	NO_3^-	ΣC_B	A^-	—
	4/1/90	Snowmelt	-28	ΣC_B	A^-	NO_3^-	Cl^-
	5/16/90	Rain	-26	A^-	ΣC_B	NO_3^-	—
	4/3/89	Snowmelt	-25	ΣC_B	A^-	Al	Cl^-
Fly Pond Outlet	3/27/89	Snowmelt	17	ΣC_B	NO_3^-	A^-	—
	3/12/90	Snowmelt	19	ΣC_B	A^-	NO_3^-	—
	4/10/90	Snowmelt	25	ΣC_B	A^-	SO_4^{2-}	—
	4/4/89	Snowmelt	31	ΣC_B	SO_4^{2-}	NO_3^-/A^-	
	4/3/90	Snowmelt	39	ΣC_B	SO_4^{2-}	NO_3^-/A^-	
Seventh Lake Inlet	3/12/90	Snowmelt	-20	ΣC_B	NO_3^-	A^-	—
	3/27/89	Snowmelt	-18	ΣC_B	A^-	NO_3^-	—
	11/16/89	Rain	-9	A^-	NO_3^-	ΣC_B	—
	5/16/90	Rain	-9	A^-	ΣC_B	NO_3^-	—
	5/6/89	Rain	-8	A^-	ΣC_B	NO_3^-	Cl^-

[a] Episodes with incomplete ion chemistry not included in analysis.

[b] Snowmelt includes rain-on-snow events.

[c] ΣC_B = sum of base cations; A^- = organic acids.

[d] — = no ion change that contributed to ANC depression.

Table 4. Rank (1 = most important) of Ion Changes Contributing to ANC Depressions During Episodes with Lowest Minimum ANC Values in Catskill Streams

Stream	Start Date[a]	Hydrologic Stimulus[b]	ANC Minimum (μeq/L)	Rank of Ion Changes Contributing to Episodic ANC Depressions			
				1[c]	2[c]	3[c]	4[d]
Biscuit Brook	4/10/90	Rain	-6	NO_3^-	ΣC_B	A^-	—
	5/5/89	Rain	-2	ΣC_B	NO_3^-	A^-	—
	1/25/90	Snowmelt	-2	NO_3^-	A^-	ΣC_B	—
	9/19/89	Rain	-2	A^-	NO_3^-	ΣC_B	—
	3/12/90	Rain	-2	NO_3^-	A^-	—	—
Black Brook	10/17/89	Rain	17	ΣC_B	NO_3^-	A^-	—
	5/5/89	Rain	18	ΣC_B	NO_3^-	A^-	—
	4/10/90	Rain	25	ΣC_B	NO_3^-	A^-	—
	9/18/89	Rain	36	ΣC_B	A^-	NO_3^-	—
	11/16/89	Rain	36	ΣC_B	NO_3^-	A^-	—
East Branch Neversink River	10/18/89	Rain	-45	A^-	ΣC_B	NO_3^-	—
	9/19/89	Rain	-39	A^-	ΣC_B	SO_4^{2-}	NO_3^-
	4/10/90	Rain	-37	NO_3^-	ΣC_B	A^-	—
	1/25/90	Snowmelt	-34	NO_3^-	A^-	ΣC_B	—
	10/31/89	Rain	-32	A^-	ΣC_B	NO_3^-	SO_4^{2-}
High Falls Brook	5/5/89	Rain	12	ΣC_B	NO_3^-	A^-	—
	10/19/89	Rain	21	ΣC_B	NO_3^-	A^-	—
	1/25/90	Snowmelt	25	NO_3^-	ΣC_B	A^-	—
	2/22/90	Rain	27	ΣC_B	NO_3^-	A^-	—
	4/10/90	Rain	28	ΣC_B	NO_3^-	A^-	—

[a] Episodes with incomplete ion chemistry not included in analysis.
[b] Snowmelt includes rain-on-snow events.
[c] ΣC_B = sum of base cations; A^- = organic acids.
[d] — = no ion change that contributed to ANC depression.

Table 5. Rank (1 = most important) of Ion Changes Contributing to ANC Depressions During Episodes with Lowest Minimum ANC Values in Pennsylvania Streams

Stream	Start Date[a]	Hydrologic Stimulus	ANC Minimum (μeq/L)	Rank of Ion Changes Contributing to Episodic ANC Depressions			
				1[b]	2[b]	3[b]	4[c]
Baldwin Creek	3/30/89	Rain	-1	ΣC_B	Cl^-	—	—
	5/6/89	Rain	4	ΣC_B	NO_3^-	Cl^-	—
	6/20/89	Rain	4	A^-	NO_3^-	Cl^-	—
	3/24/89	Rain	5	SO_4^{2-}	Al	Cl^-	—
	2/15/89	Rain	6	ΣC_B	SO_4^{2-}	—	—
Benner Run	11/16/89	Rain	-15	SO_4^{2-}	A^-	—	—
	5/14/89	Rain	-10	SO_4^{2-}	A^-	—	—
	5/9/89	Rain	-9	SO_4^{2-}	ΣC_B	A^-	—
	2/2/90	Rain	-6	ΣC_B	SO_4^{2-}	—	—
	2/15/90	Rain	-5	SO_4^{2-}	A^-	ΣC_B	—
Linn Run	3/4/89	Rain	-17	ΣC_B	NO_3^-	SO_4^{2-}	A^-
	4/17/89	Rain	-15	ΣC_B	—	—	—
	11/16/89	Rain	-13	ΣC_B	NO_3^-	A^-	Cl^-
	2/14/89	Rain	-11	ΣC_B	SO_4^{2-}	NO_3^-	—
	4/1/90	Rain	-10	SO_4^{2-}	ΣC_B	A^-	NO_3^-
Roberts Run	6/20/89	Rain	-52	ΣC_B	A^-	—	—
	6/3/89	Rain	-45	ΣC_B	SO_4^{2-}	A^-	Cl^-
	6/25/89	Rain	-39	ΣC_B	A^-	NO_3^-	—
	2/2/90	Rain	-33	ΣC_B	A^-	Al	—
	3/29/89	Rain	-28	ΣC_B	A^-	—	—
Stone Run	6/3/89	Rain	-41	SO_4^{2-}	ΣC_B	A^-	—
	1/16/90	Rain	-38	SO_4^{2-}	ΣC_B	A^-	—
	2/2/90	Rain	-33	A^-	SO_4^{2-}	—	—
	2/15/90	Rain	-31	SO_4^{2-}	ΣC_B	NO_3^-	—
	4/10/90	Rain	-25	ΣC_B	SO_4^{2-}	—	—

[a] Episodes with incomplete ion chemistry not included in analysis.
[b] ΣC_B = sum of base cations; A^- = organic acids.
[c] — = no ion change that contributed to ANC depression.

tions during episodes. Organic acid pulses, a natural source of acidity, also were important contributors to ANC depressions in Adirondack streams and, to a lesser extent, in the Catskill and Pennsylvania streams. However, SO_4^{2-} or NO_3^- pulses during episodes in study streams from all three regions augmented the base cation decreases and organic pulses to create episodes with lower pH and ANC and higher Al concentrations than would have occurred from natural processes alone. In addition, large baseline concentrations of SO_4^{2-} and NO_3^- reduced episodic minimum ANC, even when these ions did not change during episodes (Figure 6).

We examined episodic acidification in 13 streams that were specifically selected for the ERP. It is not possible to make direct regional estimates of episodic acidification from these data. However, the results should be reasonably representative of episodic acidification responses and processes in similar streams in the Catskills, the Adirondacks, and the Northern Appalachian Plateau of Pennsylvania.

Effects on Episodic Acidification on Fish Populations in Streams

Results from the ERP clearly demonstrate that episodic acidification can have long-term adverse effects on fish populations. Streams that experienced episodic acidification had significantly ($p < 0.05$) lower levels of brook trout density and biomass than nonacidic streams. Differences in trout abundance between episodically and chronically acidic streams were not statistically significant ($p > 0.05$). Brook trout density and biomass were also significantly ($p < 0.001$) correlated with the qualitative rankings of stream chemical severity ($r = 0.83$ for brook trout density and 0.92 for biomass; Figure 7). With one exception, acid-sensitive fish populations occurred only in ERP streams with median weekly pH > 6.0 (Black Brook, High Falls Brook, Biscuit Brook, Benner Run, Baldwin Run) and were absent from streams that were chronically acidic or that experienced moderate to severe episodic acidification (Bald Mountain Brook, Seventh Lake Inlet, East Branch Neversink River, Linn Run, Stone Run, Roberts Run). Likewise, young-of-the-year brook trout were abundant (indicative of successful reproduction during the study period) in Fly Pond Outlet, Black Brook, High Falls Brook, Biscuit Brook, Benner Run, and Baldwin Creek, but were absent or rare in Bald Mountain Brook, Buck Creek, Seventh Lake Inlet, East Branch Neversink River, and Linn Run.

In situ bioassays demonstrated that fish exposed to episodic acidification can experience significant mortality. Fish mortality during bioassays was significantly ($p < 0.05$) lower in reference streams (Fly Pond Outlet, Black Brook, High Falls Brook, Baldwin Run, Benner Run) than in

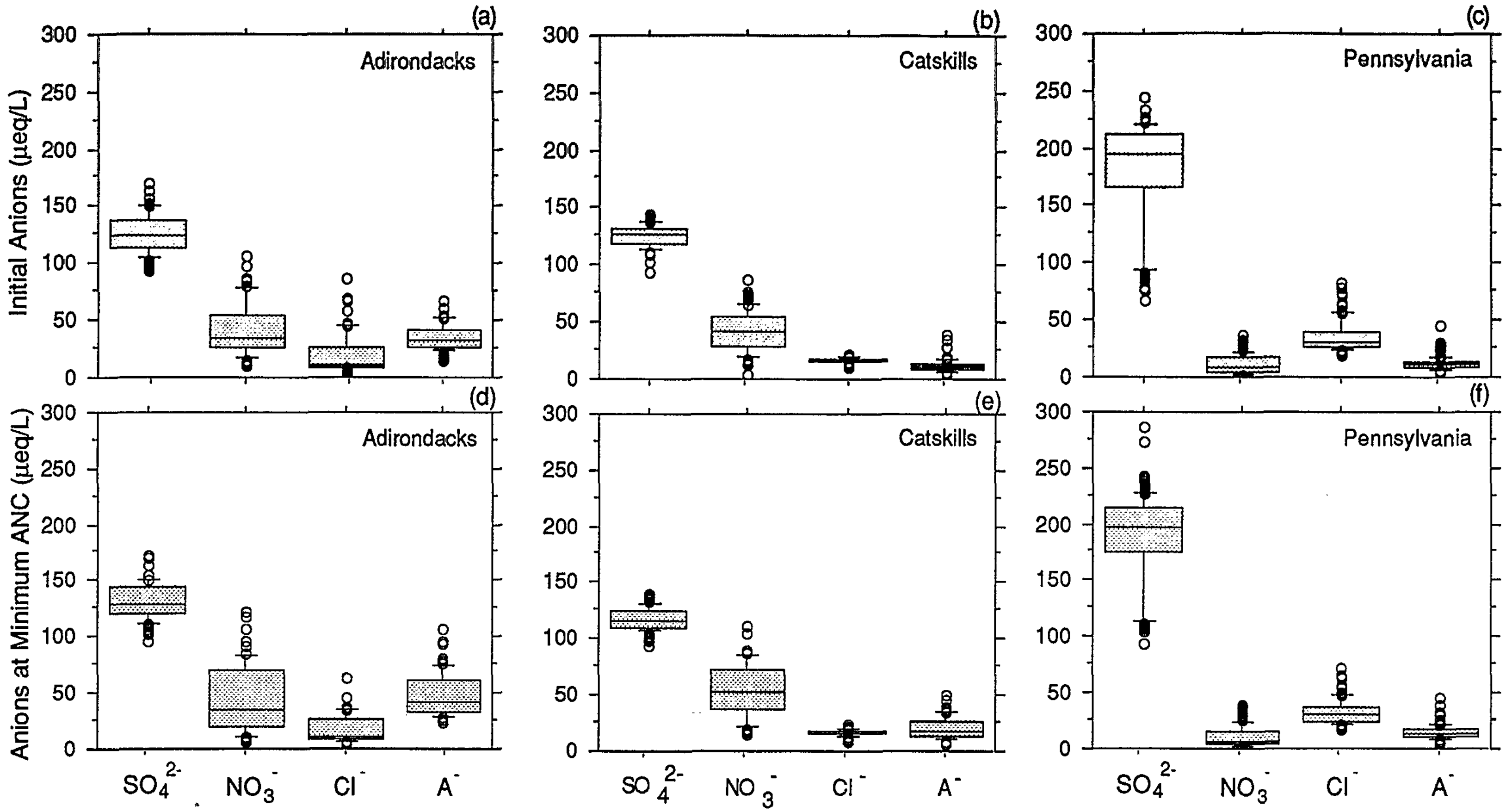

Figure 6. **Anion concentrations for (a) Adirondack, (b) Catskill, and (c) Pennsylvania streams at the beginning of episodes, and anion concentrations for (d) Adirondack, (e) Catskill, and (f) Pennsylvania streams at the time of minimum ANC. Organic acid (A^-) concentrations are estimates. Line in box indicates median; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.**

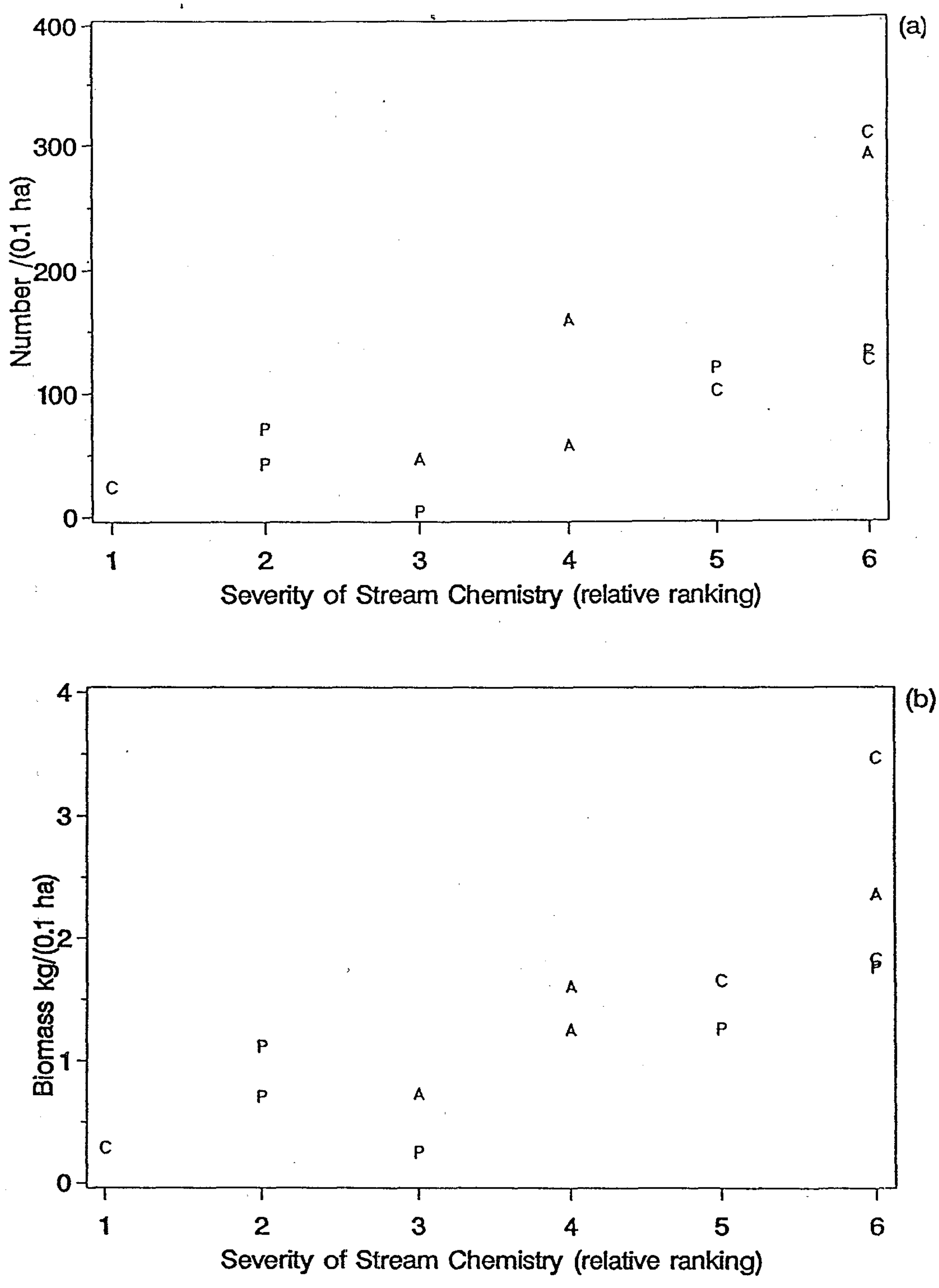

Figure 7. **(a) Mean density (number per 0.1 ha) and (b) biomass (kg/0.1 ha) of brook trout (average of fall 1988, 1989, and spring 1989, 1990 surveys) in ERP study streams ranked according to overall severity of chemical conditions in the stream (from most severe, 1, to least severe, 6). Rankings are explained in the text. Streams are labeled by region: A = Adirondacks, C = Catskills, and P = Pennsylvania.**

nonreference streams. Mortality rates were significantly higher in bioassays with acidic episodes than in bioassays with ANC > 0, but similar to bioassays that had chronically acidic conditions (ANC ≤ 0). Results were consistent across all fish species (Figure 8).

Chemical conditions toxic to fish occurred at some time during the study in all ERP streams except the five reference streams. Maximum observed mortality rates were generally highest in those streams with the most severe chemical conditions: > 80% in East Branch Neversink River, Stone Run, Buck Creek, and Linn Run; between 40% and 50% in Roberts Run and Bald Mountain Brook; 20% to 30% in Seventh Lake Inlet and Biscuit Brook; and < 20% in all five reference streams. Because bioassays were not conducted during periods with the most severe chemistry in each stream, these results provide only a qualitative indicator of the toxicity of ERP streams. All streams also had at least one bioassay with low mortality (< 10%), indicating that toxic conditions do not occur throughout the year.

A net downstream movement of radio-tagged brook trout was observed in all streams and study periods that experienced stressful chemical conditions (e.g., Figure 9). Little to no net downstream movement occurred in streams with relatively high pH (> 5.1–5.2) and low Al_{im} levels (< 150–160 μg/L) throughout the study period. Downstream fish movement either was associated with chronically acidic conditions at the start of the experiment or coincided with the occurrence of one or more episodes with Al_{im} > 160 μg/L for 1.5 or more days. Radio-tagged brook trout died when exposed to high concentrations of aluminum during an episode in Linn Run. During the same episode, radio-tagged trout survived if they avoided exposure to peak Al levels.

All ERP streams except the East Branch of the Neversink River had chemical conditions during low flow considered suitable for fish survival and reproduction (pH ≥ 6.0; Al_{im} < 60 μeq/L). Thus, stream assessments based solely on chemical measurements during low flow do not accurately predict the status of fish communities in small streams.

Episode Characteristics that Determine the Severity of Effects on Fish

Inorganic aluminum was the single best predictor of fish mortality during *in situ* bioassays. Calcium, pH, and DOC were also important predictors of brook trout mortality; at a given Al_{im} concentration, lower mortality occurred in bioassays with lower minimum pH, higher calcium, and higher DOC.

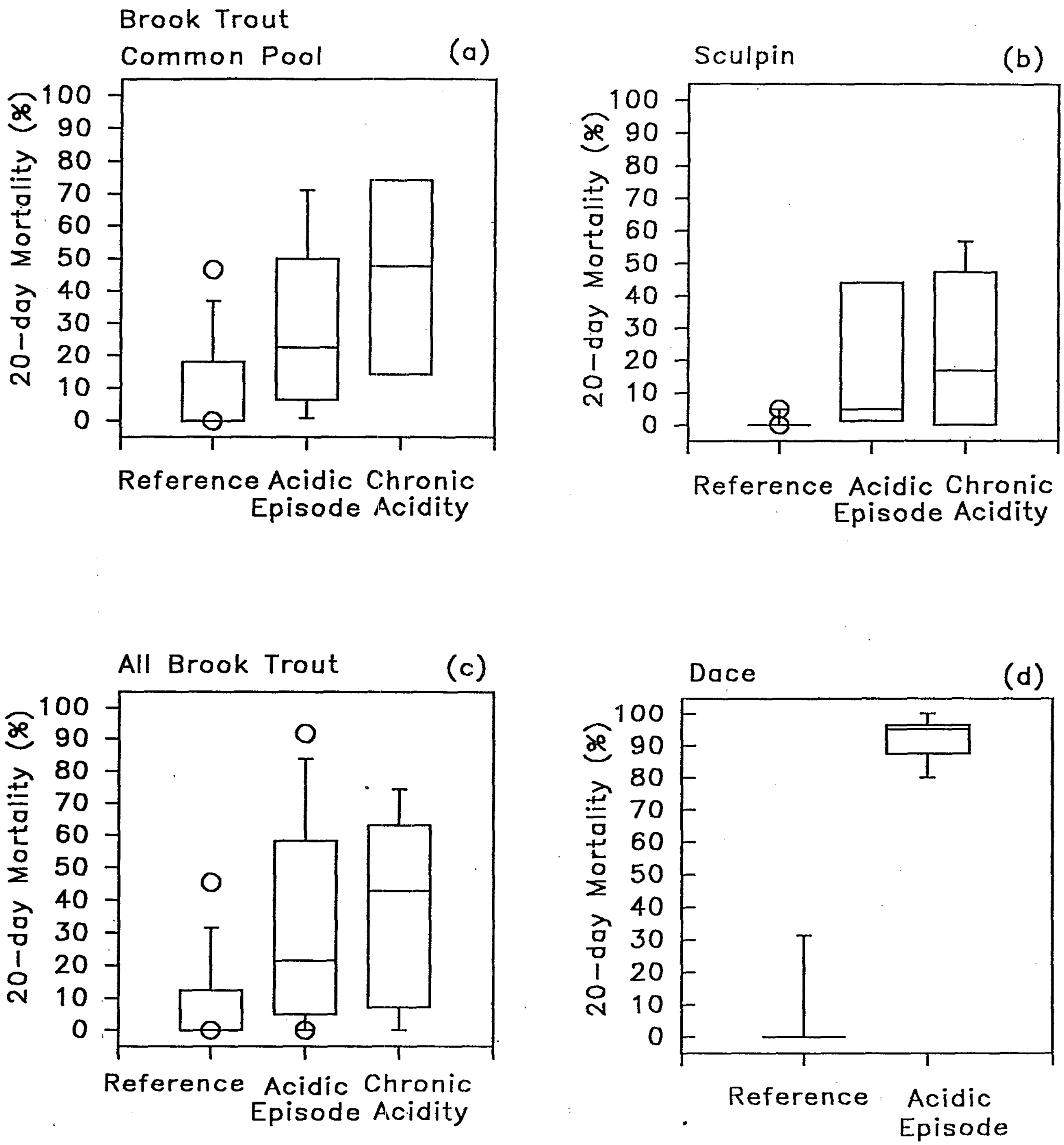

Figure 8. **Box plots of percent mortality after 20 days in *in situ* bioassays classified according to ANC: reference (nonacidic with ANC always > 0); chronic acidity (ANC always ≤ 0); and acidic episode (initial ANC > 0 with at least two consecutive values ≤ 0 during 20-day period). Line in box indicates median % mortality; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.**

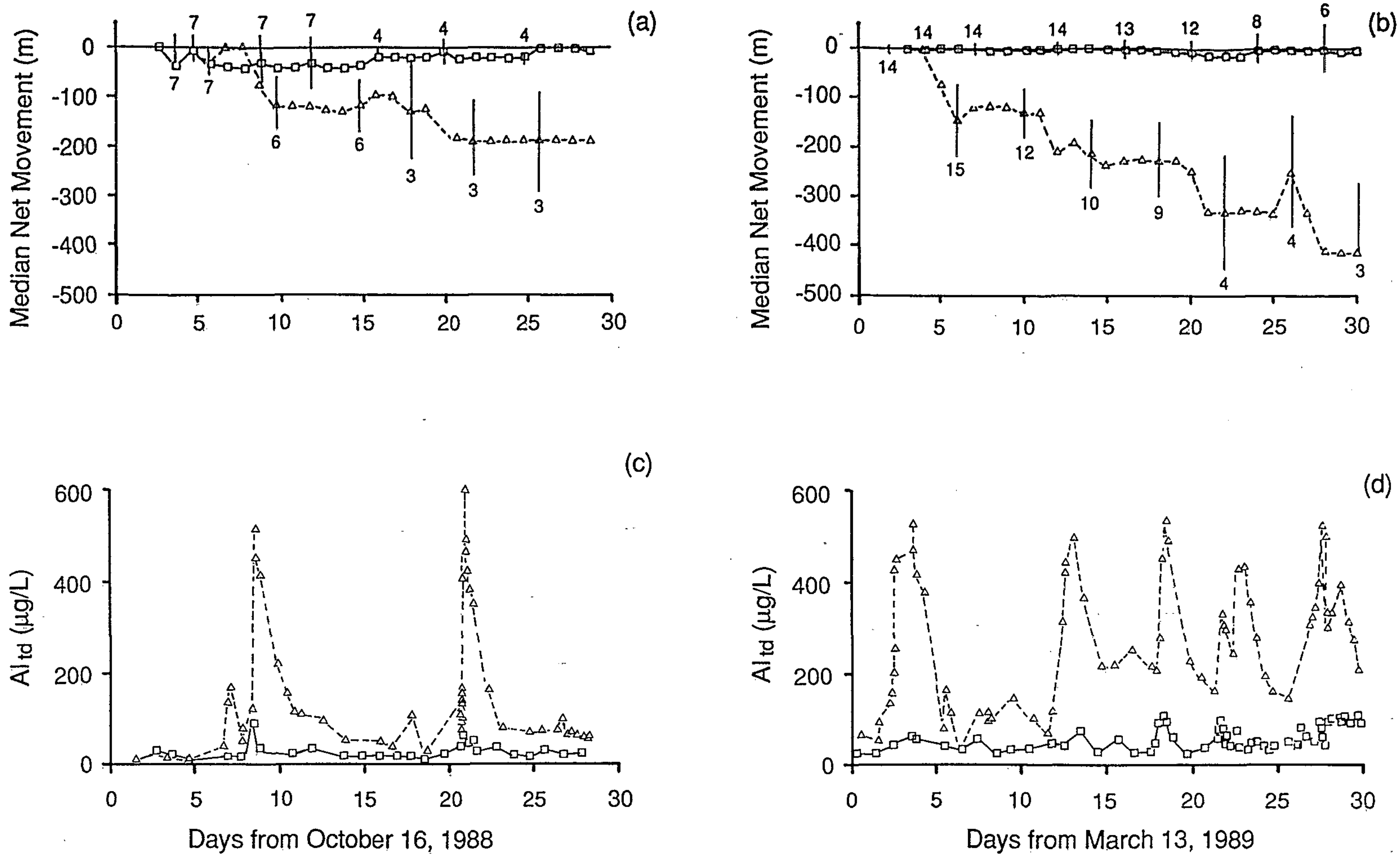

Figure 9. Total dissolved aluminum (Al_{td}) concentrations at continuous monitoring stations and median net movement of brook trout in Linn Run (triangles) and Baldwin Creek (squares). Negative values for movement indicate downstream relative to initial location. Sample size and ± 1 SE (vertical bars) are shown for fish movement on representative days (Source: Gagen, 1991).

Brook trout density and biomass in ERP streams were significantly ($p < 0.05$) correlated with both stream pH and Al_{im} concentrations, although rank correlations were slightly higher for pH than for Al_{im}. Because pH and Al_{im} are highly correlated, it is difficult, based on field data alone and given the small number of study streams, to distinguish the relative importance of pH and Al_{im}.

The relationships between Al_{im} and pH, and between Al_{im} and ANC, varied among ERP streams. High levels of Al_{im} (> 200 μg/L) commonly occurred in Linn Run at pH ≤ 5.4, but only at pH ≤ 5.2 in Stone Run, Bald Mountain Brook, Buck Creek, and Seventh Lake Inlet, and at pH < 5.0 in Roberts Run and East Branch Neversink River. [No Al_{im} levels above 200 μg/L occurred in the remaining six ERP streams.] Thus, predictions of potential effects on fish based solely on pH or ANC may be misleading.

In general, fish exposed for longer periods of time to high Al_{im} levels had higher mortality rates. However, the single best predictor of brook trout and sculpin mortality was the time-weighted median Al_{im} concentration during the 20-day bioassay period, as opposed to more complex expressions of chemical exposure incorporating peak levels and duration.

Blacknose dace are more sensitive to high Al_{im} than brook trout or sculpin. Dace mortality was best predicted by an integrated function of duration and Al_{im} concentrations. High mortality is expected to occur with Al_{im} > 250 μg/L for two or more days.

During radiotelemetry studies, some brook trout were able to move downstream or into alkaline microhabitats and avoided exposure to low pH and high Al during episodes. However, in most cases, the majority of radio-tagged fish were exposed to relatively high, potentially lethal Al levels (Figure 10). Fish behavioral avoidance and the occurrence of refugia can partially, but not entirely, mitigate the adverse effects of episodic acidification on fish populations. Recolonization from groundwater seeps and more alkaline tributary streams can maintain low densities of fish in streams that experience toxic episodes, but is not sufficient to sustain fish densities or biomass at levels near those expected in the absence of adverse acid-base chemistry.

Brook trout are fairly mobile, frequently moving more than 1 km. Thus, of the fish species common in small headwater streams, brook trout are best able to take advantage of refugia. Sculpin, by contrast, generally move only short distances (e.g., < 10 m in a summer). Sculpin were as, or more, tolerant of high Al_{im} in bioassays than brook trout. Yet, sculpin populations are absent from streams that maintain low densities of brook trout. We hypothesize that toxic

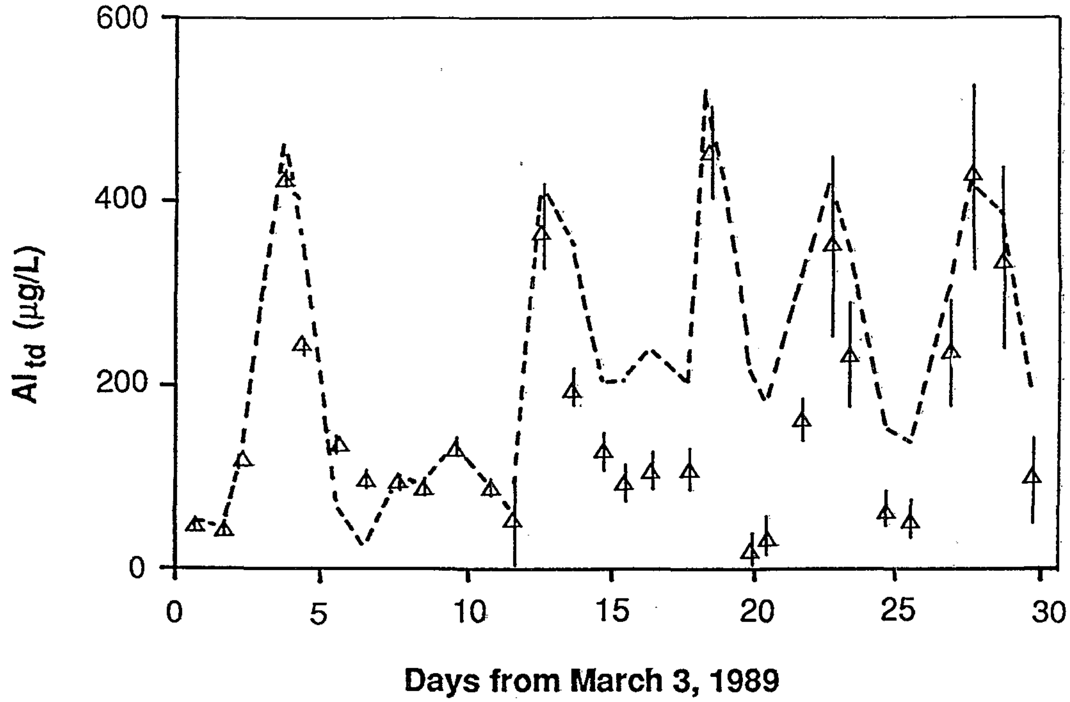

Figure 10. Median stream total dissolved Al (Al_{td}) concentration at locations of radio-tagged fish (triangles; vertical bars = ± 1 SE) and Al_{td} concentrations of concurrent samples collected at the Linn Run continuous monitoring station (broken line) (Source: Gagen, 1991).

episodes have a more severe and long-lasting effect on sculpin populations, compared to brook trout populations, because of differences in fish mobility.

Major Conclusions

- Episodes were a common occurrence in the study streams of all three regions, and acidic episodes were common when ANC values were ≤ 50 µeq/L immediately before the episode. When acidic episodes occurred, they were accompanied by depressed pH levels and elevated Al_{im} concentrations.

- Acidic deposition, as evidenced by stream water SO_4^{2-} and NO_3^- during episodes, contributed significantly in two ways to the occurrence of acidic episodes with low pH and high Al levels in all three regions. Pulses of SO_4^{2-} (in Pennsylvania streams) and NO_3^- (in Catskill and

Adirondack streams) during episodes augmented natural processes to create episodes with lower ANC and pH and higher Al_{im} concentrations than would have occurred from natural processes alone. In addition, large baseline concentrations of SO_4^{2-} (all regions) and NO_3^- (Catskills and Adirondacks) reduced episodic minimum ANC levels, even when these ions did not change or decreased slightly during episodes.

- Episodic acidification can have long-term adverse effects on fish populations. As a result, stream assessments based solely on chemical measurements during low flow do not accurately predict the status of fish communities in small streams.

- Fish exposed to low pH and high Al_{im} for longer periods of time experienced higher mortality. Time-weighted median Al_{im} concentration was the single best predictor of brook trout mortality.

- Fish behavioral avoidance only partially mitigated the adverse effects of episodic acidification in small streams and was not sufficient to sustain fish density or biomass at the levels expected in the absence of acidic episodes.

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SECTION 1
INTRODUCTION

Episodic acidification refers to short-term decreases of acid neutralizing capacity (ANC) that often accompany rainstorm runoff and snowmelt events (Wigington et al., 1990). Typically, if a stream or lake experiences an episodic ANC decrease—an episode—there are accompanying changes in the concentrations of other chemical solutes, such as H^+ and Al. Short-term exposures to low pH and elevated Al during episodes can cause significant stress and increased mortality of aquatic biota (J. Baker et al., 1990a).

The Episodic Response Project (ERP), originally funded as a component of the U.S. Environmental Protection Agency's (EPA) Aquatic Effects Research Program (AERP), was designed to address major knowledge gaps concerning episodic acidification. With the exception of the ERP, AERP research focused mostly on chronic acidification, that is, long-term changes in surface water acid-base chemistry and associated changes in biological communities. The National Surface Water Survey (NSWS) measured the current, chronic, acid-base chemical status of surface waters in regions of the United States potentially sensitive to acidic deposition (Linthurst et al., 1986; Landers et al., 1987; Kaufmann et al., 1988). The Direct/Delayed Response Project (DDRP) projected future changes in annual average surface water chemistry for a range of alternative future deposition scenarios (Church et al., 1989, 1992). Biological responses to chronic changes in acid-base chemistry were evaluated as part of the Little Rock Lake whole-lake acidification experiment (Brezonik et al., 1986; Watras and Frost, 1989) and other AERP projects. Because of these and other studies, a relatively sound knowledge base exists regarding chronic acidification and its effects.

However, many uncertainties remain regarding the occurrence, causes, and biological consequences of episodic acidification. For example, the NSWS used index samples collected at specific times of the year and specific locations to assess the current chemical status of surface waters. The DDRP projected future chemical changes based on index chemistry and a variety of soil and watershed characteristics. These projects yielded valuable research results that were used to address critically important policy questions related to acidic deposition. However, assessments based on index conditions have not adequately reflected the influence of episodes. It has not been possible to accurately estimate the worst-case chemical conditions associated with episodes for the populations of surface waters potentially sensitive to acidic deposition. The processes and forcing factors controlling episodes have remained poorly quantified. Furthermore, a very important factor is that the degree and severity of biological effects of episodic acidification, especially population-level effects on fish, has remained uncertain.

1.1 PROJECT OBJECTIVES

The ERP was conducted to address key uncertainties regarding episodic acidification. The project objectives were as follows (Thornton et al., 1988):

1. Determine the magnitude, duration, frequency, and characteristics of episodic chemical changes that accompany hydrological events (snowmelt and rainstorms) in streams.

2. Evaluate the effects of episodic acidification on fish populations in streams.

3. Define key characteristics of episodes that determine the severity of effects on fish populations.

4. Develop and calibrate regional models of episodic chemistry that link atmospheric deposition to biologically relevant chemistry during episodes.

1.2 PROJECT SCOPE

Episodic acidification is of concern in regions of the United States susceptible to adverse impacts to aquatic ecosystems because of acidic deposition. The ERP research efforts focused on three priority areas: the Northern Appalachian region of Pennsylvania and the Catskill Mountains and Adirondack Mountains of New York. These regions were selected because of three factors: the importance of their stream resources, the likely occurrence of acidic episodes, and the high probability that episodes are an important factor affecting the current status of fish populations in these areas (Thornton et al., 1988; Wigington et al., 1990). Wigington et al. (1990) concluded that (1) in the United States, acidic episodes occur most often in the Northeast and Mid-Atlantic regions, including the Adirondacks, Catskills, and Northern Appalachian region of Pennsylvania, and (2) atmospheric deposition seems to have the greatest influence on minimum ANC and pH of episodes in these areas. All three regions have a relatively high percentage of chronically acidic surface waters [14% of the lakes in the Adirondacks and 6% of the upper stream reaches in the Poconos/Catskills and Northern Appalachian Plateau regions (Linthurst et al., 1986; Kaufmann et al., 1988)]. In addition, preliminary modeling analyses by Eshleman (1988) estimated that the numbers of acidic systems in these regions could increase 3–6 times, depending on the region.

Episodic acidification occurs in both lakes and streams. ERP research efforts were conducted only in streams, however, for three reasons. First, the available evidence suggested that episodes probably have more significant impacts on fish populations in streams than in lakes (J. Baker et al., 1990a). Episodes in lakes are often accompanied by a high degree of spatial variability that may mitigate the effects on fish and other biota. Second, sampling episodic chemical conditions and biological responses to episodes is much more difficult in lakes than in streams, because of the spatial variability in lakes as well as the safety problems associated with collecting samples during spring snowmelt on lakes with thin ice covers. Third, episodic responses in streams are more directly linked to the watersheds. Therefore, understanding episodic acidification in streams is a necessary precursor to understanding the more complex episodic responses of lakes.

ERP field research did not directly address the regional extent of episodic acidification. Eventually, to aid in decisions regarding acidic deposition controls, we would like to know the number, area, and geographic distribution of waters that experience episodes severe enough to cause significant adverse biological effects. As part of the ERP planning process, we decided, however, that (1) insufficient information was available to determine what characteristics of episodes were most important in controlling biological effects and, therefore, most important to measure, and (2) regional surveys of episode chemistry, similar to the NSWS assessment of chronic acidity, are not logistically feasible because of the transient nature of episodes (Thornton et al., 1988). For these reasons, the ERP was designed as an intensive study, rather than an extensive regional survey. Detailed field monitoring and research were conducted at a relatively small number of selected sites. Five types of monitoring data were collected at the ERP study sites: (1) atmospheric deposition quantity and quality, (2) stream discharge, (3) stream chemistry, (4) fish population status and fish responses to episodes, and (5) qualitative information on stream benthic invertebrates.

Results of the ERP research are presented in this report. In addition, ERP data are being used to develop and refine models with which, together with the NSWS data, it may be possible to estimate the regional extent of biologically significant episodes. The results from these model development efforts are not included in this report but will be described in subsequent journal articles.

1.3 PROJECT ORGANIZATION

The ERP was a cooperative research effort involving scientists from a number of different institutions and agencies. Field research was conducted by regional cooperators in three areas of the United States:

1. The Adirondack Lakes Survey Corporation (Walter A. Kretser and Howard A. Simonin, principal investigators) in the Adirondack Mountains of New York.

2. The U.S. Geological Survey (Peter S. Murdoch, principal investigator) in the Catskill Mountains of New York.

3. The Environmental Resources Research Institute at Pennsylvania State University (David R. DeWalle, principal investigator) in the Northern Appalachian Plateau of Pennsylvania.

The U.S. EPA Environmental Research Laboratory in Corvallis, Oregon (ERL-C), served as the project lead. The U.S. EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV), developed and guided the ERP quality assurance/quality control (QA/QC) program. EMSL-LV also developed the field-based data management system. ERL-C performed central database management functions. The Pacific Northwest Laboratory designed and coordinated deposition monitoring for the project, working in cooperation with the U.S. EPA Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina.

1.4 REPORT SCOPE AND ORGANIZATION

This report describes the major findings of the field component of the ERP and thereby addresses the first three of the four objectives listed in Section 1.1. The stream chemistry section describes the occurrence and characteristics of episodes and explains how ion changes during episodes may indicate the causes of episodic acidification. Biology results include measures of fish toxicity, behavioral responses, and population status in the study streams in relation to stream chemistry and selected episode characteristics. An important objective of the report is to compare these chemical and biological responses among the three ERP regions. More intensive analyses of the data collected for any one region are being conducted by the individual regional cooperators, for publication in the peer-reviewed literature.

Funding constraints have hindered completion of a full analysis of the ERP data set. The ERP budget was reduced substantially in the third and final year of the project (1990), during the final stages of the original National Acid Precipitation Assessment Program (NAPAP). As a result, most field research was completed, but few resources were left for data analyses by cooperators or ERL-Corvallis staff. The analyses presented in this document have been accomplished through the persistent efforts of a relatively small group of people. Consequently, the report contents reflect very difficult choices regarding the most critical analyses to be performed and presented. Two criteria guided the prioritization of work for the report. First, analyses should address the ERP objectives as directly as possible. Secondly, the work should be a logical step on which subsequent analyses could be based. Some analyses originally planned could not be conducted. For example, the report provides only a brief description of deposition characteristics during the ERP study period. However, analyses that explicitly examine the linkage between acidic deposition and episodic acidification could not be included. Some of the biology sections rely on summaries of analyses conducted by the field cooperators, separately for each region, rather than analysis of the integrated data set.

Additional work involving ERP data is continuing. Modeling analyses, to address the fourth ERP objective, are being conducted by Keith N. Eshleman (University of Virginia), Trevor D. Davies (University of East Anglia, UK), Martyn Tranter (University of Bristol, UK), and P.J. Wigington, Jr. (ERL-C). Furthermore, both the individual field cooperators and ERL-Corvallis staff are planning future analyses of the ERP data. Results from these efforts will be published in peer-reviewed journals.

The remaining sections of this report are organized as follows:

- Chapter 2, Importance of Episodic Acidification, provides a brief review of the current understanding and uncertainties regarding the extent, severity, causes, and biological effects of episodic acidification.
- Chapter 3, Study Areas, provides a general description of the regions studied as well as the specific study sites (including information on atmospheric deposition).
- Chapter 4, Methods, provides an overview of the field, analytical, and data analysis methods used to collect and interpret the ERP data, including procedures for QA/QC.
- Chapters 5 and 6 present and discuss project results, organized by topic area:
  - Chapter 5, Stream Hydrology and Chemistry
  - Chapter 6, Effects on Fish
- Chapter 7, Summary and Conclusions, reiterates the major findings and conclusions of the ERP.

SECTION 2

IMPORTANCE OF EPISODIC ACIDIFICATION

This chapter provides a brief overview of our current understanding of the extent, severity, causes, and biological importance of episodic acidification in streams. It provides the background information necessary for interpreting the results from the ERP and identifies the key knowledge gaps and uncertainties that the ERP was designed to address. This summary is based primarily on the recent NAPAP state of science and technology reports on episodic acidification (Wigington et al., 1990) and the biological effects of acidification (J. Baker et al., 1990a).

We define acidification as a decrease in surface water ANC. Acidic waters have no ability to neutralize strong acids, that is, ANC $\leq$ 0. Episodic acidification, therefore, is the process by which a lake or stream experiences a transient, short-term decrease in ANC, usually during a hydrologic event, over a time scale of hours to weeks. A hydrologic event is an increase in stream discharge or flow resulting from rainfall or snowmelt. Thus, episodes make up the subset of hydrologic events during which ANC decreases; during acidic episodes, ANC $\leq$ 0.

Although acidification and episodes are defined on the basis of a decrease in ANC, changes also occur in a large number of other water chemistry variables. Of particular concern for aquatic biota are the decreases in pH and the increases in inorganic aluminum that accompany surface water acidification. Laboratory experiments have demonstrated that both low pH and elevated levels of inorganic aluminum are toxic to fish and other biota (Schofield and Trojnar, 1980; Baker and Schofield, 1982; Clarke and LaZerte, 1985; Ingersoll, 1986; France and Stokes, 1987; Holtze and Hutchinson, 1989).

2.1 CHARACTERISTICS OF EPISODES

Figure 2-1 presents a hydrograph (representation of discharge over time) and a chemograph (representation of chemical concentration over time) for an idealized hydrologic event and an associated episode. It illustrates several important episode characteristics. Episode *magnitude* has two components: (1) the maximum change in the concentration of ANC or other chemical variable of interest, such as pH or inorganic aluminum, represented by the change from point A to point B along the Y-axis in the figure, and (2) the absolute minimum value (or maximum, for variables such as aluminum that increase during episodes) that occurs during the event (point B).

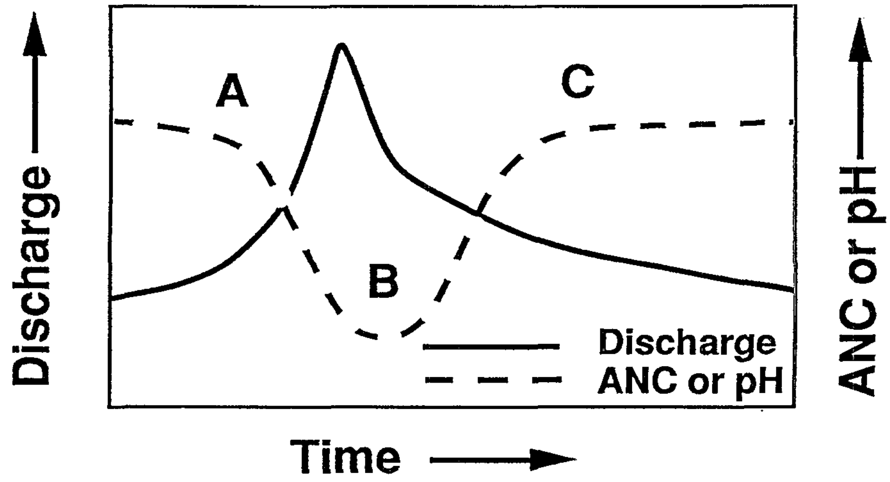

Figure 2-1. Variation of streamflow and ANC (or pH) for an idealized episode.

Episode *duration* is the amount of time that the ANC or pH depression (or elevated aluminum) lasts, that is, the time from point A to point C along the X-axis. For some purposes, duration is also specified as the amount of time below (or above) a given threshold value, such as ANC ≤ 0 or biologically significant thresholds of pH and inorganic aluminum. Available information, discussed further in Section 2.4, indicates that episode magnitude and duration are the two most important features determining the severity of the toxic effects on aquatic biota.

Aquatic systems rarely behave, however, in the idealized fashion illustrated in Figure 2-1. Multiple rainstorms or combinations of rain and snowmelt frequently produce complex hydrographs and chemographs that make it difficult to describe episode magnitude and duration. As a result, one of the most challenging tasks facing scientists is to select an appropriate index of episode chemical severity that can be consistently applied to assess the biological significance and impacts of episodic acidification in streams.

The nature of the hydrologic events that occur in a watershed provides important information about the possible characteristics of episodes in that system. For example, the duration of an event also defines the maximum possible episode duration. In northerly regions, where large snowpacks accumulate, hydrological events in the spring may last several weeks or more as the snow gradually melts. Rainstorms, on the other hand, produce hydrological events ranging from several hours to several days in low-order streams. Thus, episodes in small streams associated with individual rainstorms are likely to be no more than a few days long. Rainstorm generated episodes may last several weeks in large rivers. During the spring snowmelt period, shorter, more severe episodes may be superimposed on longer snowmelt episodes.

Numerous researchers have reported strong correlations between stream discharge and concentrations of selected chemistry variables, such as pH, ANC, and sulfate (Johnson et al., 1969; Lewis and Grant, 1979; Sharpe et al., 1984; Eshleman, 1985). In such situations, the stream hydrograph may also be used to estimate, with quantifiable uncertainty, stream chemistry and episode magnitude. Several limitations to this approach have been noted, however. In particular, concentration-discharge relationships often vary seasonally with differences in antecedent conditions (e.g., the amount of time since the last storm event) and with the rising and falling limb of the discharge curve. For example, for a given level of discharge and pH, inorganic aluminum concentrations are generally higher during the early phases of snowmelt, as water levels rise, than during later phases of the event (Sullivan et al., 1987; Hooper and Shoemaker, 1985). Possible explanations include changes in hydrological flowpaths over the course of the event (see Section 2.3) and the redissolution of aluminum from the streambed during the initial pH decline (Norton et al., 1992). Patterns of chemical changes during events and concentration-discharge relationships vary among regions as well as among stream systems within a given region (Wigington et al., 1990).

Frequency refers to the number of occurrences of episodes, of a given magnitude and duration, during a specified period (e.g., year). Because of their linkage to hydrological events, episodes are stochastic or probabilistic in nature. Some years are dry and tend to have few significant hydrological events and therefore few potential episodes. In other years, wetter conditions prevail, allowing a greater opportunity for hydrological events and episodes to occur more frequently. Only by monitoring episodic acidification in an aquatic system for several years can the full range of the system's response be reasonably assessed.

Additional complexity arises from the spatial variability of chemical conditions during episodes. Seeps, springs, and tributaries that deliver water to streams can create refugia with chemical characteristics quite different from those in the main body of water. In addition, in most stream systems, ANC and pH generally increase with increasing distance downstream (Johnson et al., 1981; Driscoll et al., 1987b; Kaufmann et al., 1988). As stream order and watershed size increase, the contribution of groundwaters, with higher ANC and pH, to stream baseflow tends to increase (Winter, 1984; Freeze and Cherry, 1979). One would also expect episodes to be less severe in higher order streams, although relatively few studies have been conducted (e.g., Hooper and Shoemaker, 1985) on longitudinal trends in episodic chemistry to confirm this assumption.

2.2 EXTENT AND SEVERITY OF THE PROBLEM

Episodic acidification is widespread. Throughout the United States, Canada, and Europe, streams and drainage lakes usually experience at least some loss of ANC during hydrological events (Wigington et al., 1990). Although some exceptions exist, that is, systems that experience no change or even an increase in pH or ANC during events, these systems or episodes represent a small proportion of those studied.

Although the occurrence of episodes is almost universal in the United States, episode magnitude varies widely both among regions and among systems within the same region (Figure 2-2). According to available studies, streams and lakes in the Northeast most consistently experience episodes with low minimum values of ANC and pH. Every northeastern state for which data are available (New York, Vermont, New Hampshire, Maine, and Massachusetts) has streams or lakes that experience episodes with minimum pH < 5.0 and/or minimum ANC < 0 (with pre-episode conditions of pH 5.5 or greater). In the southwestern Adirondacks, some streams with baseflow ANC > 200 μeq/L may become acidic during snowmelt events (Galloway et al., 1987), and many Adirondack streams and lakes with pre-episode ANC up to 75 μeq/L become acidic during episodes (Colquhoun et al., 1984; Schaefer et al., 1990). Episodes with minimum ANC < 0 or minimum pH < 5.0 have also been recorded in the Mid-Atlantic region, specifically in the Valley and Ridge area of Pennsylvania and the Atlantic Coastal Plain of Maryland (Lynch et al., 1986; Sharpe et al., 1984; Correll et al., 1987). Outside the Northeast and Mid-Atlantic regions, most of the episodes recorded have not resulted in acidic conditions, although only limited data are available.

Despite a large amount of published information, significant knowledge gaps remain concerning the extent and severity of episodic acidification, primarily because measuring episodic acidification is a difficult and expensive task. Adequately capturing the temporal dynamics and spatial variations in chemistry during episodes requires large investments in field personnel and instrumentation. In many of the existing studies, samples were collected too infrequently to provide highly accurate data on episode magnitude and duration. Studies that use sampling intervals that

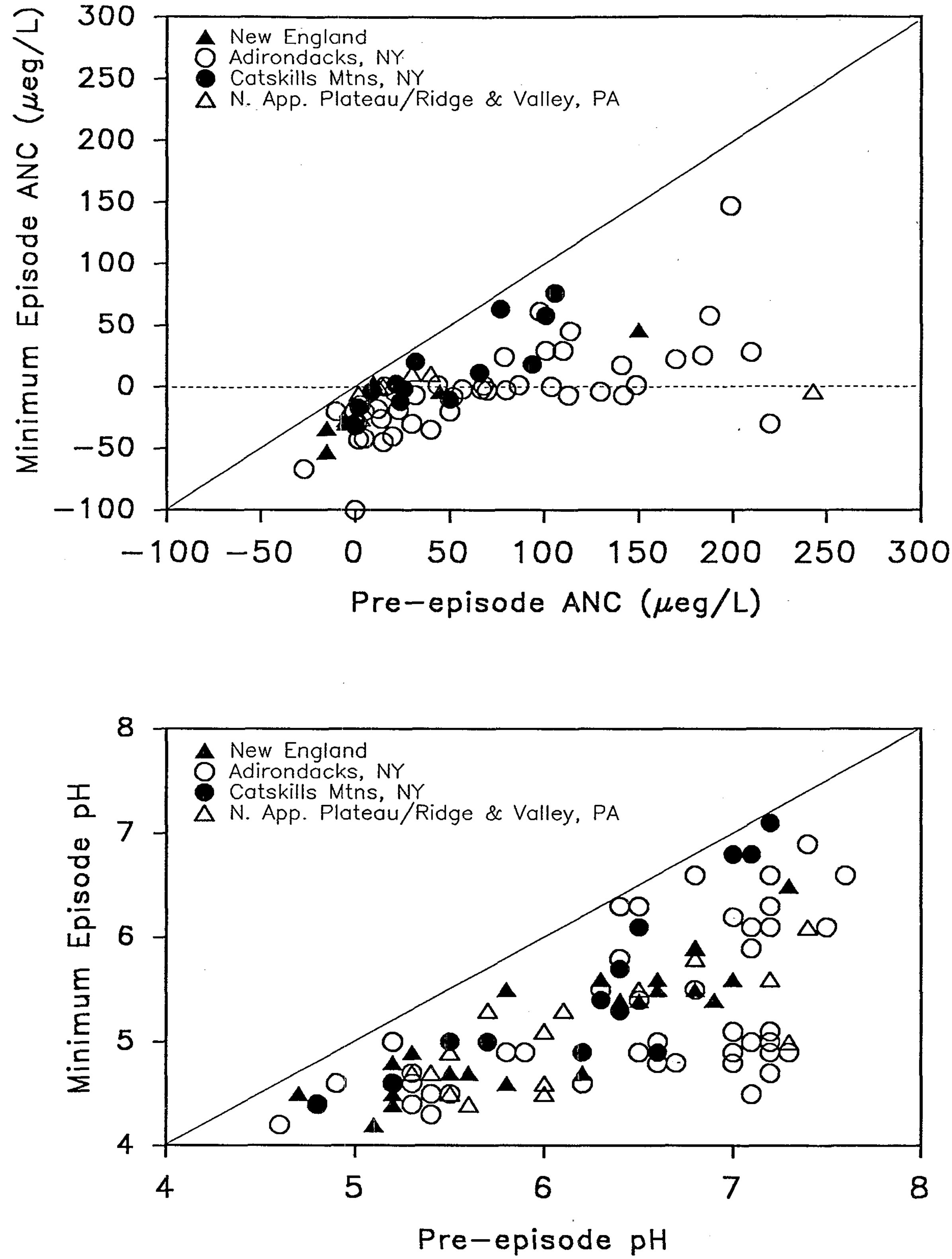

Figure 2-2. **Minimum ANC and pH for the episode with the lowest recorded minimum ANC or pH value for streams and lakes in the Northeast (including Pennsylvania). Each symbol represents an individual stream or lake (data from Wigington et al., 1990).**

are long in comparison to the rate of chemical change are likely to underestimate the total magnitude of the change, the minimum ANC, and, to some degree, the duration of episodes. Furthermore, variables of interest, such as inorganic aluminum, often were not routinely measured.

At present, there are not enough data for any region of the United States to estimate the regional extent, magnitude, duration, and frequency of episodic acidification. In particular, it has proven to be logistically infeasible to conduct statistically rigorous surveys that would allow for population estimates of episode chemistry comparable to the regional population estimates of chronic acidity provided by the National Surface Water Survey (NSWS) (Linthurst et al., 1986; Landers et al., 1987; Kaufmann et al., 1988).

The best approach for achieving population-level estimates of episodic acidification will probably be to link improved regional databases with simple modeling approaches. Eshleman (1988) conducted a preliminary analysis, using a two-component mixing model together with the NSWS chemistry data, to generate worst-case estimates of the minimum ANC during episodes in streams in six regions of the eastern United States (Table 2-1). His results suggest that the estimated proportion of acidic streams (ANC $\leq$ 0) would increase by 40–640%, compared to the NSWS results in the six regions, if the effects of episodic acidification were taken into account. Neither the model nor the model coefficients used by Eshleman (1988) have been fully validated, however. Thus, these results must be considered preliminary. Data from the ERP are being used to refine and improve these and other models, with the objective of providing improved regional estimates of the extent and magnitude of episodic acidification.

2.3 CAUSES OF EPISODIC ACIDIFICATION

Several processes and factors influence the nature and severity of episodic acidification. Physical factors, such as watershed hydrology, as well as chemical interactions are important.

2.3.1 Watershed Hydrology

The changes that occur in water flowpaths through the watershed during hydrological events are an important determinant of the characteristics of episodes in receiving streams and lakes. During periods of baseflow, relatively alkaline water is derived from the lower part of the mineral soil and deeper groundwater storage zones (Velbel, 1985) (see Figure 2-3). During hydrologic events, on the other hand, water is routed primarily through upper soil layers (Potter et al., 1988; Chen et al., 1984), which are more acidic because of natural processes or acidic deposition.

Table 2-1. **Population Estimates of the Number and Proportion of Acidic Reaches (ANC ≤ 0) Based on Index Conditions and Worst-Case Episodic Conditions Using the Two-Component Mixing Model (from Eshleman 1988)**

Subregion	Node[a]	Index Conditions (ANC ≤ 0		Episodic Conditions (ANC ≤ 0)	
		Number of Reaches	Proportion (%)	Number of Reaches	Proportion (%)
Poconos/Catskills (1D)	(lower) (upper)	0 209	0.0 6.4	157 746	4.8 23.0
Southern Blue Ridge (2As)	(lower)	0[b]	0[b]	39	2.2
Valley and Ridge (2Bn)	(lower) (upper)	0[b] 636	0[b] 4.9	47 1,126	0.3 8.6
Northern Appalachian Plateau (2Cn)	(lower) (upper)	326 499	3.8 5.8	2,379 3,224	28.0 37.2
Ozarks/Ouachitas (2D)	(lower) (upper)	0[b] 0[b]	0[b] 0[b]	0[b] 75	0[b] 1.8
Southern Appalachians (2X)	(lower) (upper)	0[b] 121	0[b] 2.5	243 364	4.8 7.4
Piedmont (3A)	(lower) (upper)	0[b] 0[b]	0[b] 0[b]	0[b] 0[b]	0[b] 0[b]
Chesapeake Area (3B)	(lower) (upper)	772 1,334	6.8 11.8	1,727 3,132	15.3 27.8
Florida (3C)	(lower) (upper)	225 678	14.5 39.2	520 963	33.5 55.7

[a] Preliminary estimates are given for both upper and lower sampling nodes for nine NSWS subregions.
[b] No acidic reaches were sampled; although the best estimate is zero, the upper 95% confidence bound on the estimate does not preclude a certain number of acidic systems in the target population.

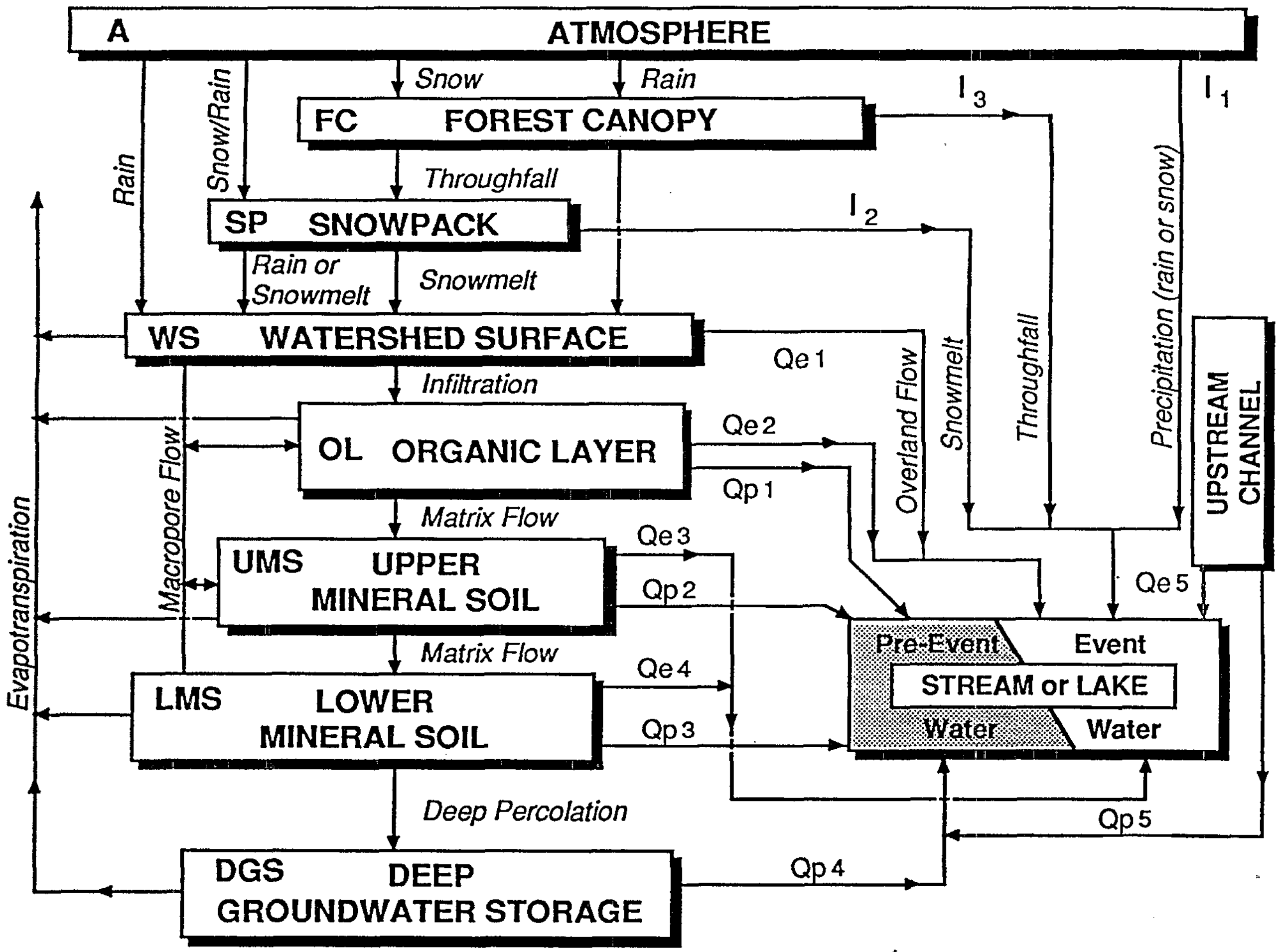

Figure 2-3. Episodic acidification conceptual model. I_n = direct input; Q_{en} = event water; Q_{pn} = pre-event water (from Wigington et al., 1990).

Differences in the characteristics of these two water sources will determine the degree of episodic acidification.

A considerable body of literature has demonstrated that streamwater during events is composed of (1) *event water* derived directly from the rainstorm or snowmelt driving the hydrologic event (flowpaths Qe1–Qe4 in Figure 2-3) and (2) *pre-event* water residing in the watershed before the rainstorm or snowmelt occurred (Qp1–Qp4 in Figure 2-3) (Wigington et al., 1990). Results from natural isotope studies suggest that pre-event water typically accounts for 30–90% of the water transported during hydrological events (Hooper and Shoemaker, 1986; Eshleman, 1988).

As water moves through the watershed system, it may be chemically altered by numerous biogeochemical reactions. Basic differences exist between the opportunities for event water and for pre-event water to be modified by these biogeochemical processes. By definition, event water moves rapidly through the system and generally has less opportunity to interact with soils and rock. For watersheds receiving acidic deposition, this means that event water is less likely to be neutralized before being delivered to a waterbody (Winter, 1984). Pre-event water resides in the soil/geologic complex for a longer period of time, increasing the opportunity for neutralization reactions to take place (Anderson and Bowser, 1986). The combination of the various sources of event and pre-event water determines the net chemical characteristics of water delivered to a stream or lake at any moment in time.

2.3.2 Natural Processes that Contribute to Episodic Acidification

Four important natural processes can produce episodes: (1) dilution, (2) nitrification, (3) organic acid production, and (4) the sea-salt effect. If present, weathering and oxidation of mineral S within the watershed can also induce episodic acidification. However, we focus our discussion on the four more commonly important processes.

Dilution occurs when precipitation water of low ionic strength (event) is mixed with higher ionic strength pre-event water in soil water or in a lake or stream. For dilution to occur, modification of the precipitation water by chemical reactions in watershed soils must be limited by either little physical contact or a short interaction time. Dilution can lower ANC, but dilution alone cannot cause an acidic episode. Episodes caused by dilution are characterized by decreases in base cation concentrations (sodium, potassium, calcium, and magnesium), which are derived largely from watershed soils.

Nitrification is the biological conversion of organic nitrogen and reduced forms of inorganic nitrogen, such as ammonium, into nitrate. The end products of these reactions include hydrogen ions (H^+) as well as nitrate anions (NO_3^-). Nitrification typically occurs in the organic layers of soils. Thus, waters moving through these upper soil layers during events are likely to flush out any accumulations of nitrate and acidity from nitrification. Episodes caused by nitrification are characterized by relatively high nitrate concentrations (Galloway et al., 1987; Peters and Driscoll, 1987).

Organic acids are also produced in soil organic layers, as byproducts of the partial decomposition of organic matter. A high proportion of the organic acids in wetland systems is exported directly to surface waters. In forest soils, on the other hand, organic acids generated in the organic layer tend to be adsorbed onto the mineral surfaces in the lower horizon mineral soils. When flowpaths bypass these mineral soils, however, as during some events, forest soils also can export organic acids (Turner et al., 1990). Hence, the production of organic acids in the organic layer and the minimal adsorption of these acids during transit to the watercourse are prerequisites for episodes stimulated by organic acids. Episodes caused by organic acid production typically are characterized by an increase in the streamwater organic anion content and, depending on the ion exchange characteristics of the organic layer, a possible decrease in base cation concentrations.

The sea-salt effect occurs when base cations from atmospheric deposition displace H^+ ions from the soil complex; these H^+ ions may then be exported to streams and lakes. Two conditions are required for this process to be a significant episode-generating mechanism. First, there must be an ample supply of neutral salts in wet or dry deposition. Therefore, the sea-salt effect generally occurs only in areas along oceanic coastlines. Second, H^+ ions must be readily available on the soil cation exchange complex. Thus, the sea-salt effect can cause episodic acidification only in watersheds with soils that have been chronically acidified by either natural or anthropogenic factors. The chronic acidification of soils by acidic deposition, therefore, could theoretically lead to episodes stimulated by sea salts, or episodes of greater magnitude, in regions where otherwise the atmospheric deposition of neutral salts would have relatively little impact on surface water acidity. In the United States, the sea-salt effect has been documented in coastal streams of Maine (Health et al., 1992; Kahl et al., 1992); in Europe, there have been numerous examples of streamwater acidic episodes caused by the sea-salt content of particular rainfall events (Harriman and Wells, 1985; Langan, 1985, 1987; Howells and Brown, 1987).

2.3.3 Role of Acidic Deposition

Acidic deposition can contribute to episodic acidification by (1) providing direct inputs of acidic waters to surface waters, (2) conditioning watersheds, via the accumulation of sulfate and nitrate anions and H^+ from atmospheric deposition in the upper layers of watershed soils during relatively dry periods, and (3) lowering the chronic ANC of some systems and thereby lowering the minimum ANC values attained during episodes.

Several mechanisms exist through which acidic waters from atmospheric deposition can be delivered to streams and lakes without significant interaction or neutralization within the watershed. For example, the snow and ice cover on a lake melts directly into the lake, with no watershed contact. Snowmelt and rain on snow may travel over frozen surfaces to a receiving stream or lake. Precipitation (or throughfall) may fall directly into a water body, or travel through macropores in the soil with minimal soil contact. Under certain circumstances, all of these flowpaths can be important, resulting in a more or less direct transfer of acidic deposition into episodic acidification.

The second way in which acidic deposition can influence episodes is by conditioning watersheds, much like the natural processes of nitrification and organic acid production described in Section 2.3.2. Sulfate and nitrate anions and the associated H^+ ions delivered to a watershed by wet and dry deposition may be stored in upper soil layers during dry periods and flushed from the system during especially large hydrological events (Lynch and Corbett, 1989; Turner et al., 1990). By increasing NH_4^+ pools in watershed soils, atmospheric deposition of NH_4^+ may also contribute to nitrification (Aber et al., 1989).

Finally, in some watersheds with low pre-episode ANC levels (< 25 μeq/L), chronically high sulfate concentrations appear to create conditions that allow other processes to create acidic, high-aluminum conditions with relatively small ANC depressions during episodes (Galloway et al., 1987). Nitrate pulses, organic acid pulses, and the sea-salt effect are examples of processes that work in conjunction with high chronic sulfate concentrations to create acidic episodes.

Both natural and anthropogenic processes, therefore, may cause episodic acidification. In some areas of the United States, especially in the Northeast and Mid-Atlantic regions, sufficient evidence exists to conclude that acidic deposition has significantly increased the severity (minimum ANC and pH; maximum aluminum) of episodes in some waters (Wigington et al., 1990). The relative importance of acidic deposition and other factors varies among regions, among surface waters, and even among events within a given lake or stream.

Episodes induced by organic acids have been documented or implicated in a number of studies in the United States, for example, Raven Fork, North Carolina (Jones et al., 1983), Camp Creek, Washington (Lefohn and Klock, 1985), several small streams near the coast of Maine (Haines, 1987; Haines et al., 1990; Kahl et al., 1992), and wetland and upland streams in the Bickford Watershed, Massachusetts (McAvoy, 1989), as well as in some catchments in Canada and Europe (Borg, 1986; Kerekes et al., 1986a,b; Seip et al., 1979). In other instances, organic acids have been discounted as major contributors to episodes, for example, in Pancake Creek in the Adirondacks, New York (Driscoll et al., 1987a,c), and in the inlets and outlets to Harp Lake, Ontario (Servos and Mackie, 1986; LaZerte and Dillon, 1984).

In the United States, nitrate seems to have the greatest influence on episodes in the Northeast, where it is the anion most consistently associated with episodes, especially during the winter and spring. For example, Schaefer et al. (1990) concluded that nitrate was an important contributor to episodic ANC depressions in Adirondack lakes with relatively low pre-episode ANC ($< 25\ \mu eq/L$). However, the relative contributions of acidic deposition and natural nitrification to these nitrate pulses are somewhat uncertain. Galloway et al. (1987) calculated that the mass of nitrate accumulated in snowpack was sufficient to account for all of the nitrate transported into two of their three study lakes in the Adirondacks. On the other hand, studies by Peters and Driscoll (1987) and Rascher et al. (1987) suggest that in the western part of the Adirondacks, nitrate is generated primarily by nitrification within the forest floor.

Aber et al. (1989) proposed a unified theory that accounts for the relative influence of nitrogen pools within forest systems and nitrogen deposited by atmospheric deposition. They defined nitrogen saturation as a situation in which the inputs of atmospheric nitrogen exceed the demand for this element by watershed plants. In addition, Aber et al. (1989) hypothesized that nitrate can accumulate in forest soils in areas receiving elevated levels of nitrogen inputs from the atmosphere that exceed the nitrogen requirements of forests. Atmospheric inputs of nitrogen add to forest nitrogen pools, including the forest floor. In areas receiving large inputs of nitrogen via atmospheric deposition, nitrate liberated by nitrification of organic nitrogen stored in the forest floor, then, is a product both of background nitrogen in the forest and nitrogen introduced by atmospheric deposition.

In watersheds with elevated nitrogen deposition regimes, the transition of forests from a condition in which virtually all nitrogen received from atmospheric deposition is retained by the forest to a condition in which stream waters draining the forest have high nitrate concentration year round (nitrogen saturation) can be considered as a series of stages (Stoddard, in press; Kahl et al., 1993). According to the hypothesis of nitrogen saturation stages, increased nitrate export during episodes is an indicator of an intermediate stage of nitrogen saturation.

Sulfate pulses have been identified as an important contributor to ANC depressions during episodes in many of the streams studied in Pennsylvania, the Southeast, and the Upper Midwest (Jones et al., 1983; Schnoor et al., 1984; Lynch and Corbett, 1989; Barker and Witt, 1990; Elwood et al., 1991). In some instances, in the Southern Blue Ridge Province and the Upper Midwest, these sulfate pulses can be linked, at least partially, to internal mineral sources of sulfate in the watershed (Elwood et al., 1991; Schnoor et al., 1984). Studies in Pennsylvania, on the other hand, suggest that atmospheric deposition is the primary source of sulfate, stored in the watershed during relatively dry periods and then exported during wet periods (Barker and Witt, 1990; Lynch and Corbett, 1989).

The importance of various causes of episodic acidification also seems to vary depending on the pre-episode ANC level in the stream or lake. In the Adirondacks, Schaefer et al. (1990) found that decreases in base cations (i.e., dilution) were very important contributors to episodic ANC depressions in lakes with large initial ANC levels. In lakes with low pre-episode ANC ($< 25\ \mu$eq/L), however, nitrate increases were more important than base cation decreases. Other studies in the United States and Canada have confirmed this pattern (Kennedy et al., 1989; Molot et al., 1989).

More research is needed in all regions of the United States and elsewhere to better quantify the effects of acidic deposition and natural processes on episodic acidification. In addition, our current understanding of how flowpaths change during episodes is largely qualitative. These uncertainties imply major knowledge gaps that limit our ability to quantitatively project episodic acidification and the importance of acidic deposition. This report is a step in addressing these gaps.

2.4 BIOLOGICAL EFFECTS

In general, we assume that acidic episodes are biologically significant. But definitive, lasting effects on biological communities resulting specifically from episodic acidification, as opposed to chronic acidification, have been demonstrated in relatively few systems (J. Baker et al., 1990a).

Many uncertainties remain concerning the biological significance of episodic acidification and the characteristics of episodes that are most important in determining biological effects.

2.4.1 Evidence for Effects

There is no doubt that fish and other organisms can experience significant mortality when exposed to adverse chemical conditions for even short time periods. Numerous laboratory bioassays have demonstrated that, in waters with sufficiently low pH and/or elevated aluminum, mortalities can occur within 1 to 5 days (Schofield and Trojnar, 1980; Baker, 1981; France and Stokes, 1987; Holtze and Hutchinson, 1989; Schweinforth et al., 1989). In addition, increased mortality of fish and benthic invertebrates exposed *in situ* to episodic acidification has been observed in several field studies (Hultberg, 1977; Sharpe et al., 1983; Andersson and Nyberg, 1984; Harvey and Whelpdale, 1986; Schofield et al., 1986; Lacroix and Townsend, 1987; Gunn, 1989). In general, the more severe the conditions, the more rapid the toxic response. The more acid-sensitive the organism, the more likely it is to be significantly affected during short-term exposures.

Although it is clear from both laboratory and field bioassays that short-term exposures to low pH and elevated aluminum can increase mortality, examples of studies that definitively link episodic acidification to population-level effects in the field are relatively rare. This may reflect in part (1) the difficulty in distinguishing between effects from short-term and long-term acidification, (2) the complexity of population responses to acidification, and (3) the need to account for the coincident physical stresses on fish during periods of high discharge, which can have direct adverse effects and also increase fish sensitivity to adverse chemical conditions. Evidence for the importance of episodes includes the following:

- Records of fish kills during acidic episodes, although limited primarily to fish kills of Atlantic salmon and seatrout (sea running brown trout) in Norwegian rivers (e.g., Jensen and Snekvik, 1972; Leivestad et al., 1976; Hesthagen, 1989) and fish kills in hatcheries (Schofield and Trojnar, 1980; Jones et al., 1983).

- A few observations of changes in biological communities through time that apparently resulted from episodic acidification, specifically long-term declines in Atlantic salmon and seatrout populations associated with the fish kills in Norwegian rivers noted above (Leivestad et al., 1976) and the observed loss of acid-sensitive benthic invertebrates in stream systems in Sweden (Engblom and Lingdell, 1984) and Ontario (Hall and Ide, 1987) that now experience episodic acidification.

- Whole-system experiments demonstrating the response of benthic invertebrate communities (increased drift and loss of acid-sensitive species) and periphyton (increased periphyton biomass) to short-term pulses of acid and aluminum (Planas and Moreau, 1986; Ormerod et al., 1987; Weatherley et al., 1988; Hall, 1990).

- Comprehensive studies combining bioassay data on species sensitivity with information on life history dynamics and variations in surface water chemistry to estimate the potential importance of episodes.

  - Gunn (1987, 1989) and coworkers evaluated the effects of episodes on lake trout populations in Ontario lakes and concluded that episodic acidification during snowmelt did not appear to be a major factor responsible for the observed long-term decline of some populations.

  - France and Stokes (1987), on the other hand, concluded that observed pH depressions in Plastic Lake, Ontario, were likely to cause significant mortality of the amphipod *Hyalella azteca*, severe enough to cause a long-term reduction in population abundance.

  - Lacroix and coworkers (Lacroix, 1985, 1989a,b; Lacroix et al., 1985; Lacroix and Townsend, 1987) conducted detailed studies of Atlantic salmon survival and growth in Nova Scotia rivers. Loss rates of Atlantic salmon parr (age 0+ and age 1+) increased during periods of minimum pH associated with fall rains and increased water flow. Mortality rates during *in situ* bioassays also increased following pH declines associated with fall rainstorm events. Based on these results, Lacroix (1989b) concluded that pH decreases below 4.6–4.7 for periods longer than 20 days, or several days at pH 4.4–4.6, severely reduce parr densities and can completely eliminate year-classes of both age 0+ and age 1+ parr in Nova Scotia rivers.

2.4.2 Episode Characteristics That Influence Biological Response

We would expect the following factors to influence the effects of episodic acidification on aquatic biota: duration, magnitude, frequency, rate of change, chemical composition, timing, and spatial extent and distribution. Unfortunately, the data available to evaluate and quantify these relationships are quite limited, highly diverse, and difficult to integrate.

Several investigators have concluded that episode duration and magnitude are probably the most important factors controlling the toxic effects of episodes; for example:

- Curtis et al. (1989) exposed brook trout embryos continuously for 90 days (through the feeding fry stage) to low pH and to four variations of intermittent cycles. The primary determinant of fish survival was the peak H^+ concentration (minimum pH). For intermittent exposures using the same minimum pH, mortality correlated principally with exposure duration, rather than with the frequency of the pulse or the length of the recovery period.

- Gagen and Sharpe (1987a) observed that significant mortality of yearling brook trout in Linn Run, Pennsylvania, occurred only when total dissolved aluminum exceeded 200 μg/L for at least one day (Figure 2-4). Lower concentrations or shorter durations had minimal effect on fish survival.

- Schweinforth et al. (1989) found that survival of smallmouth bass and rainbow trout fry exposed to 4-hour, 12-hour, and 36-hour pulses of acid and aluminum was closely correlated with measures of both exposure magnitude and duration. In general, measures of minimum pH and maximum aluminum were better predictors of survival than were integrated expressions of dose (concentration over time). In all cases, fish survival was distinctly better after brief 4-hour pulses than after 12- or 36-hour exposures.

Although the results vary among species, life stages, and test conditions, increases in exposure duration, particularly in the range of 0.5 to 5 days, and in exposure magnitude clearly affect the severity of biological response. Acidic episodes with ANC $\leq$ 0 μeq/L and pH < 5.0 (and associated levels of inorganic aluminum) lasting 2–5 days have been shown to adversely affect a diversity of aquatic biota. Episodes of moderate severity (pH < 5.5 for 1–2 days) may cause significant effects on organisms that are relatively acid sensitive, including many species of minnows and mayflies (J. Baker et al., 1990a).

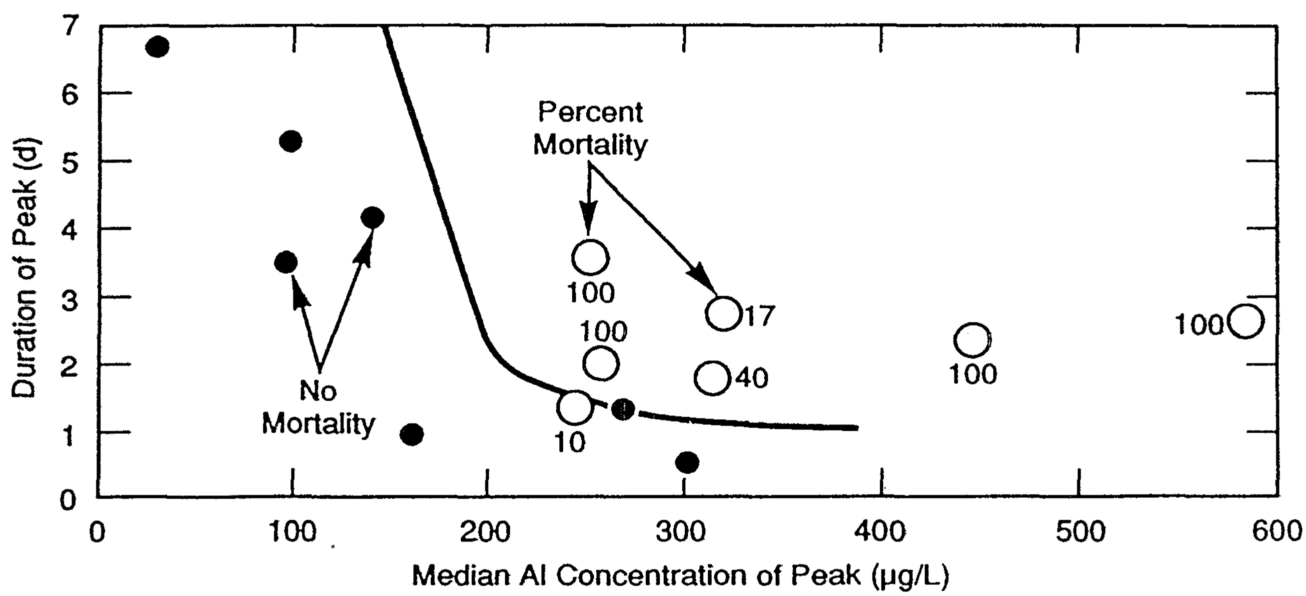

Figure 2-4. **Brook trout mortality in Linn Run (Pennsylvania) as a function of duration and median total dissolved Al concentration of coincident peaks in Al concentration. The hand-fitted curve separates data into regions of Al concentration and duration where mortality is and is not expected (source: Gagen and Sharpe, 1987a).**

The three most important chemical parameters affecting fish survival in acidified waters are pH (the H^+ ion), inorganic aluminum, and calcium (Schofield and Trojnar, 1980; Brown, 1982a,b, 1983; Baker and Schofield, 1982; Chester, 1984; Ingersoll, 1986; J. Baker et al., 1990a). During episodes, concentrations of these three ions often do not change in synchrony. For example, although pH and inorganic aluminum levels generally are highly correlated (Driscoll et al., 1980), aluminum levels for a given pH have been observed to be higher during the early stages of spring melt than later in the melt and higher during midwinter thaws than during the major spring melt (Hooper and Shoemaker, 1985; Hendershot et al., 1986; see Section 2.1). Base cations, calcium included, often experience an initial brief peak in concentration during events, followed by substantial dilution and a decline in concentration (Johannessen et al., 1980). These shifts in the relative concentrations of H^+, aluminum, and calcium through time and among different events may further complicate attempts to predict episode toxicity.

J. Baker et al. (1990a) present an integrated index, termed the acidic stress index, that expresses the combined effects of pH, inorganic aluminum, and calcium on fish mortality. Although they were developed using chronic, constant-exposure bioassays, these functions also may be useful for interpreting fish responses to episodes. J. Baker et al. (1990a) developed separate indices for several different fish species of varying acid sensitivity. All are based on laboratory bioassays with fish larvae soon after swim-up and the initiation of feeding. The model for brook trout fry, for example, is as follows:

$$ASI = \frac{100}{1 + \exp[-23.49 + 5.35*pH + (2.97 \times 10^{-3})*Ca - (1.93 \times 10^{-3})*Al]}$$

where ASI is the acidic stress index, equivalent to the expected percent mortality of brook trout fry when exposed to constant levels of pH, inorganic aluminum, and calcium for 21 days. Calcium (Ca) is expressed in μeq/L and inorganic aluminum (Al) in μg/L.

The sensitivity of fish and other organisms to acidic conditions varies with age and among life stages. Generally, early life stages (eggs and larvae/fry) tend to be more sensitive than older individuals (Kwain, 1975; Baker and Schofield, 1985). In many cases, these highly sensitive life stages occur only at certain times of the year and in specific locales. Brook trout, for example, show a strong preference for spawning in areas of groundwater upwelling with fairly high pH (Johnson and Webster, 1977). Brook trout eggs and yolk-sac fry may be reared, therefore, in an environment with pH substantially higher than in the overlying water column. Only after the fry emerge from the spawning bed, which occurs during spring or slightly before snowmelt, may brook trout early life stages be exposed to acidic waters and episodes. Thus, the timing and spatial distribution of episodes relative to the occurrence of sensitive life stages may be critical to population success.

Some organisms (e.g., adult fish) are able to detect and avoid acidic waters. Avoidance reactions to potentially lethal waters with low pH and/or elevated aluminum have been demonstrated experimentally in the laboratory (van Coillie et al., 1983; France, 1985; Gunn and Noakes, 1986; Pedder and Maly, 1986; Peterson et al., 1989) and observed in some field situations. For example, Muniz and Leivestad (1980) observed behavior of brown trout in a single tributary stream with higher pH during snowmelt in the River Gjov, Norway. Fish confined in cages in the main river died within one week. During the reacidification of Cranberry Lake in the Adirondacks, New York, following an earlier treatment of lime, large numbers of the brook trout that had been stocked in the lake were collected in the lake outlet emigrating from the lake as the pH dropped from 6.5 to 5.0 during a period of increased discharge (Gloss et al., 1989). More than 50% of the fish in the lake were lost due to emigration. Finally, several field studies have demonstrated that acid-sensitive stream benthic invertebrates (e.g., the mayfly *Baetis rhodani*) often respond to acid or aluminum stress with dramatic increases in downstream drift (Hall et al., 1980, 1985; Bernard, 1985; Raddum and Fjellheim, 1984; Ormerod et al., 1987; Weatherley et al., 1988; Hopkins et al., 1989). At least in the initial stages of response, this increase in drift probably reflects behavioral avoidance by organisms attempting to escape adverse chemical conditions.

Thus, the degree to which episodes affect fish and other biota may be largely a function of (1) the mobility of the organism, (2) the availability and accessibility of alternate habitats or refuge areas that are less acidic and otherwise suitable for survival, and (3) the ability of biota to recolonize the area after the episode without long-term adverse effects on the fish population or biological community. In streams, refugia may include tributaries with higher pH, areas further downstream where pH levels are generally higher, or zones of groundwater inflow.

Although theoretically sound, most statements regarding the biological importance of the timing and spatial extent of episodic acidification have not been specifically tested and proven in the field. In addition, comprehensive studies of the effects of episodic acidification on fish communities in streams are lacking. This report begins to address these uncertainties.

SECTION 3
STUDY AREAS

ERP field research took place in three regions, the Adirondack Mountains of New York, the Catskill Mountains of New York, and the Northern Appalachian Plateau of Pennsylvania. In each region, we conducted intensive studies of the chemistry and biological effects of episodes at 4–5 sites (Figure 3-1). Study streams were selected based on the following criteria:

- Range of baseflow chemistry, but focusing on streams likely to be adversely affected by episodic acidification (i.e., those with baseflow ANC between 0 and 100 μeq/L).
- Range of expected episode severity, based on existing data or preliminary water chemistry samples collected during site selection.
- Physical suitability for fish survival and reproduction, and similar size and quality fish habitat.
- Indigenous fish populations, of the species of interest, present in at least some part of the stream system at some time of the year.
- At least one reference stream per region, with similar physical and baseflow chemical characteristics as the other streams but relatively stable pH during events and no anticipated adverse effects on fish populations in the stream.

Because of the intensity of field activities, logistical considerations also influenced site selection. These factors included ease and availability of access, ease of installing chemical and hydrological monitoring equipment, ease of fish sampling and monitoring, proximity to central research facility or field station, and proximity of sites to each other, to minimize travel times between sites. The sites selected for the ERP are considered generally representative of other streams in regions with baseflow ANC between 0 and 100 μeq/L. Brook trout occurred in all 13 ERP streams. Brief descriptions of these regions and the physical characteristics of the ERP study streams and associated watersheds are provided in the following subsections.

3.1 CHARACTERISTICS OF STUDY SITES

3.1.1 Adirondack Mountains

The Adirondack Mountains form a large (24,000 km^2) forested upland and mountainous region in northern New York (Driscoll et al., 1991). Geologically, the Adirondack Mountains are among the oldest landforms in eastern North America and are similar in origin to the Laurentian Shield of Canada. The bedrock is predominantly granitic gneisses and metasedimentary rocks. Surficial

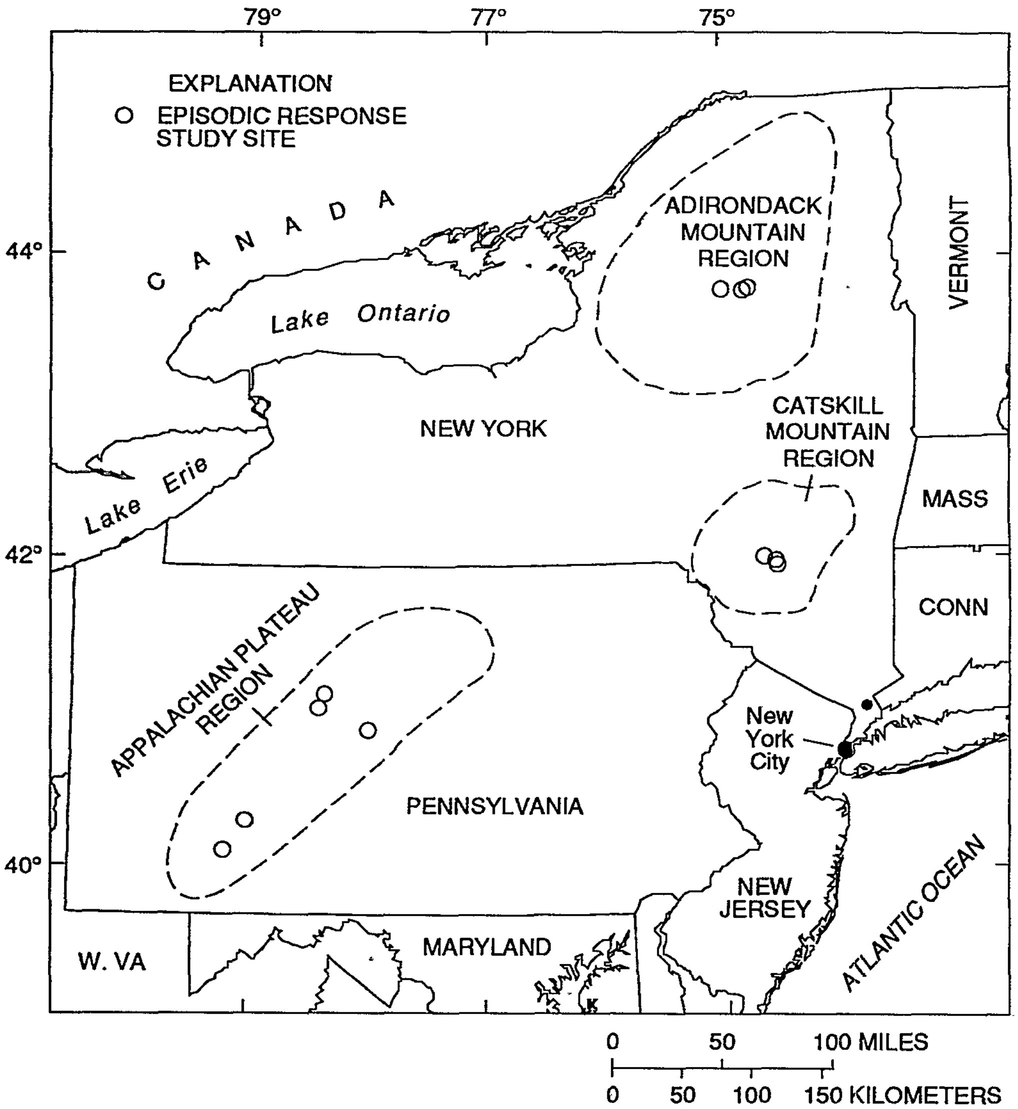

Figure 3-1. Location of the three Episodic Response Project regions (adapted from Ranalli et al., 1993).

deposits in the region are the result of glacial activity. The soils, developed from this glacial till, are typically acidic Spodisols. The thickness of the glacial till and soil layers generally decreases with increasing elevation.

The four ERP study streams are located in the southwestern highlands area of the Adirondacks (Figure 3-2), where elevations range from 400 to 800 m. All the streams are in the Oswegathchie-Black watershed, within 10 km of Eagle Bay, New York. The southwestern Adirondacks and Oswegathchie-Black watershed, in particular, have the highest proportion of low pH (< 5.0) and fishless lakes in the Adirondacks (Kretser et al., 1989). In addition, numerous prior studies have documented the adverse effects of chronic acidification on fish communities in the area (Driscoll et al., 1980; Schofield and Driscoll, 1987; J. Baker et al., 1990b).

The study area is surrounded almost entirely by state forest lands within Adirondack State Park that have not been logged or burned since the late 1800s. The principal forest cover type is a northern hardwood/conifer mixture, including sugar maple (*Acer saccharum*), red maple (*Acer rubrum*), yellow birch (*Betula alleghaniensis*), and American beech (*Fagus grandifolia*) interspersed with red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), eastern hemlock (*Tsuga canadensis*), and eastern white pine (*Pinus strobus*).

The bedrock, surficial geology, and soil types in the ERP watersheds are typical of the Adirondack region; differences among the four watersheds appear relatively minor (Kretser et al., in press). Soils are predominantly well drained, loamy soils overlaying bedrock and sandy glacial till ranging in depth from 20 to 66 cm. All of these soils are quite acidic in the upper organic-rich horizons and low in available nutrients and base saturation. The Fly Pond Outlet and Bald Mountain Brook watersheds contain the highest percentage of deep soils (Becket and Skerry series). Both watersheds contain deep soils to the southeast and thin, rocky, steep terrain to the north and west. The Buck Creek catchment is characterized by steep terrain with numerous boulders, rock ledges, and thin soils (Becket-Lyman series). The Seventh Lake Inlet watershed is a combination of moderately sloping terrain with deep bouldery soils (24% Becket-Skerry) and bedrock outcrops.

Three streams—Buck Creek, Bald Mountain Brook, and Seventh Lake Inlet—are typical first or second order Adirondack streams (Table 3-1). Minimum watershed elevations range from 560 m to 570 m for the four streams; maximum elevations range from 710 m to 775 m. All of the Adirondack study streams are relatively small and short (< 2.7 km), compared with the study streams in the Catskills (3.7–8.4 km) and Pennsylvania (5.0–8.8 km).

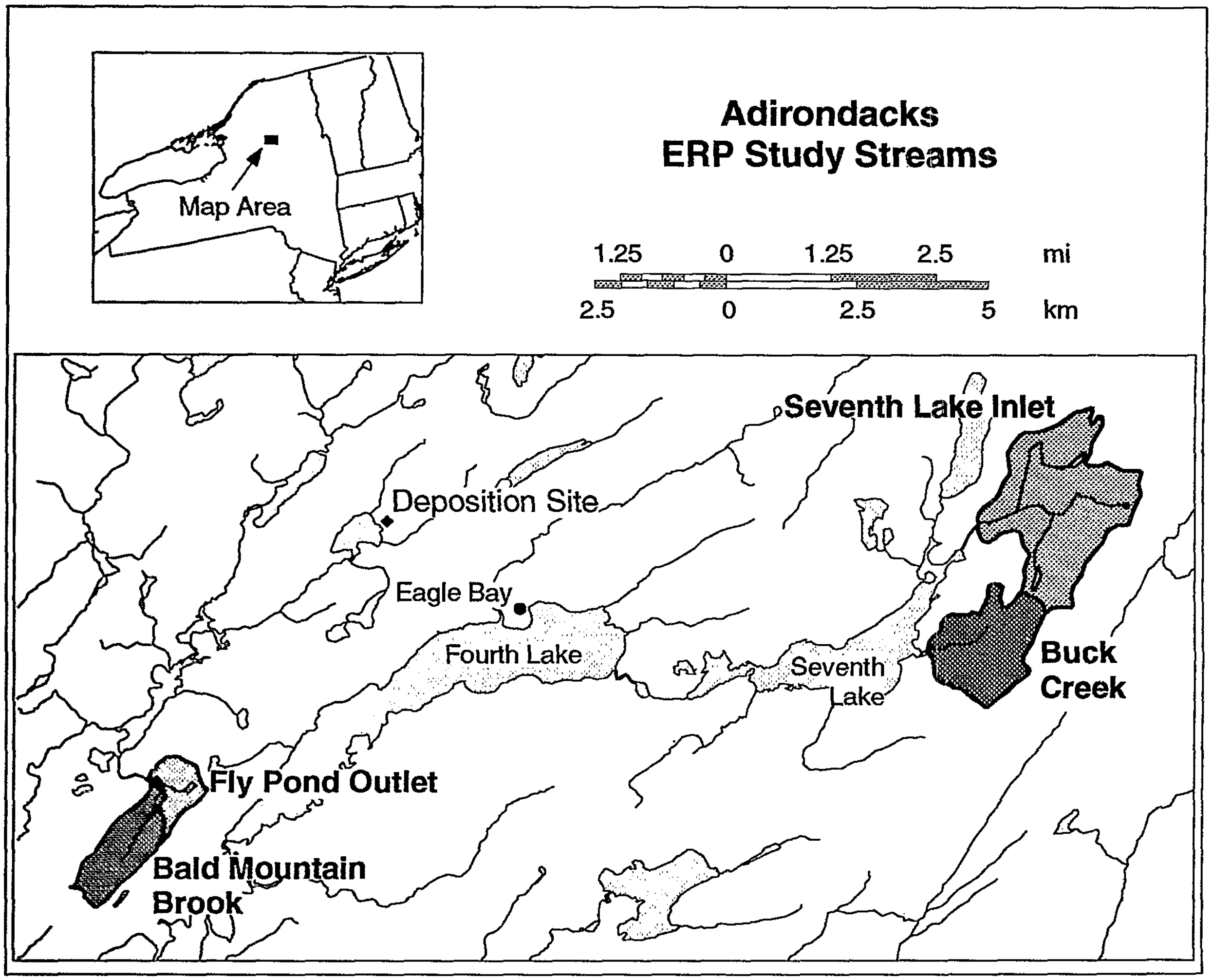

Figure 3-2. Location of Adirondack study streams.

Table 3-1. Physical Characteristics of the Four ERP Study Streams in the Adirondack Mountain Region, New York

	Fly Pond Outlet	Bald Mountain Brook	Buck Creek	Seventh Lake Inlet
Stream Gage:				
Latitude (N)	43°45'05"	43°45'03"	43°44'39"	43°45'49"
Longitude (W)	74°54'34"	74°54'39"	74°43'20"	74°42'11"
Watershed				
Area (km^2)	0.9	1.8	3.1	6.4
Max. elevation (m)	710	715	775	725
Min. elevation (m)	563	570	560	570
Lake or pond present	Yes	No	No	Yes
Wetland present	Yes	Yes	Minor	Yes
Soil series	Lyman Becket	Lyman Becket	Becket-Lyman Becket-Skerry	Lyman Becket-Skerry Becket-Lyman Adams-Croghan
Stream				
Order	1	1	2	2
Length (km)	0.8	2.2	2.1	2.7
Gradient (m/km)	9	25	50	31

As its name implies, Fly Pond Outlet is the outlet of a small pond. It is the smallest of the ERP streams, with a watershed area of 0.9 km^2, mean stream width of 1.6 m, and mean stream depth of 6 cm in the intensively studied reach. The stream gradient, 9 m/km, is also the lowest of the four Adirondack ERP streams. Substrate in the study reach is primarily sand, gravel, and silt. Fly Pond (2.4 ha), upstream of the study area, is the primary water source for Fly Pond Outlet. Several wetland areas also occur in the Fly Pond Outlet watershed above the ERP study reach. With circumneutral water chemistry, Fly Pond Outlet was the reference stream for ERP biological studies in the Adirondacks.

Bald Mountain Brook, immediately adjacent to Fly Pond Outlet, is nearly twice as large (watershed area 1.8 km^2, mean width 3.0 m) and more than twice as steep (gradient 25 m/km) as Fly Pond Outlet. Stream substrate consists primarily of gravel with large amounts of cobble and boulder. The Bald Mountain Brook study reach, at 143 m long, is the shortest of the ERP study reaches. A natural falls at the upper end of the study reach restricts fish movements further upstream. Immediately below the study reach, Bald Mountain Brook and Fly Pond Outlet join, flowing from this point 1.2 km downstream before draining into West Lake. Extensive wetland areas occur in the upper portions of the Bald Mountain Brook watershed.

Buck Creek and Seventh Lake Inlet drain directly into Seventh Lake; the ERP chemistry study sites were located 100 m and 700 m upstream from the lake in Buck Creek and Seventh Lake Inlet, respectively. Seventh Lake Inlet is the largest of the Adirondack ERP streams, with a drainage area of 6.4 km^2 and mean width of 5 m in the study reach. Three small ponds and numerous beaver ponds occur in the upper watershed. Gravel and boulder are the major substrate types; the numerous boulders in the study reach provide excellent cover for fish. Buck Creek drains an area of 3.1 km^2. The mean width at the study reach was 3.1 m, with a relatively steep gradient of 50 m/km. The pool/riffle ratio (53%) was the highest among the four Adirondack study streams. Gravel is the major substrate type, with large amounts of cobble and boulder.

3.1.2 Catskill Mountains

The Catskill Mountains, which form the northeastern end of the Appalachian Plateau, are the uplifted remnants of a massive Devonian delta that fed into a shallow inland sea to the west (Stoddard and Murdoch, 1991). The high ridges are predominantly erosional remains, and the physiography suggests that the relief is due largely to stream action. The bedrock consists of sandstone and interspersed conglomerates (60%) and mudstone or siltstone (40%). Soils are generally Entisols and Inceptisols.

Surface waters within the Catskills are almost entirely streams; ponds and lakes are rare, especially in the upper watersheds. Precipitation, stream discharge, and stream chemistry have been monitored in a number of Catskill streams since the early 1980s (Murdoch, 1988; Stoddard and Murdoch, 1991; Murdoch and Stoddard, 1992). However, relatively few studies have been conducted on the potential effects of acidification on stream biota. Although many streams in the region exhibit ANC ≤ 0 during high-flow events, few are chronically acidic (Murdoch, 1988).

Four first, second, or third order streams were selected for the ERP: the upper reaches of the East Branch of the Neversink; Biscuit Brook and High Falls Brook, both of which are tributaries to the West Branch of the Neversink; and Black Brook, a tributary to the Beaverkill (Ranalli et al., 1993) (Figure 3-3). Black Brook and High Falls Brook are relatively well buffered. Both streams were considered reference streams for the ERP, although High Falls Brook can experience large ANC declines during major storms.

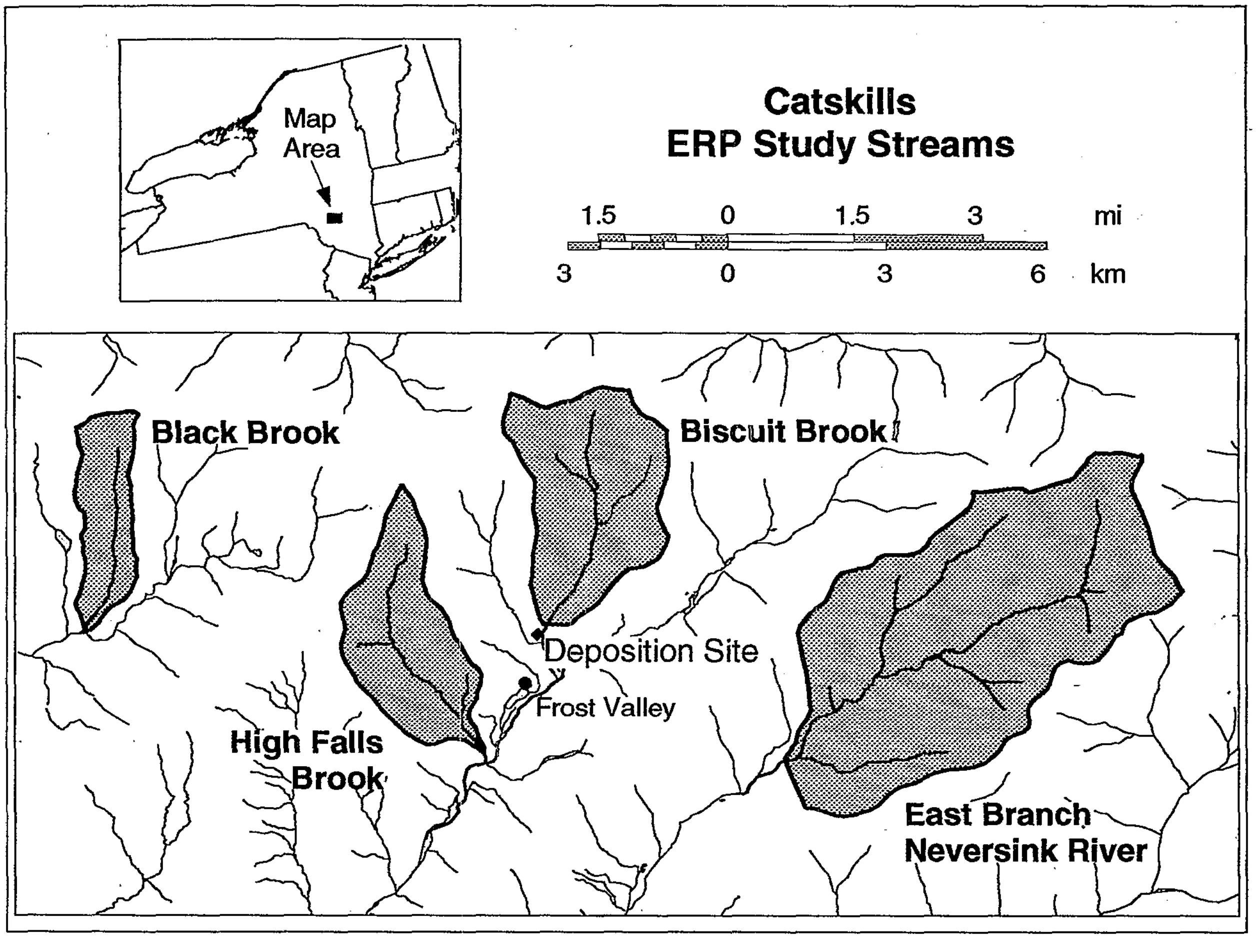

Figure 3-3. Location of Catskill study streams.

Low-order basins in the Catskills are generally characterized by steep gradients; thin, glaciated soils with extensive bedrock outcrop; and bedrock or large cobbles in stream channels. Stream gradients tend to be steeper than in comparable Adirondack Mountain streams, and Catskill streams typically flow through fewer wetlands and ponds than Adirondack streams. In general, the Catskill ERP study streams drained larger watersheds (3.7–23.1 km^2), occurred at higher elevations (591–1,280 m), and were substantially longer (3.7–8.4 km) than the Adirondack ERP study streams (Tables 3-1 and 3-2). The East Branch of the Neversink was the largest stream studied in the ERP.

Surficial deposits in the headwater valleys of the Catskills are a combination of continental-glacier-derived deposits oriented in the direction of regional ice movement and reworked or secondarily scoured alpine-glacier deposits oriented perpendicular to the valley. Rich (1934) reported thick till and thinner ground moraine from repeated glaciations in most of the upper Beaverkill and upper East Branch Neversink valleys and pockets of thick drift in the lower High Falls and Biscuit Brook basins. Morainal loops, consisting of unstratified till deposited at the end of local valley glaciers, occur midway up the Biscuit Brook basin and in the headwaters of the East Branch Neversink and Beaverkill basins. Many glacial deposits in the headwaters are thin, and many streams are incised to bedrock.

Surficial material in the Catskills consists primarily (at least 90%) of local rock and sediment. The percentage of exotics, particularly carbonate-bearing sediments, varies locally and could be a significant factor explaining chemical differences among streams. Way (1972) found calcite and pyrite in the shale along Route 17 to the south of the study area and along Route 28 to the northeast. However, no evidence of pyrite has been found in the ERP watersheds.

Soils in the Catskills are generally categorized in the Arnot-Oquaga-Lackawanna association, which are excessively drained to well-drained soils mainly on steep slopes (Ranalli et al., 1993). Soils in the ERP study area are varied, but are predominantly shallow boulder soils on steep slopes and are conducive, therefore, to rapid precipitation runoff; they are also moderately to extremely acidic. The Lackawanna soils in the East Branch of the Neversink watershed contain a fragipan of very low permeability at depths of 45 cm to 90 cm. Runoff from these soils is rapid. The Biscuit Brook and High Falls Brook watersheds contain mainly Arnot and Oquaga soils, well drained and moderately permeable with no fragipan; these soils range in thickness from 35 cm to 60 cm. The Black Brook watershed contains Wellsboro soils on gentle slopes near the stream channel; these are deep, bouldery loam soils that contain a fragipan below a depth of 50 cm.

Table 3-2. **Physical Characteristics of the Four ERP Study Streams in the Catskill Mountain Region, New York.**

	Black Brook	High Falls Brook	Biscuit Brook	East Branch Neversink
Stream Gage:				
Latitude (N)	42°00′42"	41°58′40"	41°59′43"	41°58′01"
Longitude (W)	74°36′13"	74°31′21"	74°30′05"	74°26′54"
Watershed				
Area (km^2)	3.7	7.1	9.8	23.1
Max. elevation (m)	1,140	1,170	1,120	1,280
Min. elevation (m)	681	591	628	651
Lake or pond present	No	No	No	No
Wetland present	No	No	No	No
Soil series	Wellsboro	Arnot Oquaga	Arnot Oquaga	Lackawanna
Stream				
Order	1	2	2	3
Length (km)	3.7	4.9	4.5	8.4
Gradient (m/km)	45	60	45	26

Alluvial deposits are present in the flood plains of Black Brook and the East Branch Neversink near the ERP chemistry monitoring sites.

All the ERP Catskill watersheds are covered largely by northern hardwood forest, including American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), and yellow birch (*Betula alleghaniensis*) (Stoddard and Murdoch, 1991). Hemlock (*Tsuga canadensis*) also occur throughout the region, primarily along stream banks. The upper watersheds became a state preserve in 1870, and many of the Catskill watersheds contain first-growth forests at elevations above 730 m.

3.1.3 Northern Appalachian Plateau in Pennsylvania

Most of the western portion of Pennsylvania falls within the Northern Appalachian Plateau, an area of high hills and low mountains ranging in elevation from 180 m to more than 1,000 m. Forest cover of oak and mixed northern hardwoods dominates the landscape in areas of high elevation and high relief. More than 90% of the stream basins in the region are underlain by sandstones, shales, and siltstones (L. Baker et al., 1990). Unlike the Adirondack and Catskill regions, the Northern Appalachian Plateau areas in Pennsylvania were not glaciated during the late Wisconsinan era.

Five streams were studied for the ERP: Linn Run and Baldwin Creek in the Laurel Hill area of southwestern Pennsylvania and Roberts Run, Stone Run, and Benner Run in the northcentral part of the state (Figures 3-4 and 3-5). Several prior studies have evaluated episodic acidification and the toxic effects of episodes on fish in streams in the Laurel Hill area (Sharpe et al., 1983, 1984; Gagen and Sharpe, 1987a,b). Periodic fish kills of trout stocked in the spring have been reported in Linn Run, on the western slope of Laurel Hill, since the early 1960s (Sharpe et al., 1984). Linn Run State Park pumped well water into Linn Run during the periods April 7 to June 27, 1989, and April 3 to June 22, 1990. The pumping, which was below the sampling station, was done to maintain trout that were stocked 0.5 km below the ERP study reach on Linn Run during these periods. Baldwin Creek and Benner Creek in southwestern and northcentral Pennsylvania, respectively, served as reference streams for the ERP in the two areas.

All the ERP study streams in Pennsylvania are second order (DeWalle et al., 1993). Baldwin Creek drains an area of 5.3 km^2; watershed areas for the other four streams are similar, ranging between 10.0 km^2 and 11.6 km^2 (Table 3-3). Watershed elevations range from maximum elevations of 701–893 m in the five watersheds to 439–582 m at the ERP stream gages. Stream gradients are moderate in the three northcentral streams (35–39 m/km), but steeper in the two Laurel Hill streams (58 m/km in Linn Run and 112 m/km in Baldwin Creek). Except for Linn Run, the stream channels appear stable, with stones ranging from 20 cm to 60 cm commonly covering the bottom. Areas with sandy deposits and exposed bedrock also occur. The stream bed in Linn Run consists of boulders, smaller rocks, and gravel, similar in size to the substrate in the other study streams, but not well anchored and less stable.

Both the northcentral and southwestern study areas are underlain primarily by sandstone with some shale bedrock. Dinicola (1982) provided additional detail on the geology of Laurel Hill, an anticlinal mountain (oriented northeast-southwest) within the Allegheny Mountain system. Major rock units exposed in the Laurel Hill study area include Allegheny group sandstones and shales, Pottsville group sandstones, Mauch Chunk shale, Loyalhanna limestone, and Pocono sandstone.

Soils in the region are acidic, and are composed of residual material weathered from noncalcareous bedrock of sandstone and shale (DeWalle et al., 1993). Soils on the upper part of the study basins, which approach 30% slope, are sandy loam in texture and extremely rocky. Major soil series in the Laurel Hill watersheds are Calvin, Gilpin, Dekalb, and Cavode. Hazleton and Clymer soils occur in the three northcentral study watersheds; Cookport soils also occur in the Roberts Run and Stone Run watersheds in northcentral Pennsylvania.

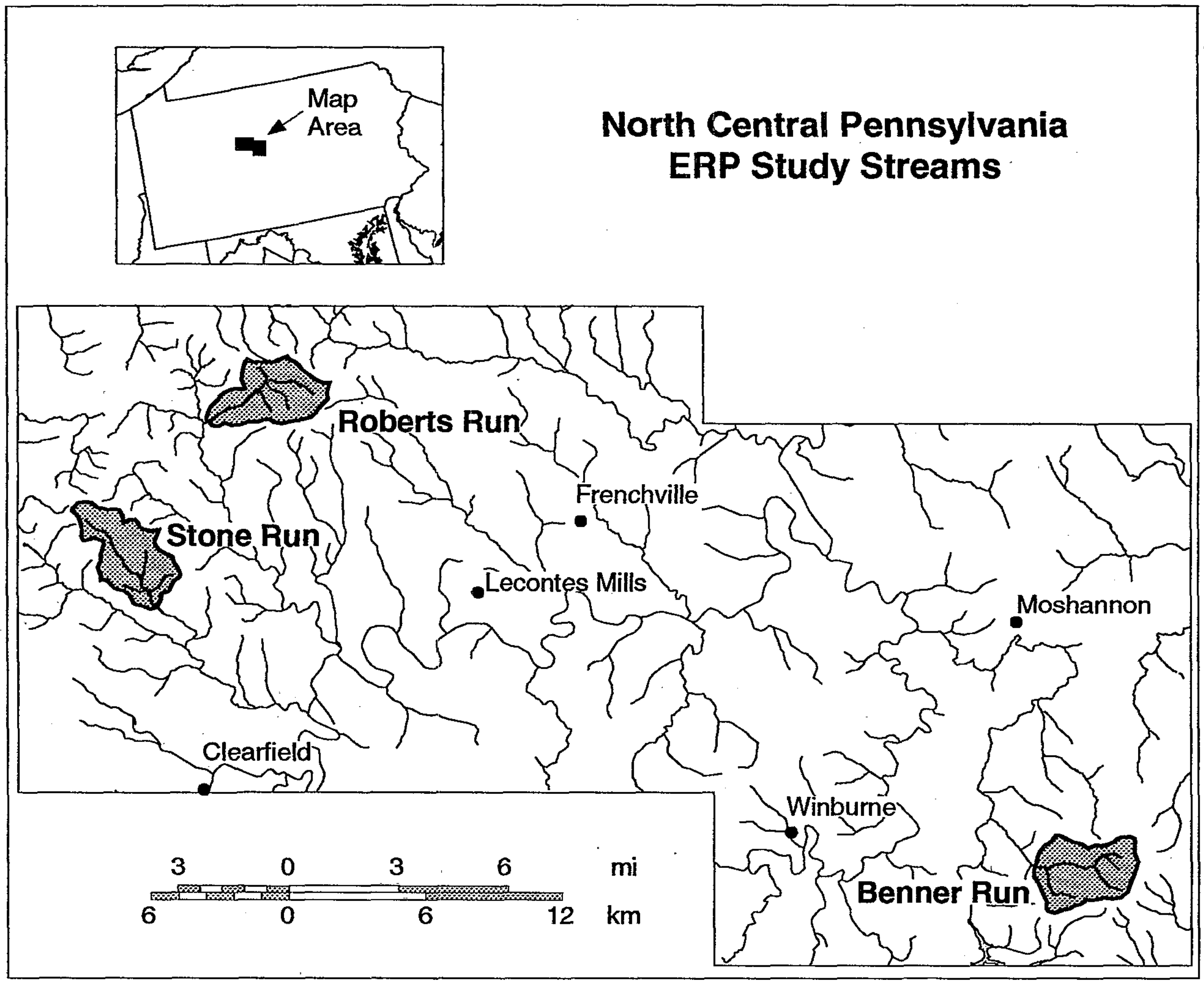

Figure 3-4. Location of three study streams in north central Pennsylvania.

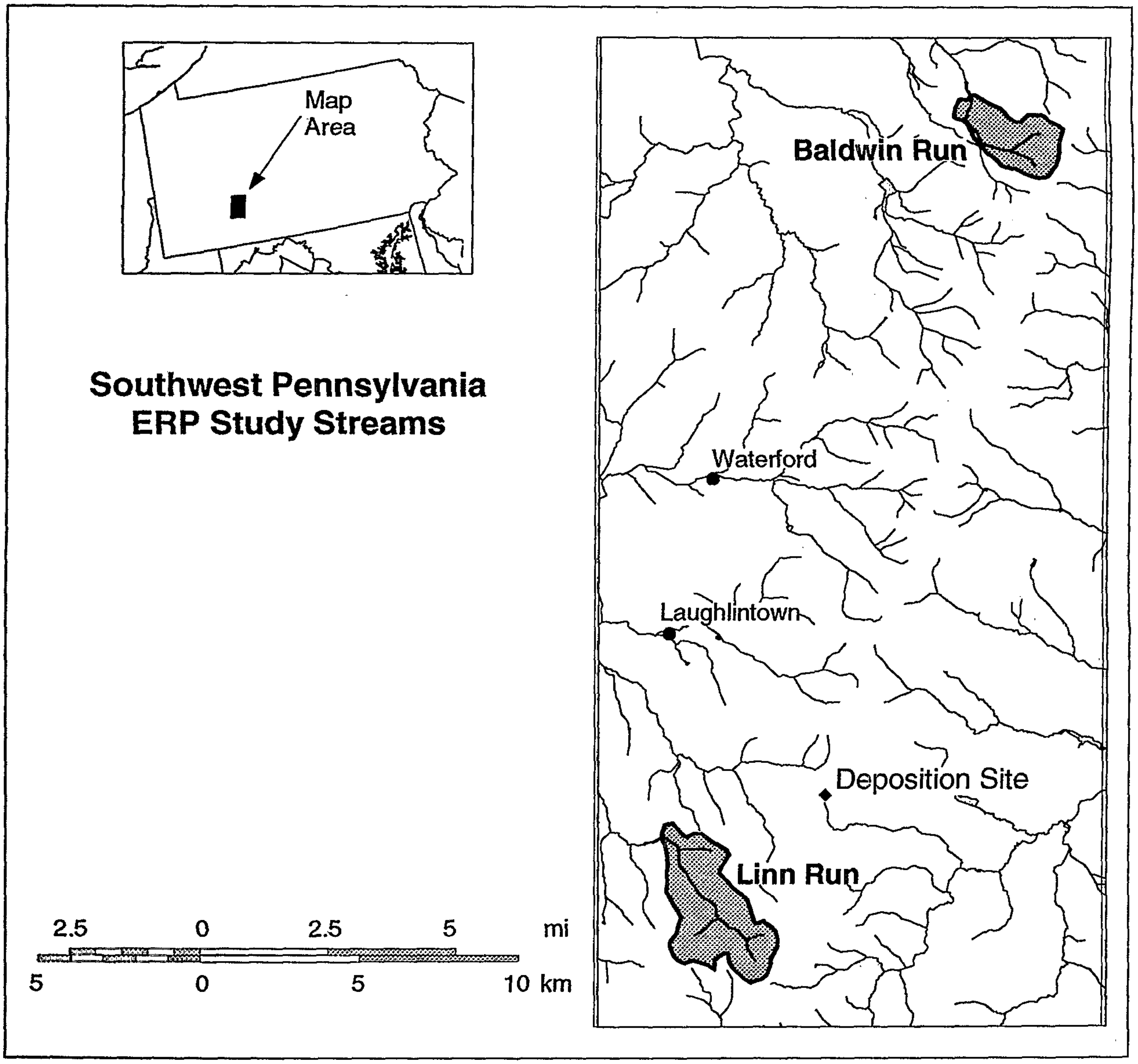

Figure 3-5. Location of two study streams in southwest Pennsylvania.

Table 3-3. Physical Characteristics of the Five ERP Study Streams in the Northern Appalachian Plateau, Pennsylvania

	Benner Run	Roberts Run	Stone Run	Baldwin Creek	Linn Run
Stream Gage:					
Latitude (N)	40°56′04″	41°10′12″	41°05′52″	40°21′05″	40°08′40″
Longitude (W)	78°01′22″	78°24′22″	78°26′48″	79°03′04″	79°12′37″
Watershed					
Area (km^2)	11.3	10.7	11.6	5.3	10.0
Max. elevation (m)	749	733	701	832	893
Min. elevation (m)	582	509	494	439	573
Lake or pond present	No	No	No	No	No
Wetland present	No	Yes	No	No	No
Soil series	Hazleton Clymer	Cookport Hazleton Clymer	Cookport Hazleton Clymer	Calvin Gilpin	Calvin Dekalb Cavode
Stream					
Order	2	2	2	2	2
Length (km)	5.4	8.1	6.4	5.0	8.8
Gradient (m/km)	36	39	35	112	58

The five basins are completely forested with large pole-sized to mature deciduous tree species predominating (DeWalle et al., 1993). The stands on the study watersheds appear to have regenerated from logging conducted early this century. Some timber cutting has been conducted on several of the basins. Salvage logging of scattered trees killed by gypsy moth defoliation was conducted in some of the upland areas of the Roberts Run catchment during the period of data collection. Tree defoliation and mortality, caused by gypsy moths, was also observed on the Stone Run watershed. However, no salvage logging was performed during the study periods. In 1973 and 1974, clearcuts were made in the uplands of Benner Run, which cover approximately 12% of the total watershed area. No detailed forest inventory exists for the study watersheds. However, red oak (*Quercus rubra*), scarlet oak (*Quercus coccinea*), chestnut oak (*Quercus prinus*), red maple (*Acer rubrum*), and black cherry (*Prunus serotina*) are common species of deciduous trees. Eastern hemlock (*Tsuga canadensis*) are common in the riparian areas of the streams. Eastern white pine (*Pinus strobus*) is scattered in the uplands. Extensive wetland areas exist in the Roberts Run watershed.

3.2 DEPOSITION

As discussed in Section 1.4, we were unable to perform analyses to evaluate the role of atmospheric deposition characteristics on episodic acidification in the study streams. This section provides a brief summary of wet deposition measured at ERP deposition stations.

Precipitation sampling began in August 1988 at Biscuit Brook in the Catskills, in December 1988 at Moss Lake in the Adirondacks, and in February 1989 at Linn Run in Southwest Pennsylvania. Periods of continuous sampling ended in January 1990 at Linn Run, in May 1990 at Biscuit Brook, and in June 1990 at Moss Lake. Data from the Pennsylvania State University MAP3S site were collected during the period January 1989 through June 1990. Figures 3-6 through 3-9 present monthly ion wet deposition and precipitation water equivalent.

The central and southwest Pennsylvania deposition collection sites received the largest monthly loadings of H^+ and SO_4^{2-} and had the greatest monthly variations of these ions (Figures 3-8 and 3-9) (Barchet, 1991). Distinct seasonal fluctuations in ion concentrations were clearly evident only at Moss Lake. In general, SO_4^{2-} concentrations were highest during the warmer months and lowest during the winter months. At the other sites, large month-to-month changes in ion concentrations masked seasonal variation. Sulfate and NO_3^- together accounted for more than 80% of the anions at all sites. Sulfate contributed a higher percentage of the total anion concentrations during summer than in winter.

Wet deposition, which occurs intermittently, is one of two atmospheric pathways for chemical inputs to watersheds (Barchet, 1991). The other pathway, dry deposition, occurs continuously. However, the ERP did not attempt to measure dry deposition. Research at NOAA dry-deposition sites near some of the ERP sites suggests that, over an annual period, dry deposition of S (SO_2 and SO_4^{2-} aerosol) and N (HNO_3 and NO_3^-) species is a factor of 0.30 to 1.00 for S and 0.48 to 0.81 for N of the wet deposition rate (Barchet, 1991). As the distance from emission sources increases, the relative contribution of dry deposition to total deposition decreases. For the ERP, the Pennsylvania sites would be expected to have higher proportions of dry deposition than the Adirondack sites, with the Catskill sites intermediate.

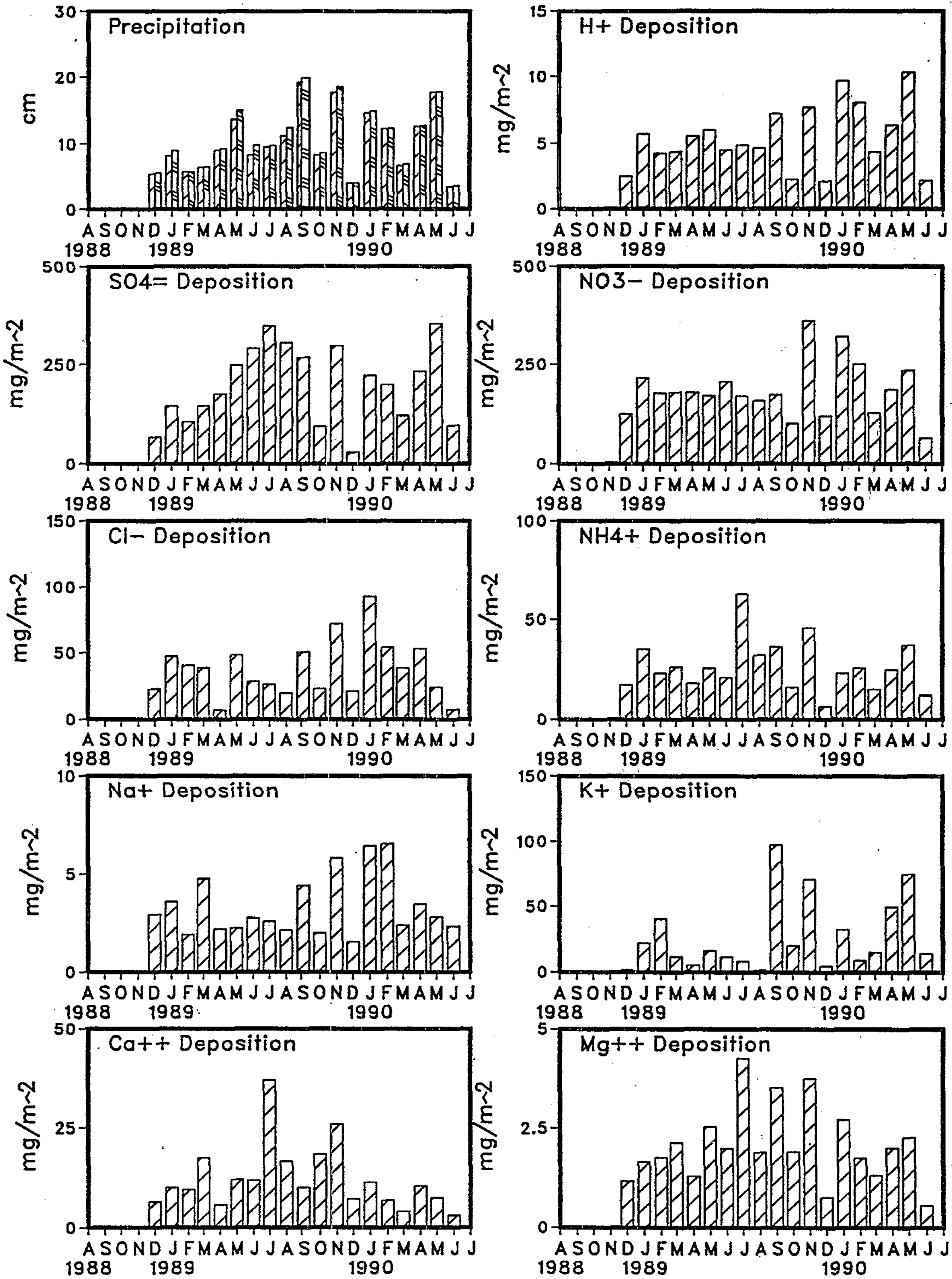

Figure 3-6. Monthly precipitation water equivalent depth and precipitation-weighted average ion deposition for the Moss Lake wet deposition collection site in the Adirondacks (adapted from Barchet 1991). Two precipitation values shown are for rain gage (left) and the greater of rain gage or wet deposition bucket (right).

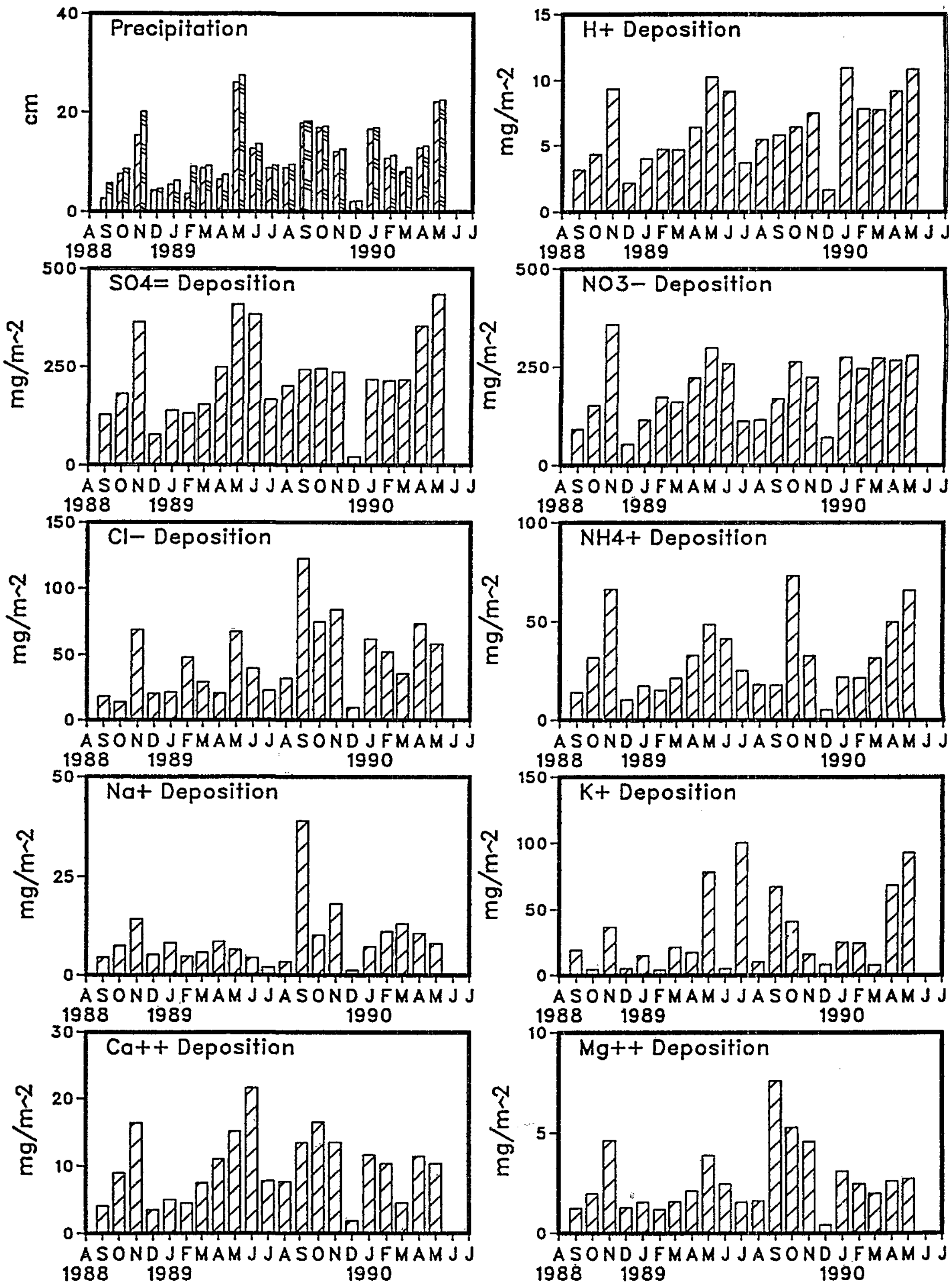

Figure 3-7. **Monthly precipitation water equivalent depth and precipitation-weighted average ion deposition for the Biscuit Brook wet deposition collection site in the Catskills (adapted from Barchet 1991). Two precipitation values shown are for rain gage (left) and the greater of rain gage or wet deposition bucket (right).**

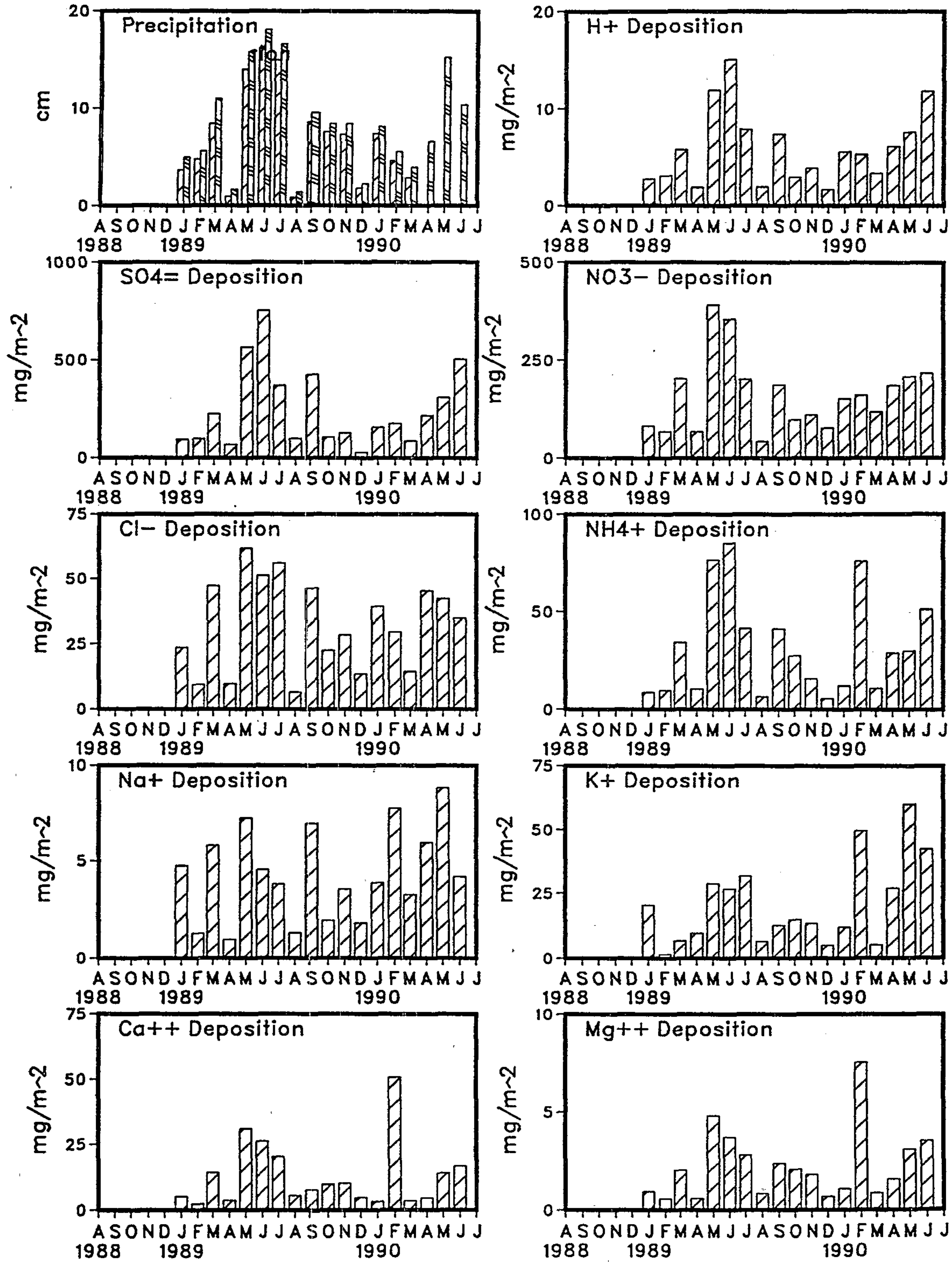

Figure 3-8. **Monthly precipitation water equivalent depth and precipitation-weighted average ion deposition for the Pennsylvania State University wet deposition collection site in central Pennsylvania (adapted from Barchet 1991). Two precipitation values shown are for rain gage (left) and the greater of rain gage or wet deposition bucket (right).**

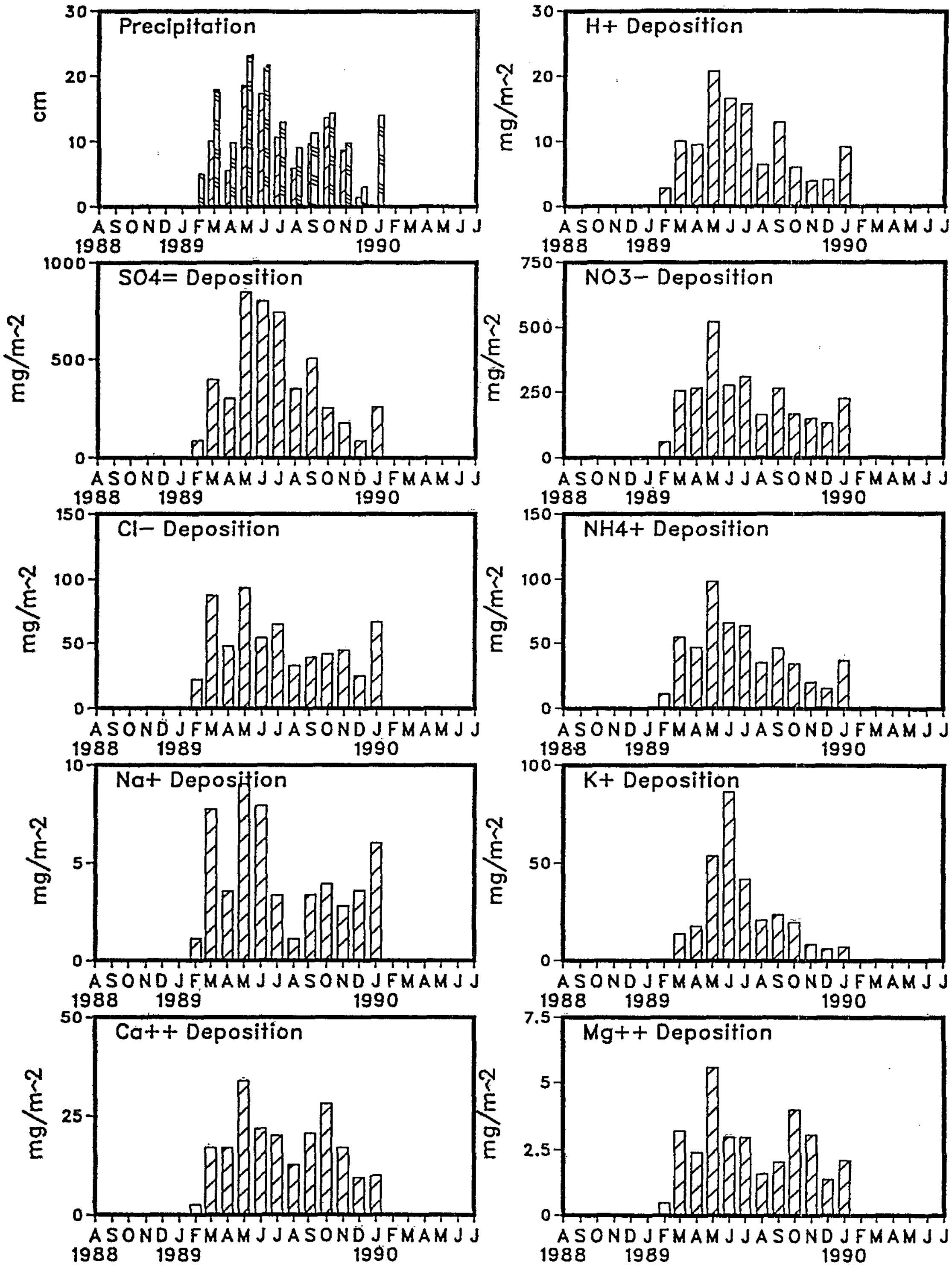

Figure 3-9. Monthly precipitation water equivalent depth and precipitation-weighted average ion deposition for the Linn Run wet deposition collection site in southwest Pennsylvania (adapted from Barchet 1991). Two precipitation values shown are for rain gage (left) and the greater of rain gage or wet deposition bucket (right).

SECTION 4
METHODS

This section describes the field, analytical, and data analysis methods used to collect the ERP data. The introductory paragraphs provide an overview of the (QA/QC) program. The sections that follow briefly summarize the methods for each major component of the ERP: atmospheric deposition (Section 4.1), stream discharge (Section 4.2), stream chemistry (Section 4.3), biological effects (Section 4.4), and database management (Section 4.5). Further information on the ERP methods and QA/QC procedures are provided in the Methods Reports prepared by each regional cooperator (Kretser et al., in press; Ranalli et al., 1993; DeWalle et al., 1993), and in the ERP quality assurance project plan (Peck et al., 1988).

The primary purpose of the QA/QC program, an integral part of the ERP, was to maximize the probability that data collected during the project met or exceeded data quality objectives, and thus would allow scientifically sound interpretations of the data. Peck et al. (1988) established objectives for seven data quality indicators (representativeness, completeness, comparability, precision, bias, detection limits, and tolerable background levels). Procedures were established to (1) ensure that collection and measurement techniques were standardized among all participants, (2) monitor performance of the various measurement systems being used in the ERP to maintain statistical control and to provide rapid feedback so that corrective measures could be taken before data quality was compromised, (3) allow for periodic assessment of the performance of measurement systems and their components, and (4) verify and validate that reported data are sufficiently representative, unbiased, and precise so as to be suitable for their intended use. Appendix B summarizes the performance of ERP water quality laboratories. Additional QA/QC information is included subsections that follow.

4.1 ATMOSPHERIC DEPOSITION

4.1.1 Wet Deposition

This section briefly summarizes procedures used to collect wet deposition samples. Section 3.2 provides an overview of wet deposition characteristics during the study period. Additional details on deposition monitoring are described in Barchet (1991).

For each of the three study regions, a precipitation sampling site was selected according to standard criteria for deposition sites (Barchet, 1991). The sites, selected in August 1988, were located in clearings within deciduous or mixed deciduous-coniferous forests. Site installations, coordinated and supervised by each watershed research group, were completed in early 1989. Most sites operated through June 1990, except for the Linn Run site, which ceased operation at the end of January 1990. Field operation procedures were the same as those followed at sites in the Multistate Atmospheric Power Production Pollution Study (MAP3S) Precipitation Chemistry Network (Dana, 1982).

Figure 4-1 illustrates the locations of the three wet deposition monitoring sites established specifically for the ERP in relation to other ERP rainfall measurement and stream chemistry monitoring activities being carried out in the vicinity of those sites. A wet deposition monitoring site that was part of the U.S. Department of Energy's (DOE) MAP3S Precipitation Chemistry Network was used to provide wet deposition data for the central Pennsylvania streams in the Northern Appalachian Plateau study region [designated Pennsylvania State University (PSU) site]. The Moss Lake site in the Adirondacks was located about 6 km southeast of the Big Moose monitoring site in the Electric Power Research Institute's Operational Evaluation Network (OEN). The Biscuit Brook site in the Catskill Mountains study area was co-located along with an NADP site, which operates on a weekly sampling protocol. Biscuit Brook is 81 km north-northwest of West Point in the Hudson River valley, which is the only other NADP monitoring site within 100 km. Linn Run is 5 km east-northeast of the Linn Run ERP watershed, 20 km south-southwest of the Baldwin Creek ERP watershed, and 45 km north-northeast of a wet deposition monitoring site in Laurel Hill State Park (elevation 616 m). The PSU site is 15 km north of the Leading Ridge NADP site.

Each precipitation sampling site was equipped with an Aerochem Metrics automatic wet-only precipitation collector and a Belfort recording, weighing rain gauge. The collection bucket in the precipitation sampler was exposed only when rain or snow were detected. Each site was visited at least once per week (even during dry periods) to check on the operation of the collector and rain gauge. A daily precipitation sampling protocol was adopted for this study. Samples were sent monthly to DOE's Pacific Northwest Laboratory (PNL) for chemical analysis and archiving.

Precipitation samples received by PNL from the ERP sites were merged with other samples being analyzed as part of the MAP3S Precipitation Chemistry Network. The analytical operations of PNL's precipitation chemistry laboratory, including data entry and archiving, are described in

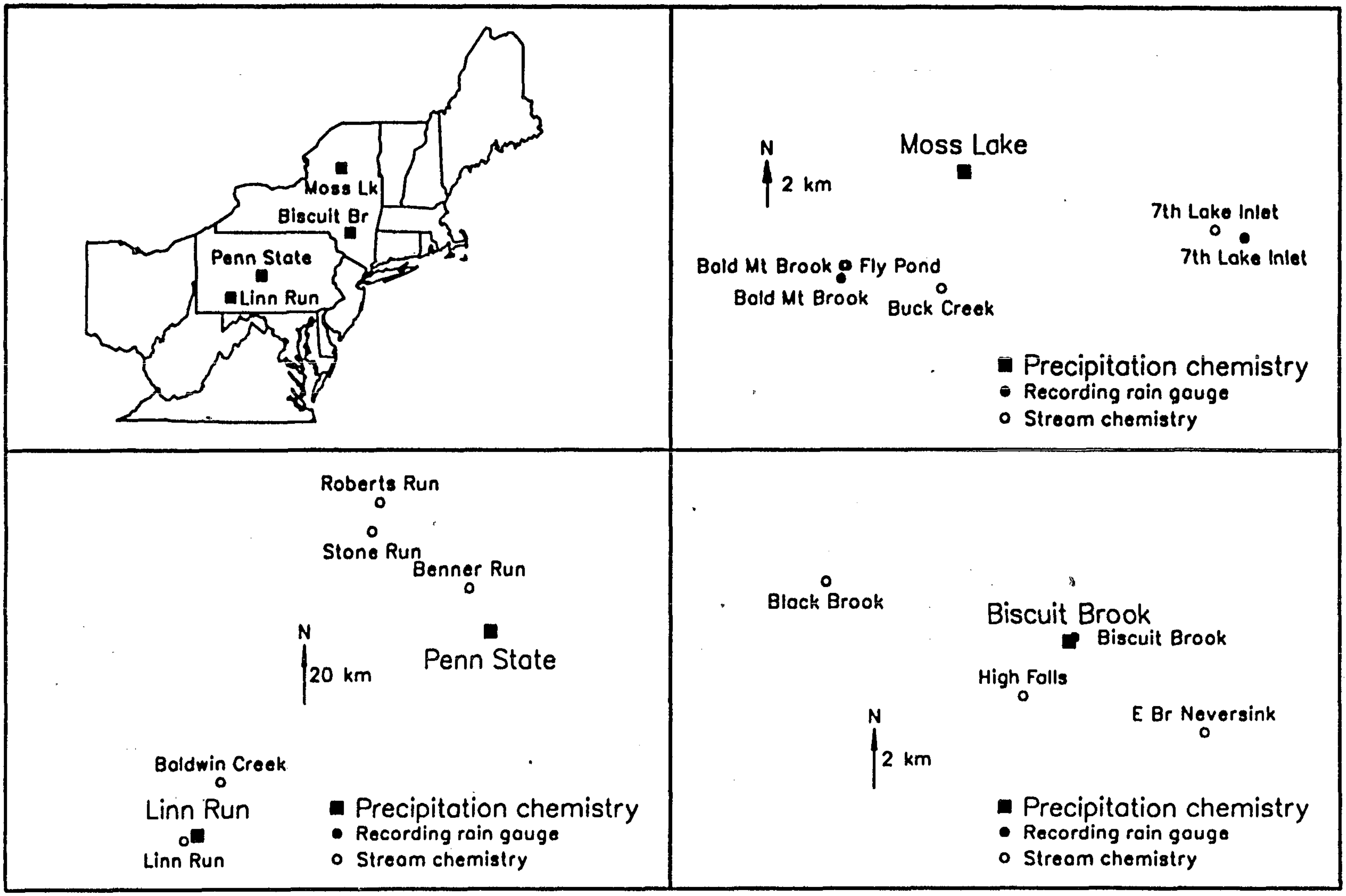

Figure 4-1. Locations of ERP wet deposition monitoring sites and other ERP rainfall measurement and stream chemistry sites (from Barchet, 1991).

detail in a series of standard operating procedures (SOPs) in Barchet (1991). Table 4-1[1] lists the analysis methods employed. For each analytical procedure, measurements of blanks were used to assess contaminants; QC standards were used to evaluate accuracy. Duplicate samples were used to determine the precision of the analyses.

4.1.2 Snow Measurements

Measurements of snowpack water equivalence and chemistry were made as part of the ERP but are not included in this report. During both winter/spring periods of the ERP, investigators in each region conducted snow surveys to determine the water equivalent and chemical characteristics of seasonal snowpacks. In the Adirondacks, snow core transects were established in the Bald Mountain Brook and Seventh Lake Inlet watersheds. Snow cores were collected weekly during 1989 and biweekly during 1990. In the Catskills, snowpack was sampled biweekly during the period of accumulation and weekly during spring snowmelt in the Black Brook, Biscuit Brook, and East Branch Neversink River watersheds. A similar procedure was followed to sample snowpacks in each of the Pennsylvania watersheds. Additional details regarding snow measurements are available in DeWalle et al. (1993), Kretser et al. (in press), and Ranalli et al. (1993).

4.2 STREAM DISCHARGE

To allow the continuous measurement of stream discharge, a stream gauging station was located on each of the study streams. In the Adirondacks and Catskills, stream stage was measured at 15-minute intervals with a pressure transducer connected to a Campbell™ CR-10 data logger. The transducer was located inside a 2-in PVC pipe that was bolted to bedrock in the stream channel as close as possible to a nonrecording staff gauge. A stage-discharge relationship was established for each stream by measuring discharge over a wide range of stages and plotting the discharge against the stage at which the discharge occurred. This relationship was used to convert stage measurements into discharge. Investigators in Pennsylvania used strip chart, water level recorders instead of pressure transducers to measure stream stage continuously. The accuracy of automated stream stage measurements was checked routinely by comparing the stage measurements of the pressure transducers or water level recorders to staff gauges located nearby in the streams.

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[1] Since this section contains so many tables, we have placed them all at the end of the section, beginning on page 61.

4.3 STREAM CHEMISTRY

This section describes the methods used to collect water samples (Section 4.3.1) and to perform chemical analyses (Section 4.3.2). Section 4.3.3 presents analyses used to estimate inorganic monomeric aluminum for water samples for which aluminum speciation was not performed. Section 4.3.4 briefly summarizes *in situ* measurements made during the ERP but not included in the report.

4.3.1 Water Sampling

A vital part of the ERP was collecting water samples often enough to characterize episodes that occurred during the study period. Because of the uncertain occurrence of episodes, ERP investigators used automated pumping samplers to collect samples during periods of high flow. Controlled by a data logger, the Instrumentation Specialties Company (ISCO^{TM}) pump samplers were programmed to collect samples at fixed time intervals (2–6 hours) or at specified changes of stage level (e.g., 0.05 ft). Water samples generally were retrieved from the pump samplers within 24 hours of collection. During periods of time when problems occurred with the data loggers or samplers, grab samples were collected by field crews during episodes to the extent possible. In addition, streamwater samples were collected manually on a weekly basis when field crews made visits to service instrumentation. During radio telemetry studies of fish movement during episodes, additional grab samples were collected. Each day during the telemetry study, a sample was collected at any location where a tagged fish was observed.

All water samples were collected in polyethylene bottles with unlined plastic caps. The samples were packed in ice and transported to laboratories in coolers. In general, one field blank sample was collected and submitted with each batch of samples to monitor container contamination.

4.3.2 Laboratory Methods

All the regional cooperators had their own laboratories for analysis of samples collected in their regions. Sample handling procedures are summarized in Table 4-2. Methods and equipment used in the analysis of water samples are summarized in Table 4-3. Most samples were analyzed for the full suite of analytes presented in Table 4-3. However, selected samples associated with radiotelemetry work (subsection 4.4.2.1) were analyzed only for pH, ANC, and total dissolved aluminum. Selected episode samples were analyzed for total monomeric and organic monomeric aluminum in addition to the other measured variables. Aluminum speciation was based upon the methods of Barnes (1975) and Driscoll (1984) and is described completely in Pagano (1990). In the laboratory, blanks, check samples, and performance evaluation samples were routinely used.

Laboratory data verification was also routinely performed using cation/anion balances and conductivity computation checks. If the measured cation/anion balance did not agree with the theoretical balance within 10%, or if conductivity calculated from individual ion measurements did not agree with measured conductivity within 15%, the sample was completely reanalyzed.

On a monthly basis, the ERP laboratories received performance evaluation samples from the EPA Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV). These samples consisted of two natural and three synthetic samples and covered the ranges of ionic values anticipated to be measured in the study. In addition, the ERP laboratories participated three times a year in a round-robin audit program administered by the Long Range Transboundary Air Pollution (LRTAP) Program. Water chemistry performance objectives and performance evaluation sample results are presented in Appendix B.

4.3.3 Estimation of Inorganic Monomeric Aluminum

As noted, concentrations of inorganic monomeric Al (Al_{im}) were measured in only a subset of the water samples collected. However, from a biological perspective, it is very important to include this chemical parameter in the characterization of episodes and biological study periods. Therefore, regression models were developed to estimate Al_{im} based on other measured chemical and physical variables. Separate models were developed for each study stream. Separate models were also evaluated for each season, for streams and seasons with sufficient data (Tables 4-4 and 4-5). Measurements of Al_{im} occurred primarily during periods of intensive biological studies in the spring and fall. Thus, season-specific models were considered only for fall 1988, spring 1989, fall 1989, and spring 1990.

Predictor variables considered included discharge, total dissolved Al, ANC, pH, DOC, sulfate, nitrate, chloride, sum of base cations, and conductivity. The log-transformed and nontransformed forms of each variable were included in maximum r^2 analyses with both log- and nontransformed Al_{im}, to identify sets of variables strongly associated with in-stream variations in Al_{im}. Based on these results, four to ten alternative models were selected for testing, including models with one or more interaction terms. For streams and seasons with sufficient data ($n \geq 30$), the data set was randomly divided into two-thirds for model calibration and one-third for model testing. Each candidate model was calibrated using ordinary least squares regression, and observed and predicted levels of Al_{im} were then compared for both the calibration data set and the test data set. The following criteria and statistics were used to select the final model:

- Lowest model mean square error, calculated using nontransformed Al_{im} data for consistency among models.
- Lowest mean square error for the test data set (sum of the squared differences between observed and predicted nontransformed Al_{im} divided by one less than the number of observations).
- No statistically significant decrease in fit for the test data set compared to the calibration data (based on the ratio of the mean square errors for the two data sets).
- All predictor variables in the model significant at $p \leq 0.1$, and preferably $p \leq 0.05$.
- Absence of significant autocorrelation, based on the Durbin-Watson D statistic (Neter and Wasserman, 1974).
- Absence of any highly influential data points, based on visual examination of residual plots and scatter plots comparing predicted and observed Al_{im}.
- Model well behaved when applied to the full data set (i.e., no unreasonable outliers or unusually high or low predicted values of Al_{im}), based on scatter plots of predicted Al_i versus pH and discharge.

The final model, used to estimate Al_{im}, was calibrated to the full data set.

For seasons with enough data ($n \geq 10$), the above steps were repeated to select the best model for estimating Al_{im} levels within that season. The need for a season-specific model, as opposed to the full-data (overall) model, was assessed by:

- Comparing the mean square errors for the season-specific and full-data models, calculated specifically for Al_{im} measurements during that season.
- T-test and signed rank tests to determine whether the full-data model estimates of Al_{im} for the season of interest were significantly biased.

If the season-specific model provided a significantly ($p \leq 0.05$) better fit than the full-data model, or if the estimates from the full-data model were significantly biased, then the season-specific model was used to estimate Al_{im} levels for that season. For each stream, if any season-specific model resulted in a significant improvement, then season-specific models were used for all seasons with enough data to calibrate a season-specific model, as long as the season-specific model did not perform significantly worse than the full-data model. For all other seasons and water samples, Al_{im} estimates were based on the full-data model. For those water samples with missing observations for one or more of the predictor variables, back-up models were used, that is, the best possible model involving only those predictor variables with no missing observations.

Some Al_{im} values (calculated as the difference between the measured total monomeric Al and measured organic monomeric Al) were zero or negative. Thus, for models involving log-transformed Al, a constant, 25 μg/L, was added to all inorganic Al observations before model calibration, and then subtracted from the model predictions.

For analyses of biological effects, the regression models just described were used to estimate Al_{im} only for those water samples where total and organic monomeric Al (required to calculate Al_{im}) were not measured. However, episode characterization analyses (See Section 6) involved only predicted Al_{im} values.

Tables 4-6 through 4-8 present the regression models that were used to estimate Al_{im} during time periods for which direct Al_{im} measurements were not made. When available, a season specific model was employed. Otherwise, an overall model was used. If samples were missing one or more predictor variables, a simpler, back-up model was used to estimate Al_{im}. Text, tables, and figures throughout the report identify whether directly measured Al_{im} or estimated Al_{im} is being reported.

4.3.4 *In Situ* Measurements

In situ measurements of stream pH, conductivity, water temperature, and air temperature were made using U.S. Geological Survey (USGS) mini-monitors rented from the USGS Instrumentation Facility in Mississippi. The mini-monitor data have not been used in primary data analyses of this report. In some regions, such as the Adirondacks, regional investigators had good success with the mini-monitor performance and were able to use the data to assist in interpreting biological results. However, in other regions, the performance of the mini-monitors was more sporadic. Each regional cooperator will use these data after a case-by-case evaluation of data quality.

4.4 BIOLOGICAL EFFECTS

Assessments of the biological effects of episodes in the study streams involved four major activities:

1. Conducting *in situ* bioassays to quantify the toxic effects of episodic acidification on fish.

2. Tracking fish movements during episodes using radiotelemetry and fish traps.

3. Monitoring fish population density and biomass.

4. Supplementing the existing populations of fish in the study reaches with transplants from other nearby stream reaches.

The methods employed for each of these research components are described in the following subsections.

Brook trout (*Salvelinus fontinalis*) was selected as the ERP target fish species. Brook trout is the sportfish most widely distributed in the small, low-ionic strength, headwater streams in the Adirondacks, Catskills, and Pennsylvania that are most susceptible to episodic as well as chronic acidification (Pfeiffer and Festa, 1980; Sharpe et al., 1987; Driscoll et al., 1991; Stoddard and Murdoch, 1991). Although brook trout are relatively acid tolerant (Baker and Christensen, 1991), this species is one of those mostly widely affected by acidification and acidic deposition, because of its distribution in a particularly sensitive habitat (J. Baker et al., 1990a). Thus, the status of brook trout populations and brook trout toxicity were selected as the primary indicators of effects of episodes on fish.

In situ bioassays were also conducted with at least one forage fish species, in addition to brook trout, in each stream. The forage species varied among regions and streams because of differences in native fish fauna. Blacknose dace (*Rhinichthys atratulus*), a highly acid-sensitive fish species, was used for bioassays in the Adirondacks; slimy sculpin (*Cottus cognatus*) were used in the Catskills; and either slimy sculpin or mottled sculpin (*Cottus bairdi*) were used in Pennsylvania, depending on the stream. All fish species caught during stream surveys (see Section 4.4.3) were recorded and included in the assessment of fish community status in the stream.

4.4.1 *In Situ* Fish Toxicity

In situ bioassays were conducted in the spring and fall, for a total of four test periods: fall 1988, spring 1989, fall 1989, and spring 1990. Test periods were selected to coincide with the expected timing of spring snowmelt and fall rainstorms. Experiments in the spring were often delayed, however, by the difficulties caused by high flows and/or ice cover on the streams. The test periods for each bioassay are presented in Tables 4-9 to 4-14.

All fish used in bioassays were wild strains, collected by electrofishing (see Section 4.4.3) from local streams with similar habitat. The objective was to test yearling brook trout in the spring, young-of-the-year brook trout in the fall, and adult or yearling forage fish in both periods. However, fish availability to some degree limited the ages and sizes of fish tested. Thus, the size (and presumably age) of fish varied (see Tables 4-9 to 4-14). We assumed all fish tested (of a given species) were equally sensitive; differences in fish size or age were not accounted for in statistical analyses.

Most tests involved organisms selected from a common pool; that is, fish of the appropriate species and size were collected from one or more circumneutral streams, combined into a common pool of fish for that region, and then randomly distributed from this pool into the bioassay test chambers in each stream in the region. Common pool tests were used to compare toxic responses among streams, since the groups of organisms tested in each stream presumably were equally sensitive to acid-aluminum stress. In some streams and test periods, bioassays were conducted with resident fish, collected from the population of fish residing in the stream (and/or from other study streams that experience episodic acidification). Comparisons between common pool and resident fish bioassays can be used to determine whether resident fish may have adapted to conditions in the stream, and thus be more tolerant of acid-aluminum stress, than the common pool fish collected from circumneutral streams.

Test fish were held in each stream in 4-L polyethylene jugs with at least two 7 x 12-cm openings, covered with 1- or 2-mm mesh fiberglass screening, to ensure adequate water exchange (after Johnson et al., 1987). The number of fish per jug varied (generally between 4 and 7), depending on the size of the fish. The total fish weight per container never exceeded 20 g wet mass in the Adirondacks and Catskills and 35 g in the Pennsylvania streams, to avoid stress from crowding. In addition, the largest fish in any bioassay container did not exceed the length of the shortest fish by more than 50%, to minimize problems with cannibalism. Multiple jugs (between 3 and 6) were used per test, so that at least 20 fish of each species were tested during most bioassays (see Tables 4-9 to 4-14). The jugs were placed within 0.6-m x 0.5-m x 0.3-m cages constructed of wood (5 cm x 5 cm) covered with 6.4- or 12-mm plastic screening. These cages were submerged and anchored near the continuous water quality monitoring station in a pool area or downstream of a large obstruction, such as a large rock, so that the test fish were not subjected to high current velocities. The jugs further reduced the velocity of the currents to which fish were exposed.

The numbers of fish in each bioassay container that were alive, dead, or visibly stressed (i.e., that had lost their equilibrium) were counted every 1–5 days. Generally, fish mortalities were checked daily during periods of storm or snowmelt events when water quality conditions were changing rapidly. Most tests lasted for a period of 20–40 days. Occasionally, tests were terminated after < 20 days if units in acidified waters experienced high levels of mortality (> 50–80%) or if weather conditions became unsuitable (e.g., in the late fall/early winter). Fish were not fed during the experiment; therefore, with longer exposure times, fish may have been increasingly stressed by starvation. For this reason, most analyses rely on the percent mortality observed after 20 days.

Percent mortalities are compared to the measured and estimated (see Section 4.3) water chemistry for the stream during the bioassay period, in particular, the magnitude and duration of episodes of low pH and elevated Al_{im} levels. For these response surface analyses, fish mortalities are expressed as the combined result from all jugs tested within a given stream, for a given species, fish source, age group, and test period. More detailed analyses, for example, assessing changes in mortality over time, are being conducted by the cooperating scientists in each region and will be published in subsequent journal papers.

Continuous records of stream chemistry were required to estimate episode magnitude and duration and median chemistry during each bioassay period. Two alternative methods were considered: (1) interpolation between chemistry samples and (2) concentration-discharge relationships. Low regression coefficients ($r^2 < 0.25$) indicated poor correlations between Al_{im} concentrations and discharge in some streams and seasons. For this reason, direct interpolation was selected as the primary basis for estimating the continuous chemical record. Chemical concentrations at any point in time were estimated from linear interpolation between measured values (both grab and event samples). Periods with inadequate chemistry data, for interpolating with reasonable confidence, were identified by comparing plots of interpolated chemistry over time to the continuous discharge record. Bioassay periods with inadequate coverage were deleted from subsequent analyses (n = 8, all of which were fall 1988 bioassays in the Catskills). The time-weighted median value for a bioassay period was defined as the chemical concentration which half the time was exceeded and half the time concentrations were below, based on the interpolated chemical record.

4.4.2 Fish Movement

Individual fish movements were tracked using radiotelemetry in each region during the fall and spring (fall 1989 and spring 1989 and 1990 in all regions; plus fall 1988 in Pennsylvania streams). In addition, fish traps were used in selected Adirondack streams to monitor upstream and downstream fish movements. Both types of information provide insight into changes in fish movement patterns during episodes and the ability of fish to behaviorally avoid stressful chemical conditions.

4.4.2.1 Radiotelemetry

Miniature radio transmitters (1–3 g) were placed in 6–15 adult brook trout per stream per experiment. The location of each fish was then determined daily or every other day using a portable radio receiver. Fish movements were tracked for a period of about 30 days or longer, or until the experiment was ended because of transmitter malfunction or regurgitation. Studies were conducted in at least one reference stream and one nonreference stream in each region per season (spring or fall). The timing and duration of each study, and streams and number and size of brook trout involved, are summarized in Tables 4-15 to 4-17. Only brook trout movements were evaluated, because forage fish (blacknose dace and sculpin) in the study streams were too small to carry the radio transmitters without adverse effects on the fish.

Brook trout for use in the radiotelemetry studies were collected using electrofishing (see Section 4.4.3) from nearby streams of similar size and habitat. In the Adirondacks and Pennsylvania, all fish collected were combined into a single common pool and randomly assigned to the study streams for tracking. Studies in the Catskills in spring and fall 1989 involved both common pool and resident fish (collected from the study stream). Brook trout weighed 30 g or more (averaging 45–70 g in most studies; see Tables 4-15 to 4-17), so that the transmitter weight never exceeded 5% of the fish's body weight.

Initially, radio transmitters were placed in the stomachs of the fish. Fish were anesthetized and the transmitter gradually pushed down the esophagus. Because of problems with regurgitation, in later seasons (fall 1989 and spring 1990), transmitters were also surgically implanted in some fish. Fish were anesthetized and transmitters inserted into the abdominal cavity through a 10–15 mm mid-ventral incision, which was then closed with three sutures. Fish were held for at least one day after ingestion and three days after surgical implantation before being released into the study streams.

Patterns of fish movement were assessed relative to chemical conditions at the ERP stream monitor (see Section 4.3) and individual fish locations. When fish moved > 25 m over a 24-hour period, water samples were collected by hand from both the initial and final fish location, and analyzed for ANC, pH, and total dissolved Al.

4.4.2.2 Fish Traps

In some Adirondack streams, fish traps were used to monitor the timing and numbers of fish moving upstream and downstream in relation to stream chemistry. Three bi-directional fish traps were installed in fall 1988, at the lower end of the study reaches in Fly Pond Outlet and Bald Mountain Brook and 80 m below the confluence of Fly Pond Outlet and Bald Mountain Brook (see Section 3). A fourth trap was installed in spring 1989 at the upstream end of the Fly Pond Outlet study reach. A natural falls at the upper end of the Bald Mountain Brook study reach restricted fish movement further upstream. All traps extended across the entire stream reach and presumably caught all fish moving either upstream or downstream.

Fish traps were operated mid-October to 10 December 1988, 1 May to 1 December 1989, and 1 May to 30 June 1990. When in operation, fish traps were checked daily; all fish caught were checked for fin clips, measured, weighed, and then released in the direction in which they were moving, either upstream or downstream of the trap.

Fly Pond Outlet and Bald Mountain Brook were the smallest of the ERP study streams. Fish traps were not constructed on other streams because of costs and potential operational problems during periods of peak discharge.

4.4.3 Fish Community Surveys

Fish communities in each study stream were surveyed to quantify the density of brook trout and the occurrence of other fish species. Sampling dates are presented in Table 4-18. Fish were collected using portable backpack electroshockers (DC battery powered units in the Adirondacks and battery and gasoline powered AC/DC units using DC current in the Catskills and Pennsylvania). Study reaches, 100–300 m in length, near the ERP stream chemistry monitor were isolated with blocking seines and sampled with at least three electrofishing passes. All fish collected in each pass were identified to species and counted. Brook trout were individually weighed and measured for total length. Forage fish (blacknose dace and sculpin) were weighed individually or as a group. Brook trout and blacknose dace were also checked for identifying marks; unmarked fish were fin clipped. After all electrofishing passes and fish processing were completed, the fish caught were redistributed throughout the study reach.

Brook trout population density (number per unit of stream area) was estimated using the Zippin removal method (Zippin, 1958; Everhart et al., 1975). Additional electrofishing passes (up to 6) were conducted until the 95% upper confidence limit was ≤ 20% of the brook trout population estimate. Population estimates were also calculated for other fish species when sufficient numbers of fish were caught. Electrofishing efficiency and the accuracy of fish population estimates were evaluated by stocking and then surveying a known number of marked brook trout in a separate 50–100-m stream section. Capture efficiencies ranged between 66% and 97% (Table 4-19).

Additional, qualitative surveys of fish communities (< 3 electrofishing passes) were conducted at other stream locations and times. In particular, longitudinal variations in fish community composition in Catskill and Pennsylvania study streams were evaluated by sampling at multiple (2–6) locations in the mainstream as well as nearby tributary streams (in June 1989 in the Catskills and May 1989 in Pennsylvania). Water chemistry samples were collected by grab sampling at each site and analyzed for ANC, pH, conductivity, and total dissolved Al.

4.4.4 Fish Transplants

Some streams had distinctly lower fish biomass than others. To ensure that differences among streams were not related to problems with fish access (e.g., natural fish barriers), additional brook trout and forage fish (blacknose dace and sculpin) were transplanted into each study reach to achieve an initial, comparable level of fish density per stream. Fish density target levels were selected to be 50% (30%–80% in the Catskills) of densities observed in circumneutral streams in the area of similar size and habitat. Brook trout targets were 2.0 g/m^2, 0.9–2.4 g/m^2, and 75 fish/0.1 ha in the Adirondacks, Catskills, and Pennsylvania, respectively. Table 4-20 shows transplant dates and the number of fish stocked in each stream.

In most cases, resident fish populations in the study streams were supplemented with additional fish, as needed, to raise fish density to the desired target. Fish for stocking were collected, using electrofishing, from other similar nearby streams, combined into a single common pool, and then distributed randomly among streams. In the Adirondacks, during one fish transplant (April 1989 for brook trout and September 1989 for blacknose dace) resident populations in the reference stream (Fly Pond Outlet) were depleted, and the stream restocked with fish from other streams, so that reference stream fish experienced a similar level of stocking and handling stress as fish in nonreference streams. All stocked fish were fin clipped to distinguish common pool transplants from resident fish. For this report, however, only changes in total fish biomass (by species, resident and transplanted fish combined) are presented.

4.4.5 Other Biological Studies

Other biological research conducted as part of the ERP, but not reported on here, includes special studies in some regions relating to fish reproductive success and qualitative surveys of benthic macroinvertebrates. The ERP study design does not explicitly address the effects of episodic acidification on fish reproductive success. However, supplemental studies were conducted by some cooperators. In the Adirondacks, hatchery-reared brook trout feeding fry were tested with *in situ* bioassays in spring 1989 and 1990. In Pennsylvania, brook trout eggs and sac fry, from wild brook trout artificially spawned in the laboratory, were exposed *in situ* from October 1989 through March 1990. Spawning surveys were also conducted in Pennsylvania streams in fall 1989 to identify the occurrence and location of brook trout redds (areas in the substrate where adult brook trout have spawned and embryos have incubated). Redds were sampled for pH, ANC, total dissolved Al, dissolved oxygen, and temperature during winter, and then excavated in mid-February (before fry emergence) to evaluate embryo survival. Because each of these special studies was conducted in only one region, neither the methods nor the results are described in this report. Simonin et al. (1993) summarize the Adirondack brook trout fry bioassays; Fiss (1991) presents results from the Pennsylvania egg and sac fry bioassays and spawning surveys. No special studies relative to fish reproduction were conducted in Catskill streams.

Qualitative data were collected on the composition of the benthic macroinvertebrate community in each ERP stream to provide general information on the suitability of fish food supplies. Each stream was sampled at least three times; on each date, five samples were collected from riffle areas with a 0.1-m^2 Surber sampler. Organisms were counted and identified to family. Results from these qualitative surveys are not summarized in this report, but are available within the ERP database (see Section 4.5.4) and presented in various reports and papers by the regional cooperators (DeWalle et al., 1991; Kretser et al., 1991; Murdoch et al., 1991).

4.5 DATABASE MANAGEMENT

The ERP was designed to record a wide variety of data pertaining to episodic acidification in streams, ranging from simple stage height measurements to complex chemical analyses and biological behavior observations. These data were collected by three different research groups in three separate regions. The database resulting from these activities had to accurately and efficiently store the project data, and it had to be designed so that the data quality would be readily apparent during future analyses. Data gathering methods had to be carefully coordinated to ensure that the resulting data could be pulled together into a single database for analysis. This section describes the methods used to manage ERP data during the project and those used to develop the final ERP database.

Databases designed to ease the chore of data entry are not necessarily the best databases for data analysis. Therefore, the overall ERP database was built in two phases: a data entry phase and a database construction phase. Data quality was assessed during and after each phase. Software was developed by the Lockheed Engineering and Science Company (LEMSCO) of Las Vegas, Nevada, to provide the tools for hand data entry of stream chemistry, biology, and research site characterization data, to allow the regions to assess the quality of these data, and to apply data quality flags. The USGS in Doraville, Georgia, also developed software to control USGS mini-monitors and data loggers used in the collection of electronic time series stream chemistry and hydrology data. Batelle's Pacific Northwest Laboratory (PNL) in Richland, Washington, handled wet deposition and precipitation data (Barchet, 1991). ManTech Environmental Technology, Inc. (METI), of Corvallis, Oregon, combined these data into the final database by integrating the files from the regional data entry efforts into a consistent structure.

4.5.1 Data Entry

Data entry was handled separately in each ERP region, and by PNL. Each regional cooperator was responsible for entering chemical, biological, and site characterization data into the regional ERP database, and for performing data quality checks. Each region also transferred data from the data loggers to computer files and formatted these data into structures suitable for addition to the final database. Regional files were submitted periodically, and at the end of the project, to METI data management personnel for inclusion in the overall ERP database.

4.5.2 Database Construction

Once data entry was complete, the data files from each region and from PNL were combined into a consistent structure. Files were merged, and some fields specific to data entry were removed to simplify the data structure. The ERP database is described in the Episodic Response Project Database User's Guide (see Appendix A).

4.5.3 Data Quality Assurance

Database quality was maintained throughout the project through the use of internal database consistency checks (within sample checks) and by comparing current versions of the database with past versions of the database. During the data entry phase, each region was responsible for checking data quality by using the tools provided in the data entry software package. Anion/cation balances were checked, as well as theoretical versus measured conductivity. These types of checks served the dual purpose of guarding against laboratory analysis problems as well as data entry problems, since problems detected by the checks could be attributable to either source of error. Once the regional databases were delivered for inclusion into the overall database, data management personnel became responsible for database integrity. Backups of each version of the database were maintained at each phase of data processing to provide a method to recover lost data or correct data processing errors. The data validation step served as a final check for data entry and data processing errors.

Data validation consisted of identifying outliers within the database through examining relationships among water chemistry variables. However, just because a datum is an outlier does not mean that it is incorrect. Therefore, a datum was not considered suspect unless it appeared to be an outlier in many of the methods. In most instances in which a datum was considered suspect, it had previously been flagged as part of the data verification step.

The methods used to identify outliers were patterned after the validation procedures used for the National Stream Survey (NSS) (Kaufmann et al., 1988). However, the procedures were updated to reflect the collection of large amounts of data at individual streams, as in the ERP, instead of small amounts of data collected at a large number of streams across a region, as in the NSS. Data were first categorized by their type: snow lysimeter, snow core, and stream grab samples. Within these classifications, each chemical constituent was investigated by region and by stream within region. Graphical methods were the primary tool used for identifying outliers. Summary statistics and box-plots (Chambers et al., 1983) were used to initially identify outliers. Scatterplot matrices and

Spearman correlation matrices were also used to identify pairs of chemical parameters with empirical linear or curvilinear relationships. These pairs were plotted in more detail and were studied carefully to identify outliers. In general, the plots studied include pH versus ANC, pH and ANC versus major cations, pH and ANC versus aluminum (total dissolved, organic monomeric, and inorganic monomeric), pH and ANC versus major anions, and conductivity versus sum of anions and sum of cations. Plots between major cations and anions were also studied when a good relationship existed. Plots of chemical variables and discharge were also examined.

The outliers were then tabulated and investigated more closely. First, ERL-C personnel discussed identified outliers with the field cooperators. If the conditions suggested that the sample values were in error, they were corrected if possible. Data that could not be corrected in this fashion, but had been identified as in error, were removed from the database. Once the rejected data had been removed, the revised data set was again subjected to these procedures.

4.5.4 Data Availability

The ERP data and the database user's guide (see Appendix A for a list of ERP publications) will be available to the public in late 1993 through the National Technology Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

Table 4-1. Parameters of Interest and Associated Measurement Methodology for the Wet Deposition Chemistry Element, Episodic Response Project

Parameter	Method	References
Precipitation Volume	Rain gauge (Belfort type or tipping bucket)	Topol and Ozdimir, 1986
pH at 25°C	Electrometric; pH meter and combination electrode	EPA 150.6; Peden et al., 1986; Dana, 1982
Conductivity at 25°C	Electrolytic; conductivity cell and meter	EPA 120.6; Peden et al., 1986; U.S. EPA, 1987
Calcium	Inductively coupled argon plasma emission spectroscopy	EPA 200.7; U.S. EPA, 1987
Magnesium	Inductively coupled argon plasma emission spectroscopy	EPA 200.7; U.S. EPA, 1987
Sodium	Inductively coupled argon plasma emission spectroscopy	EPA 200.7; U.S. EPA, 1987
Potassium	Inductively coupled argon plasma emission spectroscopy	EPA 200.7; U.S. EPA, 1987
Ammonium	Colorimetric, automated (phenate)	EPA 350.7; U.S. EPA, 1987; Peden et al., 1986
Chloride	Ion chromatography	EPA 300.6; Peden et al., 1986; U.S. EPA, 1987
Nitrate	Ion chromatography	EPA 300.6; Peden et al., 1986; U.S. EPA, 1987
Sulfate	Ion chromatography	EPA 300.6; Peden et al., 1986; U.S. EPA, 1987

Table 4-2. Sample Handling and Holding Times, Stream Chemistry Component, Episodic Response Project (adapted from Peck et al., 1988)

Analytes	Processing	Preservation[a]	Holding Time Days (Preserved)
Calcium Magnesium Potassium Sodium	Filtration (0.45 μm)[b]	pH < 2 with HNO_3; store at 4°C	28 28 28 28
Calcium Magnesium Potassium Sodium	Filtration (0.45 μm)[c]	None; store at 4°C with no head-space	14 14 14 14
Aluminum, total dissolved	Filtration (0.10 μm or 0.22 μm)	pH < 2 with HNO_3; store at 4°C	14
Aluminum, monomeric	Filtration (0.10 μm or 0.22 μm)	Extraction into methyl-isobutyl-ketone (MIBK); store at 4°C	14
Aluminum, nonlabile	Filtration (0.10 μm or 0.22 μm)	Cation exchange; extraction into methyl-isobutyl-ketone (MIBK); store at 4°C	14
Chloride Nitrate Sulfate Silica	Filtration (0.45 μm)	None; store at 4°C with no head-space	14 14 14 14
Dissolved organic carbon (DOC) Ammonium	Filtration (0.45 μm)	pH < 2 with H_2SO_4; store at 4°C	14 14
Acid neutralizing capacity (ANC) pH Conductivity	None	None; store at 4°C with no head-space	14 7 14

[a] Bulk samples maintained at approximately 4°C until processed and preserved.
[b] Applicable for samples being analyzed by atomic absorption spectroscopy.
[c] Applicable for samples being analyzed by ion chromatography.

Table 4-3. Analytes of Interest and Associated Measurement Methodology, Stream Chemistry Component, Episodic Response Project (adapted from Peck et al., 1988)

Parameter	Summary of Method	References
Field Measurements		
pH, in situ	Electrometric (USGS mini-monitor), with combination electrode	EPA 150.2 (modified); Metcalf et al., 1988
Conductivity at 25°C, in situ	Electrolytic (USGS mini-monitor)	EPA 120.6 (modified); Metcalf et al., 1988
Temperature, in situ	Thermometric; Thermistor (USGS mini-monitor)	EPA 170.1; Metcalf et al., 1988
pH, field	Electrometric, with glass combination electrode	EPA 150.6 (modified); Hagley et al., 1988
Conductivity at 25°C, field	Electrolytic, conductivity cell and meter	EPA 120.6 (modified); Hagley et al., 1988
Laboratory Measurements		
Calcium, dissolved[a]	Atomic absorption spectroscopy (flame); Ion chromatography	EPA 200.6; U.S. EPA 1987; EPA 300.7; Peden et al., 1986
Magnesium, dissolved[a]	Atomic Absorption Spectroscopy (flame); Ion chromatography	EPA 200.6; U.S. EPA, 1987; EPA 300.7; Peden et al., 1986
Potassium, dissolved[a]	Atomic absorption spectroscopy (flame); Ion chromatography	EPA 200.6; U.S. EPA, 1987; EPA 300.7; Peden et al., 1986
Sodium, dissolved[a]	Atomic absorption spectroscopy (flame); Ion chromatography	EPA 200.6; U.S. EPA, 1987; EPA 300.7; Peden et al., 1986
Ammonium, dissolved[a]	Colorimetric, automated (phenate)	EPA 350.7; U.S. EPA, 1987; Peden et al., 1986
Aluminum, total dissolved[b]	Digestion at pH < 1; analysis by atomic absorption spectroscopy (furnace)	EPA 202.2; U.S. EPA, 1987
Aluminum, monomeric[b]	Complexation with 8-hydroxy-quinoline, extraction into methyl-isobutyl-ketone, analysis by atomic absorption spectroscopy (furnace)	EPA 202.2 (modified); Driscoll, 1984; U.S. EPA, 1987
Aluminum, nonlabile[b] (organic monomeric)	Cation exchange, complexation with 8-hydroxy-quinoline, extraction into methyl-isobutyl-ketone, analysis by atomic absorption spectroscopy (furnace)	EPA 202.2 (modified); Driscoll, 1984
Chloride, dissolved[a]	Ion chromatography	EPA 300.6; U.S. EPA, 1987
Nitrate, dissolved[a]	Ion chromatography	EPA 300.6; U.S. EPA, 1987
Sulfate, dissolved[a]	Ion chromatography	EPA 300.6; U.S. EPA, 1987
Silica, dissolved[a]	Automated colorimetric (molybdate blue)	EPA 370.1 (modified); U.S. EPA, 1987
Carbon, dissolved[a] organic (DOC)	UV-promoted persulfate oxidation, IR detection	EPA 415.2; U.S. EPA, 1987
pH	Electrometric: pH meter with glass combination electrode	EPA 150.6; U.S. EPA, 1987
Conductivity at 25°C	Electrolytic, with conductance cell and meter	EPA 120.6; U.S. EPA, 1987
Acid Neutralizing Capacity (ANC)	Acidimetric titration with Gran plot analysis	EPA 310.1 (modified); U.S. EPA, 1987

[a] *Dissolved* is defined as passing through a 0.45 μm pore filter.
[b] *Dissolved* is defined as passing through a 0.10 μm or 0.22 μm pore filter.

Table 4-4. Dates Used to Define Seasons for Inorganic Monomeric Aluminum (Al_{im}) Analyses

Season	Adirondacks	Catskills	Pennsylvania
Fall 1988	10/1 – 12/15	10/1 – 12/31	10/1 – 12/31
Spring 1989	4/1 – 6/30	3/1 – 5/30	3/1 – 5/30
Fall 1989	9/15 – 12/15	9/15 – 12/31	9/15 – 12/31
Spring 1990	4/1 – 6/30	3/1 – 5/30	3/1 – 4/30

Table 4-5. Number of Measurements of Inorganic Monomeric Aluminum (Al_{im}) per Season and Stream

Stream	Fall 1988	Spring 1989	Fall 1989	Spring 1990	All (total)
Adirondacks:					
Fly Pd. Outlet	0	4	16	11	64
Bald Mt. Brook	0	3	24	16	73
Buck Creek	0	3	28	24	92
Seventh L. Inlet	0	4	27	17	84
Catskills:					
Black Brook	0	2	8	0	10
High Falls Brook	0	5	7	13	27
Biscuit Brook	0	24	19	23	69
E. Br. Neversink	0	32	22	28	86
Pennsylvania:					
Benner Run	0	30	15	23	68
Roberts Run	5	28	17	28	79
Stone Run	1	24	16	44	86
Baldwin Creek	19	29	11	17	76
Linn Run	23	35	12	44	114

Table 4-6. Models Selected to Estimate Inorganic Monomeric Al (Al_{im}) from Other Measured Physical and Chemical Variables: Adirondacks

Application[a]	Model, Al_{im} =[b]	R^2	n	RMSE[c]
Bald Mt. Brook				
Overall	$-98.85 + 0.6760(Al_{td}) + 2.741(ANC) - 0.014181(ANC*Al_{td})$	0.83	73	62.1
Fall 1989	$10^{**}(10.65 - 1.804(\log Al_{td}) - 1.134(pH) + 0.09356(DOC) + 0.0091(\Sigma C_B))$	0.82	24	52.9
Spring 1990	$-69.43 + 0.9728(Al_{td}) - 39.62(DOC)$	0.93	16	30.8
Back-up	$10^{**}(5.083 - 0.5371(pH)) - 25$	0.58	73	80.0
Buck Creek				
Overall	$-76.83 + 0.9199(Al_{td}) - 25.29(DOC)$	0.91	90	52.8
Fall 1989	$236.5 - 6.455(ANC) - 1.124(Q)$	0.73	28	46.7
Spring 1990	$-101.2 + 0.4544(Al_{td}) + 4.478(NO_3) - 14.79(DOC)$	0.97	24	30.0
Back-up	$10^{**}(5.661 - 0.6520(pH)) - 25$	0.80	90	102.7
Fly Pond Outlet				
Overall	No significant models; median measured values used for the prediction	–	68	37.6
Seventh Lake Inlet				
Overall	$393.9 + 0.5049(Al_{td}) - 15.07(DOC) - 66.00(pH)$	0.84	84	40.1
Fall 1989	$10^{**}(5.2317 - 0.5696(pH) - 0.0028(Q)) - 25$	0.69	27	41.5
Spring 1990	$-81.23 + 0.7989(Al_{td}) - 20.59(DOC)$	0.91	17	22.3
Back-up	$10^{**}(5.522 - 0.6405(pH)) - 25$	0.57	84	59.9

[a] Season specific models were applied for the seasons listed. Otherwise, the overall (full-data) model was used. For those samples with missing values for one or more predictor variables, the back-up model was used to estimate Al_{im}.

[b] Units for variables used in models: ANC, ΣC_B, NO_3 = μeq/L; Al_{im}, Al_{td} = μg/L; DOC = mg/L; pH = pH units; Q = cfs. ΣC_B = sum of base cations.

[c] RMSE = $[(\text{sum of squared prediction errors})/n]^{1/2}$.

Table 4-7. Models Selected to Estimate Inorganic Monomeric Al (Al_{im}) from Other Measured Physical and Chemical Variables: Catskills

Application[a]	Model, Al_{im} =[b]	R^2	n	RMSE[c]
Biscuit Brook				
Overall	127.5 + 0.4526(Al_{td}) – 11.43(DOC) + 1.316(SO_4) – 0.8396(ΣC_B) + 8.55(COND)	0.87	57	14.5
Spring 1989	1820 + 1.699(ANC) + 8.773(COND) – 675.4 (logSO_4) – 248.5(log ΣC_B)	0.93	20	7.9
Fall 1989	–0.4018 + 0.1983(Al_{td})	0.55	17	11.1
Spring 1990	61.10 +0.3211(Al_{td}) – 4.158(ANC)	0.91	17	12.7
Back-up	–81.89 + 5.950(COND) + 2.193(ANC)	0.58	64	68.6
Black Brook				
Overall	–965.3 + 1.959(Q) + 455.5(logSO_4)	0.76	10	11.7
Back-up	396.2 – 59.55(pH)	0.60	10	14.9
East Branch Neversink River				
Overall	435.2 – 226.2(pH) – 10.88(DOC) + 221.7(logAl_{td}) + 231.1(log NO_3)	0.82	65	43.0
Spring 1989	69.04 +0.3929(Al_{td}) – 4.693(ANC)	0.87	29	37.7
Fall 1989	–530.2 + 3.771(SO_4) + 9.953(COND)	0.71	20	26.2
Spring 1990	–2177 + 360.4(pH) + 13.13(NO_3)	0.82	23	42.0
Back-up	974.9 – 183.7(pH) + 2.891(NO_3)	0.56	75	69.9
High Falls Brook				
Overall	17.52 + 0.3797 (Al_{td}) – 16.15(DOC) + 0.7194(Q)	0.78	23	11.7
Back-up	204.0 + –41.65(pH) + 7.110(COND) – 0.6156(ΣC_B)	0.59	27	15.3

[a] Season specific models were applied for the seasons listed. Otherwise, the overall (full-data) model was used. For those samples with missing values for one or more predictor variables, the back-up model was used to estimate Al_{im}.

[b] Units for variables used in models: ANC, ΣC_B, SO_4, NO_3 = μeq/L; Al_{im}, Al_{td} = μg/L; DOC = mg/L; pH = pH units; Q = cfs; COND = μmhos/cm. ΣBC = sum of base cations; COND = conductivity.

[c] RMSE = [(sum of squared prediction errors)/n]½.

Table 4-8. **Models Selected to Estimate Inorganic Monomeric Al (Al_{im}) from Other Measured Physical and Chemical Variables: Pennsylvania**

Application[a]	Model, Al_{im} =[b]	R^2	n	RMSE[c]
Baldwin Creek				
Overall	11.60 + 8.804(Q) – 1.406(pH*Q)	0.79	74	9.8
Back-up	5.486 + 1.104(Q)	0.72	74	11.3
Benner Run				
Overall	543.3 – 89.52(pH)	0.83	68	14.9
Spring 1989	10**(5.347 – 0.6588(pH) + 0.0586(DOC) – 0.0056(Q)) – 25	0.92	30	9.3
Fall 1989	10**(5.131 – 0.5985(pH)) – 25	0.92	15	12.9
Spring 1990	405.9 – 89.40(pH) + 0.7474(ΣC_B)	0.80	22	9.8
Back-up	–44.70 + 78.53(log Q)	0.45	67	27.4
Linn Run				
Overall	10**(5.2479 – 0.0027(Al_{td}) – 0.5742(pH) + 0.0007(Al_{td}*pH)) – 25	0.90	107	57.6
Fall 1989	1098 + 0.3423(Al_{td}) + 3.270(Q) – 182.4(pH)	0.97	19	37.1
Spring 1989	10**(4.8071 + 0.3953(log Al_{td}) + 0.2106(log Q) – 1.536(log ΣC_B)) – 25	0.96	35	26.2
Fall 1989	10**(4.53 + 0.0016(Al_{td}) – 0.4743(pH)) – 25	0.98	11	20.8
Spring 1990	1141 + 0.5969(Al_{td}) – 151.2(pH) – 0.7081(ΣC_B)	0.80	42	66.5
Back-up	– 140.4 + 311.6(logQ)	0.51	111	118.1
Roberts Run				
Overall	10**(5.163 – 0.5718(pH) – 0.002969(Q)) – 25	0.92	76	28.2
Spring 1989	10**(6.892 – 0.8474(pH) – 0.3631(logQ)) – 25	0.62	28	20.7
Fall 1989	10**(5.209 – 0.5797(pH)) – 25	0.96	17	9.9
Spring 1990	10**(2.249 + 9.429(log DOC) – 1.859(log DOC*pH)) – 25	0.82	28	23.0
Back-up	10**(3.742 – 0.3638(pH) + 0.0036(SO_4) – 0.0017(ΣC_B)) – 25	0.92	79	27.1
Stone Run				
Overall	10**(7.353 – 0.9702(pH) – 0.0439(Q) + 0.0090(pH*Q)) – 25	0.96	83	35.8
Spring 1989	10**(0.2465 + 0.8306(log Al_{td}) + 1.432(log Q) – 0.5088(log Al_{td}*log Q)) – 25	0.95	23	21.1
Fall 1989	–55.85 + 2.879 (Al_{td}) – 13.25(Q) – 0.1498(Al_{td}*Q)	0.96	15	9.3
Spring 1990	1758 – 303.0(pH) + 3.391(Q)	0.88	43	34.4
Back-up	1849 – 314.5(pH) + 11.75(NO_3) – 3.974(Cl) + 0.5912(ΣC_B)	0.91	86	39.9

[a] Season specific models were applied for the seasons listed. Otherwise, the overall (full-data) model was used. For those samples with missing values for one or more predictor variables, the back-up model was used to estimate Al_{im}.

[b] Units for variables used in models: ΣC_B, SO_4, Cl = μeq/L; Al_{im}, Al_{td} = μg/L; DOC = mg/L; pH = pH units. ΣC_B = sum of base cations.

[c] RMSE = [(sum of squared prediction errors)/n]$^{1/2}$.

Table 4-9. *In Situ* Bioassays with Brook Trout in Adirondack Streams

Stream[a]	Source of fish[b]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean	STD	Mean	STD
FALL 1988									
FPO	CP	11/01/88	12/01/88	30	20	80.2	9.0	4.00	1.46
BMB	CP	11/01/88	12/01/88	30	20	74.8	8.9	3.60	1.27
BCK	CP	11/01/88	12/01/88	30	15	104.1	13.5	10.54	3.43
SLI	CP	11/01/88	12/01/88	30	20	70.7	10.9	3.25	1.07
SPRING 1989									
FPO	CP	5/26/89	6/20/89	25	20	75.6	6.5	3.60	0.55
BMB	CP	5/26/89	6/20/89	25	20	76.4	7.7	4.31	1.03
BCK	CP	5/26/89	6/20/89	25	20	78.6	7.8	4.64	1.12
SLI	CP	5/26/89	6/20/89	25	20	77.4	8.1	3.50	0.71
FALL 1989									
FPO	CP	9/27/89	11/06/89	40	20	73.2	10.9	3.05	1.32
BMB	CP	9/27/89	11/06/89	40	20	74.4	9.9	3.45	1.47
BCK	CP	9/27/89	11/06/89	40	20	67.0	12.1	2.95	1.87
SLI	CP	9/27/89	11/06/89	40	20	69.4	12.4	4.80	2.98
FPO	CP	10/06/89	11/06/89	31	20	68.4	7.2	2.20	0.89
BMB	CP	10/06/89	11/06/89	31	20	67.4	6.9	2.40	0.82
BCK	CP	10/06/89	11/06/89	31	20	70.3	7.9	3.00	1.03
SLI	CP	10/06/89	11/06/89	31	20	67.2	9.8	5.50	2.35

[a] FPO = Fly Pond Outlet; BMB = Bald Mountain Brook; BCK = Buck Creek; SLI = Seventh Lake Inlet.
[b] CP = common pool (see text for explanation).

Table 4-9. *In Situ* Bioassays with Brook Trout in Adirondack Streams (Continued)

Stream[a]	Source of fish[b]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean	STD	Mean	STD
SPRING 1990									
FPO	CP	4/30/90	5/30/90	30	20	73.2	6.5	2.65	0.75
BMB	CP	4/30/90	5/30/90	30	20	77.2	7.5	3.72	1.35
BCK	CP	4/30/90	5/30/90	30	20	76.0	6.0	3.35	0.81
SLI	CP	4/30/90	5/30/90	30	20	75.6	10.3	2.90	1.48

[a] FPO = Fly Pond Outlet; BMB = Bald Mountain Brook; BCK = Buck Creek; SLI = Seventh Lake Inlet.
[b] CP = common pool (see text for explanation).

Table 4-10. *In Situ* Bioassays with Brook Trout in Catskill Streams

Stream[a]	Source of fish[b]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean	STD	Mean[c]	STD[c]
FALL 1988									
Black	Black	11/10/88	12/15/88	35	19	75.9	10.2	--	--
	Black	11/10/88	12/15/88	35	9	129.3	12.5	57.1	9.3
Biscuit	Biscuit	11/03/88	12/14/88	41	21	76.0	15.9	--	--
	Biscuit	11/03/88	12/14/88	41	13	145.3	31.0	42.0	14.7
EBrNS	EBrNS	11/04/88	12/15/88	41	14	95.8	15.6	--	--
	EBrNS	11/04/88	12/15/88	41	6	150.7	10.1	--	--
Black	Black	11/30/88	12/15/88	15	20	69.5	6.8	3.05	0.55
High Falls	Black	11/30/88	12/15/88	15	20	77.2	9.8	3.48	0.92
Biscuit	Black	11/30/88	12/14/88	14	20	80.1	9.1	4.32	1.20
EBrNS	Black	11/30/88	12/15/88	15	20	80.4	12.4	4.41	1.80
SPRING 1989									
Black	PIN	4/08/89	4/27/89	19	21	74.8	6.4	4.27	0.39
High Falls	PIN	4/06/89	4/27/89	21	21	71.5	6.3	2.94	0.87
Biscuit	PIN	4/06/89	4/27/89	21	21	73.8	9.3	3.50	1.20
EBrNS	PIN	4/06/89	4/27/89	21	16	76.9	5.1	3.69	0.79
High Falls	H.Falls	4/06/89	4/27/89	21	21	69.0	6.4	2.38	0.74
EBrNS	EBrNS	4/06/89	4/27/89	21	21	68.8	6.6	2.62	0.80

[a] EBrNS = East Branch Neversink River.
[b] PIN = Pigeon Creek; WBrNS = West Branch Neversink River.
[c] -- = no measurements were made of fish weight.

Table 4-10. *In Situ* Bioassays with Brook Trout in Catskill Streams (Continued)

Stream[a]	Source of fish[b]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean[c]	STD[c]	Mean[c]	STD[c]
SPRING 1989	(cont.)								
High Falls	WBrNS	5/04/89	5/17/89	13	21	--	--	--	--
Biscuit	WBrNS	5/04/89	5/17/89	13	21	--	--	--	--
EBrNS	WBrNS	5/05/89	5/16/89	11	21	71.8	5.3	3.89	0.76
High Falls	WBrNS	5/19/89	6/24/89	36	21	78.4	7.4	2.64	0.88
EBrNS	WBrNS	5/19/89	6/24/89	36	21	80.5	6.1	3.55	1.06
High Falls	H.Falls	5/19/89	6/24/89	36	21	73.4	6.9	1.95	0.67
EBrNS	EBrNS	5/19/89	6/24/89	36	21	77.0	6.5	2.63	0.86
FALL 1989									
Black	WBrNS	10/04/89	11/09/89	36	21	66.6	9.6	2.52	1.17
High Falls	WBrNS	10/04/89	11/08/89	35	21	65.6	7.9	2.19	0.87
Biscuit	WBrNS	10/04/89	11/08/89	35	21	64.7	7.2	2.00	0.77
EBrNS	WBrNS	10/04/89	11/07/89	34	21	65.2	7.5	2.14	0.65
High Falls	H.Falls	10/05/89	11/08/89	34	21	72.0	5.6	2.81	0.68
EBrNS	EBrNS	10/07/89	11/07/89	31	21	68.0	4.4	2.19	0.51
High Falls	WBrNS	11/08/89	11/30/89	22	21	69.5	7.4	2.86	0.85
EBrNS	WBrNS	11/08/89	11/30/89	22	21	67.7	7.1	2.62	0.74
High Falls	H.Falls	11/08/89	11/30/89	22	21	72.2	6.0	2.98	0.72
EBrNS	EBrNS	11/07/89	11/30/89	23	21	69.4	5.5	2.95	0.67

[a] EBrNS = East Branch Neversink River.

[b] PIN = Pigeon Creek; WBrNS = West Branch Neversink River.

[c] -- = no measurements made of fish length of weight

Table 4-10. *In Situ* Bioassays with Brook Trout in Catskill Streams (Continued)

Stream[a]	Source of fish[b]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean	STD	Mean	STD
SPRING 1990									
High Falls	WBrNS	3/09/90	4/06/90	28	21	73.1	3.8	3.19	0.60
Biscuit	WBrNS	3/09/90	4/06/90	28	21	69.9	5.6	2.86	0.57
High Falls	WBrNS	4/06/90	5/06/90	30	21	74.3	6.1	2.90	0.77
Biscuit	WBrNS	4/06/90	5/06/90	30	21	75.0	5.3	3.12	0.55
EBrNS	WBrNS	4/06/90	5/06/90	30	21	74.4	5.9	3.37	0.83
High Falls	H.Falls	4/06/90	5/06/90	30	21	74.5	4.6	2.76	0.44
EBrNS	EBrNS	4/06/90	5/06/90	30	21	66.2	4.3	2.71	0.73

[a] EBrNS = East Branch Neversink River.

[b] PIN = Pigeon Creek; WBrNS = West Branch Neversink River.

Table 4-11. *In Situ* Bioassays with Brook Trout in Pennsylvania Streams

Stream	Source of fish[a]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean	STD	Mean[b]	STD[b]
FALL 1988								--	--
Benner	Benner	10/11/88	11/16/88	36	20	68.8	22.8	--	--
Roberts	Benner	10/05/88	11/10/88	36	21	67.7	20.0	--	--
	Roberts	10/05/88	11/10/88	36	39	66.6	8.5	--	--
	Stone	10/05/88	11/10/88	36	22	66.3	7.5	--	--
Stone	Benner	10/06/88	11/10/88	35	20	62.0	12.8	--	--
	Roberts	10/06/88	11/10/88	35	35	64.4	7.2	--	--
	Stone	10/06/88	11/10/88	35	33	65.5	8.6	--	--
Baldwin	Baldwin	10/13/88	11/18/88	36	36	74.5	17.9	--	--
Linn	Baldwin	10/13/88	11/18/88	36	37	73.4	20.3	--	--
	Benner	10/13/88	11/18/88	36	14	61.3	6.7	--	--
SPRING 1989									
Benner	Benner/ Roberts	2/21/89	4/04/89	42	21	63.5	7.6	2.25	0.62
Roberts	Roberts	2/23/89	4/03/89	39	21	112.6	203.2	2.30	0.48
Stone	Stone	2/22/89	4/03/89	40	21	109.5	203.9	3.00	0.00
Baldwin	Baldwin	2/27/89	4/07/89	39	21	159.8	279.0	3.20	0.63
Linn	Linn	2/28/89	4/06/89	37	42	86.9	22.0	3.00	--

[a] CP = common pool (see text for explanation).

[b] -- = no measurements made of fish weight.

Table 4-11. *In Situ* Bioassays with Brook Trout in Pennsylvania Streams (Continued)

Stream	Source of fish[a]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean	STD	Mean[b]	STD[b]
SPRING 1989	(cont.)								
Roberts	Roberts	3/14/89	4/03/89	20	21	69.0	6.4	2.50	0.52
Stone	Stone	3/14/89	4/03/89	20	21	68.0	7.6	3.10	0.74
Linn	Linn	3/20/89	4/06/89	17	21	79.8	6.9	--	--
FALL 1989									
Benner	Benner	10/30/89	11/20/89	21	35	60.9	7.5	2.37	0.94
Roberts	Stone	10/31/89	11/20/89	20	35	60.8	4.6	2.31	0.72
Stone	Stone	10/31/89	11/20/89	20	35	62.1	8.3	2.46	1.09
Baldwin	CP	11/02/89	11/22/89	20	35	72.8	8.3	3.40	0.98
Linn	CP	11/02/89	11/22/89	20	35	69.1	9.4	2.91	1.04
SPRING 1990									
Benner	CP	3/02/90	3/22/90	20	35	74.3	7.6	3.49	1.31
Stone	CP	3/02/90	3/22/90	20	35	76.2	6.6	4.40	1.14
Benner	CP	3/22/90	4/11/90	20	35	84.9	9.4	4.88	1.55
Stone	CP	3/22/90	4/11/90	20	35	82.1	8.3	5.57	1.56

[a] CP = common pool (see text for explanation).
[b] -- = no measurements made of fish weight.

Table 4-12. *In Situ* Bioassays with Blacknose Dace in Adirondack Streams

Stream[a]	Source of fish[b]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean	STD	Mean[c]	STD[c]
FALL 1988									
FPO	CP	11/01/88	12/01/88	30	20	70.6	3.4	2.80	0.62
BMB	CP	11/01/88	12/01/88	30	20	72.8	5.2	4.10	0.97
BCK	CP	11/01/88	12/01/88	30	20	71.2	6.8	3.93	1.03
SLI	CP	11/01/88	12/01/88	30	20	71.6	6.9	3.82	1.10
SPRING 1989									
FPO	CP	5/08/89	5/18/89	10	21	37.4	3.6	--	--
BMB	CP	5/08/89	5/18/89	10	21	37.4	4.1	0.50	0.00
BCK	CP	5/08/89	5/18/89	10	22	39.5	3.4	0.50	0.00
SLI	CP	5/08/89	5/18/89	10	21	38.9	3.8	0.50	0.00
FPO	CP	5/18/89	6/28/89	41	21	38.3	4.8	0.67	0.29
BMB	CP	5/18/89	6/28/89	41	21	38.0	3.7	--	--
BCK	CP	5/18/89	6/28/89	41	21	38.2	4.1	0.53	0.14
SLI	CP	5/18/89	6/28/89	41	21	37.1	4.5	--	--
FALL 1989									
FPO	CP	9/27/89	11/06/89	40	20	61.4	5.7	1.90	0.85
BMB	CP	9/27/89	11/06/89	40	20	62.2	6.2	2.20	0.77
BCK	CP	9/27/89	11/06/89	40	20	62.0	6.3	2.60	0.88
SLI	CP	9/27/89	11/06/89	40	20	61.2	6.9	6.00	2.29

[a] FPO = Fly Pond Outlet; BMB = Bald Mountain Brook; BCK = Buck Creek; SLI = Seventh Lake Inlet.
[b] CP = common pool (see text for explanation.
[c] -- = no measurements made of fish weight.

Table 4-12. *In Situ* Bioassays with Blacknose Dace in Adirondack Streams (Continued)

Stream[a]	Source of fish[b]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean	STD	Mean	STD
SPRING 1990									
FPO	CP	4/30/90	5/30/90	30	20	59.4	3.6	1.45	0.51
BMB	CP	4/30/90	5/30/90	30	20	59.5	5.7	2.20	0.70
BCK	CP	4/30/90	5/30/90	30	20	61.9	4.7	2.40	0.75
SLI	CP	4/30/90	5/30/90	30	20	61.9	5.7	2.35	0.75

[a] FPO = Fly Pond Outlet; BMB = Bald Mountain Brook; BCK = Buck Creek; SLI = Seventh Lake Inlet.
[b] CP = common pool (see text for explanation).

Table 4-13. *In Situ* Bioassays with Slimy Sculpin in Catskill Streams

Stream[a]	Source of fish[b]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean[c]	STD[c]	Mean[c]	STD[c]
FALL 1988									
Black	Black	11/10/88	12/15/88	35	21	62.5	18.2	--	--
Biscuit	Biscuit	11/03/88	12/14/88	41	20	91.5	21.9	--	--
SPRING 1989									--
Black	PIN	4/08/89	4/27/89	19	21	63.2	7.8	--	--
High Falls	PIN	4/06/89	4/27/89	21	21	59.2	9.5	2.10	1.09
Biscuit	PIN	4/06/89	4/27/89	21	21	61.8	8.7	2.60	1.14
EBrNS	PIN	4/06/89	4/27/89	21	19	59.4	6.6	2.47	0.82
High Falls	WBrNS	5/04/89	5/17/89	13	21	--	--	--	--
Biscuit	WBrNS	5/04/89	5/17/89	13	21	--	--	--	--
EBrNS	WBrNS	5/07/89	5/16/89	9	21	80.0	--	8.00	--
FALL 1989									
Black	WBrNS	10/04/89	11/09/89	36	21	63.8	8.2	2.64	1.22
High Falls	WBrNS	10/04/89	11/08/89	35	21	64.5	7.3	2.38	0.86
Biscuit	WBrNS	10/04/89	11/08/89	35	21	62.1	8.2	2.29	0.92
EBrNS	WBrNS	10/04/89	11/07/89	34	21	65.3	6.3	2.57	0.81
High Falls	H.Falls	10/05/89	11/08/89	34	21	63.8	5.7	2.10	0.62
EBrNS	EBrNS	10/07/89	11/07/89	31	21	71.0	6.3	3.60	1.36

[a] EBrNS = East Branch Neversink River.
[b] PIN = Pigeon Creek; WBrNS = West Branch Neversink River.
[c] -- = no measurements made of fish length or weight.

Table 4-13. *In Situ* Bioassays with Slimy Sculpin in Catskill Streams (Continued)

Stream[a]	Source of fish[b]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean	STD	Mean	STD
FALL 1989	(cont.)								
High Falls	WBrNS	11/08/89	11/30/89	22	21	65.6	6.6	2.76	1.04
EBrNS	WBrNS	11/08/89	11/30/89	22	21	68.0	8.9	3.24	1.14
High Falls	H.Falls	11/08/89	11/30/89	22	21	67.9	6.4	3.05	0.80
EBrNS	EBrNS	11/07/89	11/30/89	23	21	68.4	5.6	3.33	1.02

[a] EBrNS = East Branch Neversink River.
[b] PIN = Pigeon Creek; WBrNS = West Branch Neversink River.

Table 4-14. *In Situ* Bioassays with Sculpin in Pennsylvania Streams

Stream	Species	Source of Fish[a]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
							Mean	STD	Mean[b]	STD[b]
FALL 1988										
Benner	Slimy	Benner	10/11/88	11/16/88	36	55	40.2	17.0	--	--
Roberts	Slimy	Benner	10/05/88	11/10/88	36	47	52.7	21.9	--	--
Stone	Slimy	Benner	10/06/88	11/10/88	35	27	66.8	8.9	--	--
Linn	Slimy	Benner	10/13/88	11/18/88	36	21	67.6	8.0	--	--
Baldwin	Mottled	Baldwin	10/13/88	11/18/88	36	25	68.6	7.2	--	--
Linn	Mottled	Baldwin	10/13/88	11/18/88	36	23	70.8	13.0	--	--
SPRING 1989										
Benner	Slimy	SixMile	2/21/89	4/04/89	42	21	55.1	4.5	1.81	0.68
Roberts	Slimy	SixMile	2/22/89	4/03/89	40	21	56.6	5.4	2.00	0.00
Stone	Slimy	SixMile	2/22/89	4/03/89	39	21	100.3	206.0	--	--
Baldwin	Mottled	Linn	2/27/89	4/07/89	39	21	96.5	206.8	1.07	0.27
Linn	Mottled	Baldwin	2/28/89	4/06/89	37	21	100.1	206.1	--	--
SPRING 1990										
Benner	Slimy	CP	3/02/90	3/22/90	20	35	69.4	8.0	3.34	1.51
Stone	Slimy	CP	3/02/90	3/22/90	20	35	69.2	7.8	4.03	1.29
Benner	Mottled	CP	3/02/90	3/22/90	20	35	70.0	8.0	3.37	1.37
Stone	Mottled	CP	3/02/90	3/22/90	20	35	70.7	10.1	4.29	1.84

[a] CP = common pool (see text for explanation).
[b] -- = no measurements made of fish weight.

Table 4-14. *In Situ* Bioassays with Sculpin in Pennsylvania Streams (Continued)

Stream	Species	Source of Fish[a]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
							Mean	STD	Mean	STD
SPRING 1990	(cont.)									
Benner	Slimy	CP	3/22/90	4/11/90	20	35	69.2	7.1	3.17	1.07
Stone	Slimy	CP	3/22/90	4/11/90	20	35	65.5	7.7	3.31	1.13
Benner	Mottled	CP	3/22/90	4/11/90	20	35	76.2	9.3	4.80	1.86
Stone	Mottled	CP	3/22/90	4/11/90	20	35	69.8	7.3	3.71	1.27

[a] CP = common pool (see text for explanation).

Table 4-15. Radiotelemetry Studies of Brook Trout Movement in Adirondack Streams

Stream[a]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
					Mean	STD	Mean	STD
SPRING 1989								
FPO	5/22-26/89	6/20/89	25-29	8	182.0	28.6	55.8	27.6
SLI	5/22-23/89	6/20/89	28-29	7	174.1	29.2	54.7	38.2
FALL 1989								
FPO	10/04/89	11/03/89	30	9	182.1	27.8	62.1	36.8
BMB	10/04/89	11/03/89	30	10	181.2	27.2	65.3	38.8
BCK	10/04/89	11/03/89	30	9	181.1	21.2	56.7	24.5
SPRING 1990								
FPO	5/04/90	6/05/90	32	6	170.8	11.7	44.0	7.6
BCK	5/04/90	6/05/90	32	6	175.3	8.3	46.2	7.4

[a] FPO = Fly Pond Outlet; SLI = Seventh Lake Inlet; BMB = Bald Mountain Brook; BCK = Buck Creek.

Table 4-16. Radiotelemetry Studies of Brook Trout Movement in Catskill Streams

Stream[a]	Source of fish[b]	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
						Mean	STD	Mean	STD
SPRING 1989									
High Falls	PIN	4/12/89	4/27/89	15	4	182.2	9.4	57.2	6.7
	H. Falls	4/12/89	4/27/89	15	5	225.4	11.5	99.6	16.6
EBrNS	PIN	4/12/89	4/28/89	16	4	179.8	6.3	50.8	2.8
	EBrNS	4/12/89	4/28/89	16	5	185.4	13.5	63.2	15.0
FALL 1989									
High Falls	WBrNS	10/17//89	11/25/89	39	8	220.8	32.4	111.6	47.3
	H. Falls	10/17/89	11/25/89	39	5	222.6	18.3	112.4	20.5
EBrNS	WBrNS	10/17/89	11/28/89	42	4	202.8	15.9	83.2	21.2
	EBrNS	10/17/89	11/28/89	42	9	191.9	8.7	71.6	11.7
SPRING 1990									
High Falls	WBrNS	3/24/90	5/23/90	60	10	221.5	17.6	99.7	25.4
Biscuit	WBrNS	3/24/90	5/22/90	59	11	203.8	18.2	80.8	18.1

[a] EBrNS = East Branch Neversink River.

[b] PIN = Pigeon Creek; WBrNS = West Branch Neversink River.

Table 4-17. Radiotelemetry Studies of Brook Trout Movement in Pennsylvania Streams

Stream	Starting Date	Ending Date	Total No. Days	Total No. Fish	Length (mm)		Weight (g)	
					Mean	STD	Mean	STD
FALL 1988								
Baldwin	10/15-16/88	11/14/88	29-30	10	172.9	13.9	55.5	16.6
Linn	10/15-16/88	11/14/88	29-30	10	188.4	25.6	72.2	31.6
SPRING 1989								
Baldwin	3/02-03/89	4/07/89	35-36	15	176.7	20.5	45.8	17.8
Linn	3/02-03/89	4/06/89	34-35	15	179.1	19.0	48.2	14.0
FALL 1989								
Benner	11/06/89	11/28/89	22	14	174.8	16.7	48.5	15.4
Stone	11/06/89	11/30/89	24	15	179.2	14.8	53.0	16.4
SPRING 1990								
Benner	3/07/90	4/06/90	30	10	178.8	25.9	60.8	30.2
Stone	3/07/90	4/05/90	29	10	193.5	25.9	65.8	22.9

Table 4-18. Sampling Dates for Quantitative Surveys of Fish Communities in ERP Study Reaches

Region	1988	1989	1990
Adirondacks	9/22–10/12	4/24–26 6/21–27 9/01–12 11/07–14	4/19–24 6/12–14
Catskills	10/10–12/12	5/1–6/20 1/13–29 8/22–28 10/13–11/27	6/2–6/6
Pennsylvania	7/12–14 11/15–22	3/29–4/6 6/28–30 8/22–25 11/28–12/1	4/3–10 5/31–6/5

Table 4-19. Electrofishing Efficiency Checks

Region	Date	No. Marked Fish	No. Passes	No. Fish Caught	Population Estimate	Capture Efficiency	Accuracy Population Estimate
Adirondacks	6/89	25	3	17	N/A[a]	68%	N/A
Catskills	6/89 10/89	40 40	3 3	39 26	39 28	97% 66%	97% 70%
Pennsylvania	N/A	50	4	39	40 (± 4)	78%	80%

[a] Data not available (not calculated or reported by regional cooperator).

Table 4-20. Fish Transplants

Region	Date	Stream	Brook Trout Stocked		Forage Fish Stocked[a]	
			Number	Weight[b] (g)	Number	Weight[b] (g)
Adirondacks	September 1988	Fly Pond Outlet	0	0	57	154
		Bald Mt. Brook	30	126	30	103
		Buck Creek	103	820	86	203
		Seventh L. Inlet	65	804	122	323
	April 1989	Fly Pond Outlet	51	358	71	103
		Bald Mt. Brook	26	183	44	104
		Buck Creek	112	974	113	210
		Seventh L. Inlet	100	866	185	323
	September 1989	Fly Pond Outlet			46	139
		Bald Mt. Brook			29	80
		Buck Creek			81	205
		Seventh L. Inlet			126	298
	November 1989	Fly Pond Outlet			32	83
		Bald Mt. Brook			21	63
		Buck Creek			82	193
		Seventh L. Inlet			106	278
Catskills	May-June 1989	High Falls	43	718	0	0
		Biscuit Brook	42	680	29	180
		E. Br. Neversink	50	770	50	280
Pennsylvania	October 1988 and February 1989	Benner Run	26	--	50	--
		Roberts Run	44	--	100	--
		Stone Run	77	--	50	--
		Baldwin Creek	28	--	100	--
		Linn Run	67	--	100	--

[a] Blacknose dace in Adirondack streams; slimy sculpin in Catskill streams and in Benner, Roberts, and Stone; and mottled sculpin in Baldwin and Linn.

[b] -- = no measurements made of fish weight.

SECTION 5

STREAM HYDROLOGY AND CHEMISTRY

In Section 5, we describe the hydrologic and chemical responses of the ERP streams during the course of the study. Section 5.1 provides the climatic setting during the ERP and summarizes the occurrence of major hydrologic events. Section 5.2 includes an overview of the chemical characteristics of the ERP streams and describes their chemical responses during episodes. Subsection 5.2.1 describes episodic changes of ANC, pH, and Al_{im}. In Subsection 5.2.2, we explore the role that major ions played in controlling episodes in ERP streams.

5.1 HYDROLOGIC RESPONSE

5.1.1 Climatic Conditions

We can obtain an overview of the climatic conditions during the ERP by examining long-term records for climatic stations located near the ERP watersheds (USGS 1991; and data from the NOAA National Climatic Data Center, Reston, Virginia). In the Adirondacks, nearby climatic stations are located at Old Forge, Big Moose, and Stillwater Reservoir. For the period of summer (July, August and September) 1988 through spring (April, May and June) 1989, precipitation was 75% to 125% of the 30-year normal. Summer 1989 rainfall was 125% to 150% of normal. From fall (October, November, December) 1989 to spring 1990, precipitation was near or slightly above normal. Temperatures during summer 1988 were above normal, whereas the winter (January, February, March) 1988 through summer 1989 period had near normal temperatures. During fall 1989, temperatures were below normal and during winter and spring 1990, temperatures were above normal.

Slide Mountain and Liberty are climatic stations near the ERP sites in the Catskills. For summer 1988, fall 1988, winter 1989, and summer 1989, precipitation was 75% to 125% of normal. Precipitation during spring 1989 was 150% to 200% of normal. Snowfall accumulations during the winter of 1989 were at a record low. Fall 1989 through spring 1990 had precipitation depths that were near or slightly above normal. Temperatures for summer 1988, winter 1989, and winter 1990 were above normal, whereas temperatures during spring 1989 and spring 1990 were near normal. Both fall 1988 and fall 1989 had below normal temperatures.

Phillipsburg is the climatic station closest to the ERP streams in central Pennsylvania. Two stations, Laurel Mountain and Donegal, are near the southwest Pennsylvania study sites. Both parts of Pennsylvania experienced similar meteorological conditions during the ERP. Summer 1988 through winter 1989 had precipitation levels that were 75% to 125% of normal. Spring 1989 precipitation levels were 125% to 150% of normal and summer 1989 levels returned to 75% to 125% of normal. Precipitation for fall 1989 through spring 1990 was approximately normal. Temperatures during winter 1989 and winter 1990 were above normal. Temperatures during all other seasons were normal or below normal.

5.1.2 Major Hydrologic Events

The ERP was designed to examine the chemical and biological responses of streams to episodic acidification. The study ideally would have been conducted during a period when snowmelt and rainstorms generated hydrologic events with normal or above normal flows. In practice, the hydrologic conditions during the study varied from region to region. In the Adirondacks, winter conditions allowed significant snowpacks to develop during both winters of the ERP. In each case, snowpacks > 50 cm developed, with meltwaters contributing to episodes during late winter and early spring periods. Spring and fall rainstorms also generated hydrologic events. In the Catskills, very small snowpacks developed during both winters. Most of the episodes were generated by rainstorms. A similar situation developed in Pennsylvania. No significant snowpacks accumulated in either of the winters during the ERP. Hydrologic events were generated almost exclusively by rainstorms. However, a number of the rainstorms were quite large and generated hydrologic events with large peak flows and relatively long durations.

All Adirondack streams had similar numbers of hydrologic events in response to snowmelt and rainstorms (Figures 5-1[1] through 5-4). Fly Pond outlet, the reference stream, had the smallest streamflows, and the least difference between the minimum and maximum flows (Tables 5-1[1] to 5-4). These levels reflect the influence of Fly Pond as the source of the stream. The other Adirondack streams also reached very low flows ($\leq$ 0.01 m^3/s) during the summer months and median flow rates were no greater than 0.06 m^3/s (Tables 5-1, 5-2, and 5-4). However, these streams experienced maximum flows of 0.6 to 4.1 m^3/s during the snowmelt periods of late winter and early spring. During the first year of study, the largest hydrologic event occurred during snowmelt, beginning approximately March 27 and lasting 7 days. During 1990, major hydrologic

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[1] Since this section contains so many tables and figures, we have placed them all at the end of the section. Figures appear first, beginning on page 109, then tables, beginning on page 161.

events occurred during early winter, but the main snowmelt period began the second week of March, with warming temperatures and rain.

In the Catskill Mountains, the 1989 spring snowmelt was much smaller than normal, with a period of moderately high discharge beginning February 21 and continuing through a small rainstorm in early April. The most sustained high flows occurred in late March and early April, a period of high air temperatures but little precipitation. A high flow period in late March was caused mainly by melting ice, rather than snowmelt. Snowpack accumulations during winter 1990 were also much smaller than normal. However, in late January 1990, a melt event did occur. In addition, a small hydrologic event in March 1990 was influenced by snowmelt. Rainstorms generated a number of major hydrologic events throughout the year (Figures 5-5 to 5-8). High flows ranged from 1.7 to 41.7 m^3/s (Tables 5-5 to 5-8). The East Branch of the Neversink River, because of its large drainage area, had the highest levels of discharge during hydrologic events (Figure 5-7). However, much smaller differences in flow existed between the streams during periods of low and moderate discharge (Tables 5-5 to 5-8).

During both winter periods in the Pennsylvania study areas, snowpack levels were very low and had minimal influence on hydrologic events recorded during the study. However, major rainstorms occurred during spring 1989 and to a lesser degree in spring 1990 (Figures 5-9 to 5-13). Maximum discharge ranged from 2.0 to 8.6 m^3/s, and minimum flow rates were from < 0.01 to 0.04 m^3/s (Tables 5-9 to 5-13). Linn Run had the greatest streamflows and the flashiest response to rainstorms (Table 5-11).

5.2 STREAM CHEMISTRY

Tables 5-1 through 5-13 summarize the overall maximum and minimum values of major chemical variables recorded in the ERP streams. In addition, we created a subset of the ERP database that represents weekly sampling of the ERP streams. The purpose of this activity was to be able to report the chemical characteristics of the ERP streams in a format similar to that commonly found in the literature from less intensive (non-episodic) stream chemistry studies. We chose a weekly sample for each stream that was closest in time to Tuesday at 10 AM (reference time). In all regions, a sample was available within 1 or 2 days of the designated reference time. Then, we made statistical summaries for the one-year period within the study (1989: 2/1/89 through 1/31/90) with the most complete weekly data record (Tables 5-1 to 5-13). Throughout the report, we refer to the values reported from these procedures as *weekly* statistics (e.g., weekly median).

The weekly ANC, pH, and Al data are virtually complete for all streams in all regions. For Pennsylvania streams, major ion data are missing for several weeks. The missing data are from the period November 1989 through January 1990, a time with relatively high discharge and episodes. Therefore, the Pennsylvania weekly statistics are somewhat biased away from the higher flow regimes. However, the weekly summaries still provide a qualitative picture of the major ion characteristics of the Pennsylvania streams.

As indicated in Section 3, one or two streams in each region served as references for the biological studies. The biological reference streams are Fly Pond Outlet in the Adirondacks, Black Brook and High Falls Brook in the Catskills, and Baldwin Creek and Benner Run in Pennsylvania. The discussion that follows will show that the water chemistry in the reference streams was generally favorable for fish and other aquatic biota during the ERP (see Section 6). However, as discussed in Subsection 5.2.1, Benner Run experienced occasional acidic episodes of short duration, but had the best water chemistry of the three northcentral Pennsylvania streams. The reference streams do not serve a strict reference or control function for ERP hydrochemical studies. Instead, the reference streams allow ion changes in fairly well-buffered systems to be examined along with and compared to ion changes in the streams that have acidic, high Al episodes.

All streams in the Adirondacks had 1989 weekly median ANC values of at least 10 μeq/L and median pH values > 5.3 (Tables 5-1 to 5-4). Weekly median Al_{im} values ranged from 20 to 165 μg/L. Fly Pond Outlet, the reference stream for biological studies, had the highest pH and ANC values, and the lowest Al_{im} values. Fly Pond was also the most alkaline of the 13 ERP study streams. Buck Creek had the lowest pH and ANC values, and the highest Al_{im} levels. Bald Mountain Brook and Seventh Lake Inlet weekly median ANC and pH values were only slightly greater than values for Buck Creek.

In the Catskills, Black Brook and High Falls Brook had similar weekly median ANC ($\geq$ 95 μeq/L) and pH values ($\geq$ 6.6). During the study period, the East Branch Neversink River was a chronically acidic system with a median ANC of −6 μeq/L and a median pH of 4.91 (Table 5-7). Not surprisingly, East Branch Al_{im} values are the highest of the Catskill streams. Linn Run in Pennsylvania and Buck Creek in the Adirondacks had weekly median Al_{im} values that were just slightly less than the East Branch median. Biscuit Brook had intermediate median pH and ANC levels compared to the other Catskills study streams (Table 5-5).

Two of the Pennsylvania streams were chronically acidic during 1989. The weekly median ANC values of both Roberts Run and Stone Run were < 0, and their weekly median pH values were < 5.4 (Tables 5-12 and 5-13). Although Linn Run's weekly median ANC was 30 μeq/L and its weekly median pH was 6.24, it had the highest median Al_{im} value of any stream in Pennsylvania. Baldwin Creek and Benner Run were the two reference streams for biological research. Both of these streams had weekly median ANC levels above 0, but Baldwin Creek had higher levels of pH and ANC. Neither stream had median Al_{im} levels above 11 μg/L.

Because episodes occur during periods of high streamflow, a useful way to examine the data is to compare periods of high streamflow (during episodes) with periods of low flow (not during episodes or seasons with high flow, e.g. snowmelt). We developed flow duration curves of each stream using hourly streamflow data for the entire study period, and we calculated the 20th percentile streamflow to represent low-flow conditions and the 95th percentile streamflow to represent high-flow conditions associated with moderate to large episodes. Then, we sorted the stream chemistry database by the streamflow at the times water samples were collected, and we calculated the median values of major chemical variables at streamflows ≤ 20th percentile (low flow) and ≥ 95th percentile (high flow). For each stream, we compared the discharge distributions ≤ 20th percentile and ≥ 95th percentile in the discharge database and in the stream chemistry database and found them to be very similar.

Tables 5-14 and 5-15 summarize the median water chemistry variables for low flow and high flow. The numbers presented do not attempt to deal with the seasonal variation described in Sub-sections 5.2.1 and 5.2.2, but they represent an approach that provides a simplified comparison of chemistry during major episodes (high flow) among streams. With the exception of the East Branch Neversink River, all the ERP streams had ANC values > 0 and pH and Al_{im} values suitable to support fish populations during low flow (see Section 2). In general, the low flow median pH and ANC were slightly greater than 1989 weekly median pH and ANC (Figures 5-14 and 5-15). However, low flow Al_{im} concentrations were considerably smaller than the 1989 weekly median values (Figure 5-16). During high flow, five of the streams had median ANC values < –10 μeq/L, median pH ≤ 4.8, and Al_{im} concentrations > 195 μg/L (Table 5-15 and Figures 5-14 to 5-16).

Distinctive regional characteristics are evident in the ERP stream major ion data. The five Pennsylvania streams had the highest overall SO_4^{2-} concentrations, and had four of the five highest median SO_4^{2-} concentrations (Tables 5-9 to 5-15). Benner Run, with the lowest median SO_4^{2-} value of Pennsylvania streams, had the greatest total variation of any ERP stream. The Adirondack streams had the largest DOC concentrations, the Pennsylvania streams had the lowest concentrations, and the Catskills had intermediate concentrations (Tables 5-1 to 5-15). The Adirondack and Catskill streams had similar median and maximum concentrations of NO_3^-. The NO_3^- concentrations of the Pennsylvania streams were much smaller than the NO_3^- concentrations of the Catskill and Adirondack streams. Although the Pennsylvania streams are located farthest from the coast, they generally had the highest Cl^- concentrations. Fly Pond Outlet also had large Cl^- concentrations. The primary study reach of Fly Pond Outlet is located immediately below a stretch of stream that parallels a paved road, and the stream may have been influenced by road salt. Calcium was the dominant cation in all ERP streams. As expected, the sum of base cations for all streams was directly related to ANC.

5.2.1 Episodic ANC, pH, and Al_{im}

The sampling strategy employed in the ERP allowed most episodes (and virtually all major episodes) that occurred during the study period to be reasonably well characterized, at least with regard to worst-case chemical conditions (Figures 5-1 to 5-13). Sometimes the total duration, especially the recession stages, of hydrologic events were not sampled as intensively as the rising limb and peak of the storm hydrograph. Also, each region experienced hydrologic events that were unsampled or had few samples. Nevertheless, the ERP database represents one of the most intensive temporal stream sampling efforts (related to acidic deposition) to be conducted in the United States.

Episodes that occurred during the ERP were individually identified. The senior author evaluated the time series of hydrologic and chemical data, displayed in Figures 5-1 through 5-13 (but on a much larger time scale), and separated out 19 to 33 episodes per stream that had been sampled with sufficient intensity to allow the initial conditions and the lowest ANC and pH and the highest Al_{im} values to be identified (Figure 5-17). If episodes occurred sequentially, the two episodes were separately identified even if the stream chemistry and streamflow had not returned to pre-episode conditions from the first episode in the series. For most analyses, ANC was used as the primary chemical variable for establishing the initial and minimum points of the episode.

The ERP streams exhibited a wide range of ANC depressions during episodes (Figure 5-18a). Aquatic systems with high initial ANC values tended to have larger ANC depressions. However, the lowest episodic ANC values occurred in streams with initial ANC values of < 50 μeq/L. For episodes in which pH levels dropped to 5 or below, initial pH values were ≤ 5.8 (Figure 5-18b). The magnitude of pH changes during episodes was greatest for episodes with mid-range initial pH values (5.5 to 6.8). Episodic changes of Al_{im} were highly variable (Figure 5-18c). Estimated

ERRATA

Page 92, third paragraph, line 3.

Change "19 to 33 episodes" to "13 to 26 episodes".

increases of 100 to 200 μg/L were fairly common. Episodes with higher initial Al_{im} concentrations tended to have the highest maximum Al_{im} concentrations.

A comparison of the episodic chemical characteristic of streams in the three ERP regions reveals that Roberts Run, Stone Run, Buck Creek, and the East Branch Neversink River had the lowest initial episode ANC levels (Figure 5-19). The starting ANC values were often < 0. These streams also had relatively small ANC changes during episodes, but they reached the lowest absolute ANC levels of any of the ERP streams (Figure 5-19). Fly Pond Outlet, High Falls Brook, and Black Brook had the highest initial ANC values, the greatest ANC depressions, and the highest minimum ANC values among the ERP streams (Figure 5-19). Biscuit Brook and Baldwin Creek occasionally experienced acidic episodes. Most of the other ERP streams often experienced acidic conditions during episodes. The behavior of pH during episodes was similar to that exhibited by ANC (Figure 5-20). Buck Creek, East Branch Neversink River, Roberts Run, and Stone Run had the lowest minimum pH levels, commonly with values < 4.8.

Aluminum chemistry patterns during episodes in ERP streams were somewhat different from those observed for ANC and pH. Bald Mountain Brook, Buck Creek, Seventh Lake Inlet, East Branch Neversink River, Linn Run, Roberts Run, and Stone Run all had estimated initial Al_{im} concentrations > 100 μg/L (Figure 5-21) during some episodes. Of these streams, Linn Run exhibited the greatest Al_{im} increases during episodes. Buck Creek, East Branch Neversink River, Linn Run, and Stone Run consistently had the highest estimated maximum Al_{im} concentrations (commonly > 350 μg/L) during episodes.

ERP results demonstrate that streams with the lowest ANC levels do not necessarily have the highest Al_{im} concentrations. All Adirondack streams have a similar relationship between ANC and estimated Al_{im} (Figure 5-22). Some variation in the Al_{im}-ANC relationship is evident among the Catskill streams. However, the Pennsylvania streams have very distinctive Al_{im}-ANC relationships (Figure 5-22). Linn Run and Stone Run tend to mobilize Al at higher ANC levels than the other Pennsylvania streams, an indication of differences in substances and processes controlling Al concentrations among the streams.

Plots of ANC, pH and estimated Al_{im} at the beginning of episodes and at the time of minimum episodic ANC illustrate the variance of episodic chemistry responses in the three regions during the course of the study (Figures 5-23 through 5-35). In all regions, the initial conditions of episodes have strong influences on the episodic behavior of ANC, pH and Al_{im}.

In the Adirondacks, initial ANC and pH tended to be high during the summer months, to decrease during the fall months, and to be at a minimum during snowmelt of late winter and early spring (Figures 5-23 to 5-26). Initial Al_{im} concentrations were low in the summer and high during late winter and early spring. Episodic pH and ANC decreases tended to be greatest in the summer and early fall, but the lowest pH and ANC occurred during episodes in the spring, winter, and late fall. Summer had the lowest initial and episodic Al_{im} concentrations. Episodes with the lowest minimum ANC and pH generally occurred during March 1989 and 1990 in response to snowmelt or rain and snowmelt. Buck Creek was an exception, however. Its most severe episode occurred in response to a rainstorm in November 1989. Snowmelt runoff produced episodes with the longest durations and with the highest Al_{im} concentrations.

The Catskill streams exhibited less seasonality of initial and minimum episodic ANC and pH, probably because of small snowpacks and a relatively uniform distribution of hydrologic events (Figures 5-27 to 5-30). For Biscuit Brook and the East Branch Neversink River, estimated Al_{im} values were the highest in the winter and spring periods. However, East Branch Al_{im} concentrations were much greater than Biscuit Brook Al_{im} concentrations. Estimated episodic Al_{im} concentrations in Black Brook and High Falls Brook were generally < 100 μg/L. In Biscuit Brook, the episodes with the lowest minimum values of ANC and pH and the largest concentrations of estimated Al_{im} occurred during episodes generated by spring rainstorms in May 1989 and April 1990 (Figure 5-27). A snowmelt-influenced acidic episode with elevated Al_{im} concentrations started on January 25, 1990. A fall episode during September 1989 produced acidic conditions but failed to generate high Al_{im} concentrations. The East Branch Neversink River, with the exception of a few fall or late summer episodes had acidic conditions at the beginning of episodes (Figure 5-29). The lowest minimum ANC and pH levels occurred during episodes in October 1988, September and October 1989, January 1990, and April 1990. The winter and spring episodes had large maximum Al_{im} concentrations (> 400 μg/L). However, the fall episodes had much lower maximum Al_{im} concentrations (< 300 μg/L).

Spring and late winter rainstorms produced most of the major episodes in the Pennsylvania streams during the ERP (Figures 5-31 to 5-35). Also, a few acidic episodes were recorded during fall periods. However, unlike the Catskill streams, when fall episodes occurred in the Pennsylvania streams, they generated Al_{im} concentrations similar to those of spring episodes. In Roberts Run and Stone Run (central Pennsylvania), ANC levels at the beginning of episodes were typically less than 0. Episodes with very low levels of minimum ANC or pH, or high levels of maximum Al_{im} occurred in March, May, June, and November 1989, and January and February 1990

(Figures 5-34 and 5-35). The episodes with the lowest minimum ANC values in Roberts Run and Stone Run occurred in June 1989. Pre-episode ANC values in Linn Run (southwest Pennsylvania) were usually positive. Linn Run episodes with low pH and ANC levels or high Al_{im} concentrations occurred throughout the spring and fall periods (Figure 5-33). Episodes during March and April 1989 had the lowest minimum ANC values.

The study streams can be divided into six ranked classes of chemical severity, based on ANC, pH, and Al_{im} behavior during episodes and low-flow periods.

1. The East Branch of the Neversink River was chronically acidic (median ANC $\leq$ 0) and had strong episodic ANC and pH depressions. It had the longest sustained durations of severe chemical conditions (low pH and ANC and high Al_{im}) of the ERP streams.

2. Stone Run and Roberts Run were also chronically acidic, but pH and Al_{im} levels were not as extreme as in the East Branch of the Neversink River. These streams experienced severe episodes with low pH and high Al_{im}. During summer low-flow periods, ANC levels were positive.

3. Buck Creek and Linn Run were not chronically acidic but had severe acidic episodes with low pH and ANC and high Al_{im} for long durations.

4. Bald Mountain Brook and Seventh Lake Inlet had episodes of moderate severity (low pH and ANC, but moderate Al_{im} levels) and duration.

5. Biscuit Brook and Benner Run experienced acidic episodes but they were of short duration with moderate pH levels and relatively low Al_{im} concentrations.

6. Fly Pond Outlet, Black Brook, High Falls Brook, and Baldwin Creek were classified as nonacidic (with ANC always > 0, except for one brief excursion below 0 in Baldwin Creek) and had relatively high pH and low Al_{im} throughout the study period.

The biological significance of these chemical severity classes is discussed in Section 6.

The shaded areas in Figures 5-1 to 5-13 identify the time periods during which brook trout bioassays were conducted (see Section 6.1). In the Adirondacks, the bioassay experiments occurred during major episodes. However, no bioassays were conducted during snowmelt periods, which generally had episodes with the lowest ANC and pH levels and the highest Al_{im} values. The Catskill bioassays included some of the most severe episodes measured in the Catskill streams. Bioassay experiments in Pennsylvania occurred during major episodes, but episodes with lower pH and ANC levels and higher Al_{im} levels occurred at other times during the study.

5.2.2 Contributions of Major Ions to Episodic Acidification

With the exception of organic acids (A^-), major ions in streamwater were measured by the methods described in Section 4.3.2. These measurements provided SO_4^{2-}, NO_3^-, Cl^-, and base cation data for the ERP streams. However, DOC measurements do not yield information about the ionic charge of organic acids, which is required to evaluate the role of organic acids in controlling episodes. Therefore, the ionic charge of A^- was determined indirectly.

In the Adirondacks, the definition of ANC was used as the basis for determining A^- (Munson and Gherini, 1991).

$$ANC = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [\text{other proton acceptors}] - [\text{proton donors}] \qquad (5\text{-}1)$$

$$ANC = \Sigma C_B - \Sigma C_A \qquad (5\text{-}2)$$

where: ΣC_B = the sum of base cation molarities times their equivalence charge. Base cations are $2[Ca] + 2[Mg] + [Na] + [K] + [NH_4] + X[Al]$,
where: X = charge of Al.

ΣC_A = the sum of the strong acid anions times the equivalence charge. Acid anions are $2[SO_4] + [NO_3] + [Cl] + Y[A]$,
where: Y = charge of A.

For each water sample with complete ion chemistry, the following expression was calculated:

$$D_{ANC} = (\Sigma C_B - \Sigma C_A) - \text{Gran ANC}. \qquad (5\text{-}3)$$

D_{ANC} is an estimate of A^- for a water sample, because the Gran ANC measurement includes the influence of organic acids, whereas the $\Sigma C_B - \Sigma C_A$ term does not include a value for A^-. This approach assumes that D_{ANC} is not the result of analytical error and that the charge associated with Al can be determined. The charge of Al, as represented by X in the ΣC_B definition, was estimated by the following linear expression (Eq. 5-4), which is based on data presented by Sullivan et al. (1989):

$$X = 6.5 - 0.875(pH) \qquad (5\text{-}4)$$

For each water sample, the calculated Al charge (X) was applied to the total dissolved Al value to calculate the equivalent concentration of Al.

For any given water sample, D_{ANC} was too variable to provide a reasonable estimate of A^-. Therefore, a regression approach was used to develop empirical models, by ERP region, that estimate A^- (D_{ANC}) as a function of DOC and pH in a manner similar to that of Wilkinson et al. (1992). Because DOC and pH were measured directly, a regression equation based on these analytes will provide a more stable estimate of A^-. The best model for the Adirondack ERP streams is:

$$A^- = -33.64 + 6.407(pH) + 15.08(DOC) - 1.653(pH*DOC) \quad (5\text{-}5)$$
$$R^2 = 0.65$$

We used Eq. 5-5 to estimate A^- for the Adirondack streams. We could not develop statistically significant models for the Catskills ($R^2 = 0.20$) or Pennsylvania ($R^2 = 0.06$). There are at least two reasons that could explain why a sound empirical model could be developed in the Adirondacks but not in the Catskills or Pennsylvania. First, the concentrations and ranges of DOC are both much greater in the Adirondack streams. Second, the source of the organics is likely to shift during the course of episodes because of changes in hydrologic flowpaths. Most empirical relationships used to estimate organics from anion deficit have been developed for databases of regional surveys of lakes or streams. Typically, these waterbodies have been sampled during similar hydrologic conditions and would therefore have organics contributed from fairly uniform parts of their watersheds. In the Adirondacks, the organics concentrations are higher and the characteristics of the organics may be more uniform in all hydrologic source areas than in the Catskills and Pennsylvania.

Consequently, we decided to use a literature-based estimate of organic carbon charge-density to estimate A^- for Catskill and Pennsylvania streams. We reviewed charge-density values tabulated by Kahl et al. (1989) and Wilkinson et al. (1992) from studies of a wide variety of streams and lakes in North America and Europe. We selected a mid-range charge-density value of 5 μeq/mg of DOC to estimate A^-.

A traditional anion deficit approach was not employed because dissolved inorganic carbon (DIC) was not measured in all regions, and when DIC was measured, the pH – DIC relationship did not uniformly conform to the theoretical, open-atmosphere relationship for these two variables (Stumm and Morgan, 1981). Therefore, an accurate calculation of $[HCO_3]$ could not be made.

Figures 5-36 through 5-48 show the concentrations of major ions and stream discharge at the beginning of each episode and at the time of minimum ANC (ANC_{min}) during the episode. The time of minimum ANC was used as a reference point because these ion changes are used in Section 5.2.2.1 to examine the causes of episodic ANC depressions. The reader is advised to examine the scales of the y-axes carefully because they are not uniform from stream to stream or from ion to ion. The graphs have been designed to show the maximum amount of ion variation.

In the Adirondacks, SO_4^{2-} concentrations do not appear to have consistent seasonal patterns (Figures 5-36 to 5-39). However, SO_4^{2-} is most likely to increase during episodes that occur in the summer and early fall months. Nitrate does exhibit a strong seasonal pattern in the Adirondack ERP streams. Initial and ANC_{min} NO_3^- concentrations are much greater in the winter and early spring episodes. Also, NO_3^- increased more frequently during episodes in the winter and early spring than during the remainder of the year. Chloride concentrations and episodic changes were fairly constant during the course of the study. Concentrations of A^- were much greater in the Adirondack streams than in the Catskill or Pennsylvania streams. Typically, A^- increased during episodes throughout the year, but the greatest increases tended to occur during episodes in the late summer and fall. Base cations usually decreased during episodes throughout the year, with the largest initial concentrations and changes occurring in the summer and early fall. Fly Pond Outlet experienced the greatest decreases in base cations (Figure 5-38).

Similar to the Adirondacks, SO_4^{2-} concentrations and changes in Catskill episodes did not exhibit much seasonality (Figures 5-40 to 5-43). Unlike the Adirondacks, the Catskill streams frequently exhibited large SO_4^{2-} decreases during episodes. Nitrate concentrations routinely increased during episodes in all streams except High Falls Brook (Figure 5-43). Episodic NO_3^- increases in High Falls Brook were concentrated in the winter and spring. Initial and ANC_{min} NO_3^- concentrations were somewhat greater during the winter and spring than in other seasons. Although A^- increased during episodes year round, the most dramatic increases tended to occur in late summer and fall. Chloride tended to decrease slightly during episodes, with Black Brook having the largest Cl^- decreases (Figure 5-41). Base cations also decreased during most, but not all, episodes in the Catskill streams. As expected, Black Brook and High Falls Brook had the largest base cation decreases during episodes (Figures 5-41 and 5-43).

Pennsylvania streams had the highest SO_4^{2-} concentrations (Figures 5-44 to 5-48). All the Pennsylvania streams had SO_4^{2-} increases, some quite large, during episodes. Baldwin Creek (fall and early spring), Linn Run (fall and early spring), and Benner Run (throughout the year) had the largest SO_4^{2-} pulses (Figures 5-44 to 5-46). However, strong seasonal SO_4^{2-} patterns were not evident in any of the Pennsylvania streams. Nitrate concentrations in the Pennsylvania streams were much smaller than those in the Catskill or Adirondack streams, and the central Pennsylvania streams (Benner Run, Roberts Run, and Stone Run) had lower concentrations of NO_3^- than did the southwest Pennsylvania streams (Baldwin Creek and Linn Run). In central Pennsylvania, Roberts Run and Stone Run had a mixture of small NO_3^- increases and decreases during episodes, whereas Benner Run consistently had NO_3^- decreases. In southwest Pennsylvania, NO_3^- decreases were common during episodes in both Linn Run and Baldwin Creek (Figures 5-46 and 5-44). Concentrations of A^- typically increased during Pennsylvania episodes. However, A^- concentrations and changes did not exhibit any seasonal patterns during the study. Although both Cl^- increases and decreases occurred during episodes in the Pennsylvania streams, decreases were more common. Benner Run consistently showed some fairly large decreases in Cl^- during both fall and spring (Figure 5-45). As a rule, changes in base cations during episodes followed the typical pattern of decreasing during episodes in all streams. However, some notable exceptions occurred. Base cations increased fairly often during episodes in Baldwin Creek, Benner Run, and Stone Run. Linn Run, which most consistently had base cation decreases during episodes, had the greatest decreases during late spring (Figure 5-46).

5.2.2.1 Ion Changes

To evaluate the role of ion changes on episodic ANC depressions, we once again depend on the C_BC_A definition of ANC (see Eq. 5-2). From Eq. 5-2, we can develop the following expression:

$$\Delta ANC = \Delta\Sigma C_B - \Delta\Sigma C_A. \qquad (5\text{-}6)$$

For the ion change analyses, we slightly modified C_B by excluding Al, which allows a separate evaluation of the effects of traditional base cations (Ca, Mg, Na, K, NH_4) and Al. Consequently, we can expand Eq. 5-6 to the following:

$$\Delta ANC = \Delta\Sigma C_B + \Delta Al - \Delta SO_4 - \Delta NO_3 - \Delta Cl - \Delta A \qquad (5\text{-}7)$$

We used Eq. 5-7 as the basis for ranking the importance of ion changes for each episode. All computations were performed for the greatest ΔANC of an episode. Ion changes were calculated in equivalents. Inspection of Figures 5-36 to 5-48 reveals that ion changes can contribute to ANC depressions (–ΔANC) or reduce ANC depressions. Decreases of base cations ($-\Delta\Sigma C_B$) or Al (–ΔAl) and increases of acid anions ($+\Delta SO_4^{2-}$, $+\Delta NO_3^-$, $+\Delta Cl^-$, $+\Delta A^-$) contribute to ANC depressions. For each episode, all of the ion changes were evaluated to determine if they contributed to the ANC depression. All ion changes that contributed to episodic ANC depression were tabulated and ranked. The largest magnitude ion change was assigned a rank of 1 (most important contributor to the ANC depression). The second largest ion change was assigned a rank of 2, and so forth.

Regional and individual stream characteristics emerge upon examination of the number of episodes for which ion changes contributed to ANC depressions and the mean rank of ion change contributions to ANC depressions (Table 5-16). In the Adirondacks, base cation decreases and A^- increases most consistently contributed to ANC depressions during episodes. For Fly Pond Outlet, base cation decreases were consistently the most important contributor to ANC depressions (for episodes with sufficient data to allow ion change analysis). Base cation decreases were also the highest mean contributor to episodes in the other Adirondack streams except Seventh Lake Inlet. On average, A^- increases were the most important ion changes in Seventh Lake Inlet and were the second most important ion changes to ANC depressions in the other Adirondack streams. Nitrate increases were also very important contributors to episodes in Adirondack streams, with mean ranks just slightly less than A^- increases.

In the Catskills, base cation decreases, NO_3^- increases and A^- increases were all consistently important contributors to episodic ANC depressions (Table 5-16). On average, with the exception of the East Branch Neversink River, base cation decreases were the highest ranked contributors, NO_3^- increases were the second most important contributor, and A^- increases were the third most important ion changes. Decreases in base cations were especially important in Black Brook and High Falls Brook. For the East Branch Neversink River, base cation decreases were the most inportant ion changes and A^- increases were the second most important ion changes to ANC depressions. Sulfate increases rarely contributed to episodic ANC depressions in the Catskill streams. When SO_4^{2-} increases did contribute to ANC depressions, they were typically the second or third mean ranked ion change.

In the Pennsylvania streams, SO_4^{2-} increases and base cation decreases frequently made strong mean contributions to episodic ANC depressions (Table 5-16). In Linn Run and Roberts Run, base cation decreases were consistently the most important ion change contributing to episodic ANC depressions. However, in Baldwin Creek, Benner Run, and Stone Run, SO_4^{2-} increases contributed to ANC depressions in more episodes than did base cation decreases. Organic acids (A^-), on average, were the third most important contributor to ANC depressions in all Pennsylvania streams. Nitrate and Cl^- increases occurred less frequently than did SO_4^{2-} increases, base cation decreases, or A^- increases and generally made less important contributions to ANC depressions in the Pennsylvania streams.

In all three regions, Al typically increased during episodes and reduced ANC depressions. However, during a few episodes in some of the streams, especially in Pennsylvania, Al concentrations did decrease and make modest contributions to ANC depressions (Table 5-16).

An overview of ion changes is useful in developing a general understanding of the variance of episodic chemistry among the ERP streams. However, we are not equally interested in all episodes. We are most interested in those episodes that result in conditions harmful to aquatic biota. Because we are focusing on ANC in this section, we should be most interested in the severe episodes (lowest ANC_{min}) that result in acidic conditions for relatively long periods of time. In the Adirondacks, these type of episodes usually occurred during snowmelt periods. In Pennsylvania and the Catskills, large rainstorms induced episodes with the lowest ANC values.

For most streams in the Adirondacks, the episodes with the lowest ANC and pH values and highest Al concentrations occurred during the two snowmelt periods (1989 and 1990) and during spring rainstorms (Table 5-17). A rainstorm in November 1989 produced the most severe episode in Buck Creek. Fall rainstorms also produced major episodes in Bald Mountain Brook and Seventh Lake Inlet. Chemical behavior generally was similar among the Adirondack streams for the snowmelt episodes (Table 5-17). Sulfate and Cl^- concentrations decreased, reducing ANC depressions; base cation decreases were the first ranked contributors to ANC depressions; A^- and NO_3^- increases positively contributed to episodes and were second or third ranked (Table 5-17; Figures 5-36 to 5-39). During one snowmelt-driven episode in Buck Creek, NO_3^- increases were the most important ion change.

The ion changes controlling ANC depressions were more variable in Adirondack study streams during major rain-driven episodes than during major snowmelt episodes (Table 5-17). For Bald

Mountain Brook, base cation decreases were the most important ion changes during the two major rain-driven episodes, which occurred during fall 1989. Sulfate and A^- were the second or third ranked ion changes, but NO_3^- increases did not contribute to the ANC depressions of these episodes. Snowmelt was the driving force behind all the major Fly Pond Outlet episodes. In Buck Creek and Seventh Lake Inlet, A^- increases made the most important contributions to ANC depressions during major rain-driven episodes, regardless of whether they occurred in the spring or fall. Base cations decreases or NO_3^- increases were the second or third most important ion change during these episodes.

Unlike the Adirondacks, most of the major episodes in the Catskills streams occurred in response to spring or fall rainstorms (Table 5-18). Sulfate and Cl^- decreases reduced ANC depressions during the most episodes in Catskill streams (Figures 5-41 and 5-43). During the major episodes in High Falls Brook and Black Brook, base cation decreases were the most important contributors and NO_3^- increases (once an A^- increase) were the second ranked contributors to episodic ANC depressions (Table 5-18). Increases in A^- were consistently the third ranked ion change in High Falls Brook and Black Brook.

For Biscuit Brook, NO_3^- increases were the most important ion change in two of three of the major spring episodes (Table 5-18). Base cation decreases or an A^- increase were the second most important ion change. In the third spring episode, base cation decreases were the most important ion change; a NO_3^- increase was the second ranked ion change. Nitrate was also the most important contributor, followed by base cation decreases, to the major spring episode that occurred in the East Branch Neversink River.

During the major fall episodes in the East Branch Neversink River, A^- pulses were the most important contributors to ANC depressions (Table 5-18). Base cation decreases were second ranked and NO_3^- or SO_4^{2-} increases were the third ranked ion changes. Similarly, an A^- increase was the most important ion change during the major fall episode measured in Biscuit Brook (Table 5-18). However, a NO_3^- pulse was the second most important ion change.

The ionic responses of the Catskill streams were fairly uniform during the January 1990 snowmelt influenced episodes (Table 5-18). For all streams except Black Brook, NO_3^- pulses were the first ranked and A^- increases or base cation decreases were the second ranked contributors to ANC depressions.

All the major episodes in Pennsylvania streams were generated by rainstorms in the winter and spring (Table 5-19). Base cation decreases were usually the most important ion change for major episodes in Roberts Run and Linn Run. In Roberts Run, A^- pulses tended to be the second ranked ion change. In episodes in Linn Run, the second ranked ion changes were increases in NO_3^-, pulses of SO_4^{2-}, or decreases in base cations. During one 1990 episode in Linn Run, a SO_4^{2-} increase was the first ranked ion change controlling the episodic ANC depression. Base cation decreases commonly were the most important ion change in Baldwin Creek episodes. However, SO_4^{2-} and A^- pulses were each the first ranked ion change in a major episode. Sulfate pulses were commonly the most important ion change during major episodes in Benner Run and Stone Run; base cation decreases or A^- pulses were also the most important ion change in one or more episodes.

Major episodes in the Pennsylvania streams often had fewer ion changes contributing to ANC depressions than did the major episodes in the Catskills or Adirondacks (Tables 5-17 to 5-19). Whereas the Catskill and Adirondack streams rarely had fewer than three ion changes that contributed to ANC depressions, 40% of the major episodes in Pennsylvania had only two (or in one instance, one) ion changes that controlled ANC depressions. Benner Run had the greatest number of episodes with only two ion changes contributing to ANC depressions. In each case SO_4^{2-} pulses were the most important ion change and A^- increases were the second ranked ion change. During one major episode in Linn Run, base cation decreases, alone, controlled the ANC depression.

Another way to examine the importance of ion changes is to look for patterns of ion change in relationship to the minimum ANC (ANC_{min}) of episodes. In the Adirondacks, SO_4^{2-} tends to decrease during acidic episodes, whereas NO_3^- and A^- increases are likely to be the greatest during acidic episodes (Figure 5-49). In the Catskills, SO_4^{2-} tends to decrease in episodes with a wide range of episodic ANC_{min} levels (Figure 5-50). Nitrate increases are greatest in acidic or low ANC episodes. Organic acid changes may also be somewhat greater in low ANC or acidic episodes in the Catskills. No obvious relationships exist between SO_4^{2-} changes and ANC_{min}, NO_3^- changes and ANC_{min}, or A^- changes and ANC_{min} in Pennsylvania (Figure 5-51). In the Adirondacks and the Catskills, base cation decreases are smaller for acidic episodes than nonacidic episodes. However, the Pennsylvania streams experienced much larger base cation decreases during acidic episodes than did the Adirondack and Catskill streams (Figures 5-49 to 5-51).

5.2.2.2 Ion Concentrations

In Subsection 5.2.2.1, we explore the role that ion changes played in controlling episodes in the ERP streams. As can be seen from the data, these changes are very important in determining episodic acid-base chemistry. However, the ion changes must be linked with the absolute concentrations of ions to obtain a complete picture of the ionic control of minimum episodic ANC. In all three regions, SO_4^{2-} typically had the greatest concentrations of any of the acid anions at all times during episodes (Figure 5-52). Based on a C_BC_A (Eq. 5-2) definition of ANC, SO_4^{2-} is a major contributor to the ANC_{min} of a stream or lake, even if it remains unchanged or decreases during episodes. Sulfate is especially dominant in the Pennsylvania streams.

The role of NO_3^- in episodic chemistry is another example of the importance of examining both absolute concentrations of ions and ion changes. In Pennsylvania, NO_3^- pulses can be the second most important ion change during episodes (e.g., Linn Run). However, these changes are an order of magnitude smaller than the base cation decreases that are typically the most important ion change (Figure 5-46). Whether at the beginning or at the ANC_{min} of episodes, the NO_3^- concentrations in Linn Run or the other Pennsylvania streams are much smaller than in the Adirondack and Catskill streams (Figure 5-52). In the Catskill streams, both NO_3^- increases and absolute concentrations are important (Figure 5-52; Tables 5-16 and 5-18). The NO_3^- concentrations are sufficiently great at the beginning and at ANC_{min} to make a significant impact on ANC. In the Adirondacks, NO_3^- pulses are not typically the primary control of episodic ANC, but the NO_3^- concentrations, because of their relatively high absolute levels, depressed ANC values at the beginning and during the course of episodes (Figure 5-52; Tables 5-16 and 5-17). Even though A^- typically had somewhat greater increases during episodes in Adirondack streams, NO_3^- at times had a greater effect on minimum ANC because of its greater concentrations. This was especially true during late winter and early spring.

In the Adirondacks and Catskills, Cl^- concentrations were generally the smallest of the major ions (Figure 5-52). In the Pennsylvania streams, however, Cl^- concentrations in general were greater than NO_3^- or A^- concentrations at the beginning of episodes and at ANC_{min}. Therefore, Cl^- may have exerted an influence on the acid-basis status of the water chemistry of the Pennsylvania study streams.

As previously stated, A^- concentrations in the Catskill and Pennsylvania streams were generally low (Figure 5-52). In these two areas, the influence of A^- on ANC_{min} was primarily because of A^-

changes during episodes. In the Adirondack streams, however, A^- concentrations were great enough for both absolute concentrations and for ion changes to have an important influence on ANC_{min}.

5.2.2.3 Role of Acidic Deposition

Evaluation of ion changes and concentrations, as presented in Section 5.2.2, is a useful way to understand processes controlling episodes. Data presented in the previous subsection show that episodic ANC depressions are a result of complex interactions of multiple ions. However, there is the question of what these ionic behaviors mean with regard to the effects of atmospheric deposition. Organic acids are one common natural source of acidity during episodes. Although base cation decreases are generally viewed as largely a natural process, acidic deposition can influence the magnitude of the effect. During hydrological events, and associated episodes, the source of streamflow changes from groundwater, which is dominant during baseflow periods, to surface soils and other shallow sources (Wigington et al., 1990; Swistock et al., 1989). Base cation decreases are a manifestation of the differences in cation concentrations of the major sources of streamflow before and during episodes. Because acidic deposition can contribute to the depletion of base cations in surface soils more rapidly than deeper soils, it can accentuate base cation decreases that occur during episodes (Wigington et al., 1990).

In the ERP watersheds, there is no evidence of internal sources of SO_4^{2-}. Therefore, SO_4^{2-} in the streams is predominantly, if not solely, a consequence of atmospheric deposition. Nitrate in the ERP watersheds probably is derived from a combination of natural N cycling and atmospheric deposition (Aber et al., 1989, 1991). Significant NO_3^- pulses from forested watersheds are very unlikely without large deposition of atmospheric N (Stoddard, in press). Watersheds in the Adirondacks and Catskills, in which stream water concentrations of NO_3^- are quite high, have in all likelihood been significantly affected by atmospheric deposition of N. In the remainder of this section and the report, we ascribe all SO_4^{2-} effects and a portion of the NO_3^- effects to acidic deposition. Given these assumptions, we see evidence of both natural processes and acidic deposition making important contributions to episodic acidification in the Adirondack, Catskill, and Pennsylvania study streams.

For all episodes recorded (large and small) in the three ERP regions, base cation decreases were commonly the most important ion change contributing to ANC depressions. In the Catskills and Adirondacks, the largest base cation decreases occurred during nonacidic episodes. Base cation decreases were especially dominant for episodes in circumneutral streams in the study (Black Brook, Fly Pond Outlet, and High Falls Brook). However, some base cation decreases in the Pennsylvania streams were very large even during acidic episodes.

Organic acid concentrations were greatest in the Adirondack streams, and A^- increases during episodes were commonly the second and sometimes the first ranked ion changes during major episodes. Organic acid contributions tended to be greatest in episodes with acidic or low ANC_{min} values. Organic acids were generally less important in Pennsylvania and Catskill episodes. However, A^- increases were the most important ion changes during several fall episodes in two Catskill streams. Organic acid pulses were commonly the second most important, and occasionally the most important, ion changes during episodes in the Pennsylvania streams, even though the magnitudes of A^- changes were small.

Sulfate was the dominant acid anion (C_A) virtually at all times in the study streams in all three regions. For both acidic and nonacidic episodes in the Catskills, SO_4^{2-} concentrations tended to decrease, thereby reducing ANC depressions. In the Adirondacks, SO_4^{2-} concentrations were observed to increase or decrease during episodes. However, SO_4^{2-} concentrations tended to decrease during acidic episodes. Sulfate concentrations in the Pennsylvania streams were greater than in Catskill or Adirondack streams. Based on the C_BC_A ANC definition, these large SO_4^{2-} concentrations (in all regions) provided an acidity base upon which other ion changes further modified the acid-base status of the stream waters. Another major difference between the Pennsylvania streams and the Adirondack and Catskill streams is the importance of SO_4^{2-} pulses in Pennsylvania episodes. In some major episodes, SO_4^{2-} pulses were the most important ion change contributing to ANC depressions in three of the five Pennsylvania streams and were consistently the most important ion change in two of the streams.

Nitrate behavior and contributions to episodes were different in each of the three regions. Nitrate concentrations were much greater in the Catskill and Adirondack streams than in Pennsylvania streams. In the Catskills, NO_3^- concentrations typically increased during episodes, particularly during acidic episodes. In two of the Catskill streams, Biscuit Brook and East Branch Neversink River, NO_3^- was the most important ion change contributing to ANC depressions during several episodes. In the Adirondacks, NO_3^- increases were typically the third ranked ion change during episodes. The largest NO_3^- increases occurred during acidic episodes. Even though episodic changes of NO_3^- were relatively small, NO_3^- concentrations were large throughout Adirondack episodes. Nitrate pulses in Pennsylvania streams were generally small and made little contribution to ANC depressions.

Dow (1992) calculated S and N input-output budgets for the Pennsylvania streams. Four of the five watersheds exported 66–78% of S received as wet and dry deposition. The fifth basin, Benner Run, exported only 30% of deposited S. Dow attributed this phenomenon to the Benner Run watershed soils having higher SO_4^{2-} adsorption capacities than the other Pennsylvania watersheds. Benner Run is also the watershed in which SO_4^{2-} pulses during episodes were most frequently important contributors to ANC depressions. The Pennsylvania watersheds exported only 2–15% of the N deposited, with the southwest streams having the greatest NO_3^- export, a finding supporting the general lack of large NO_3^- pulses during episodes in Pennsylvania.

Stoddard (in press) has proposed stages to describe the progression of nitrogen saturation in watersheds based on temporal patterns of NO_3^- leaching in surface waters. Stage 0 is one of very low, or immeasurable, concentrations during most of the year, and measurable concentrations only during snowmelt or during spring rain storms. The Pennsylvania watersheds are probably in Stage 0 of this scheme. At Stage 1, the seasonal pattern typical of Stage 0 watersheds is amplified. In Stage 2, NO_3^- concentrations increase during periods of baseflow and the seasonal cycle of NO_3^- is dampened. The Catskill ERP streams may be in this stage. The ERP streams in the Adirondacks may be approaching the mid to later phases of Stage 2. In Stage 3, the watershed becomes a net source of N rather than a sink. Watersheds in Stage 3 have very high NO_3^- concentrations and lack a coherent seasonal pattern in NO_3^- concentrations.

Other ion changes were less important to episodes measured in the ERP. Chloride changes and concentrations usually had relatively little impact on episodes. However, for a few episodes in some Pennsylvania streams, Cl^- increases were the second ranked ion change. In virtually all episodes, especially those that were acidic, Al increases tended to buffer ANC depressions.

Ion behavior that controlled ANC depressions during the five major episodes recorded in each stream during the study period was not necessarily the same as the ion changes most important to smaller, more frequent episodes. In the Adirondacks, the only region to have major snowpacks, the most severe episodes generally occurred during spring snowmelt. During these episodes, base cation decreases were usually the most important contributions to ANC depressions, and A^- and NO_3^- changes positively contributed to episodes and were of similar rank (2 or 3). Buck Creek experienced one major snowmelt episode in which an increase in NO_3^- was the most important ion change. The Catskills had one episode influenced by snowmelt in which NO_3^- pulses were the first ranked contributor and base cation decreases were the second ranked ion change for three of the four streams.

Within regions, the major episodes generated by rainstorms had more variable ionic controls than did snowmelt episodes. The large rain-induced Adirondack episodes occurred in the spring and fall. In these episodes, increases in A^- and decreases in base cations were the most important ion changes to ANC depressions. In major spring episodes in the Catskills, decreases in base cations or increases in NO_3^- were typically the first or second ranked ion changes contributing to ANC depressions. For a series of Catskill streams (including the ERP streams) that had been monitored for a number of years, Murdoch and Stoddard (1993) concluded that decreases in ANC are controlled primarily by dilution of base cations during the fall and early summer and by increases in NO_3^- during the initial spring snowmelt. For the major episodes in Pennsylvania, base cation decreases and SO_4^{2-} increases were usually the most important or second most important ion changes contributing to ANC depressions. Stone Run and Baldwin Creek both experienced major rain-induced episodes in which A^- increases were the most important ion changes. In Linn Run, NO_3^- pulses were the second ranked ion change in two major episodes.

Atmospheric deposition of SO_4^{2-} and NO_3^-, as evidenced by stream water SO_4^{2-} and NO_3^- during episodes, has contributed significantly to the occurrence of acidic episodes with low pH and high Al levels in all three study areas. Base cation decreases are often the most important ion change that occurs during minor and major episodes. However, base cation decreases alone cannot create acidic stream water conditions during episodes. Organic acid pulses are also important contributors to ANC depressions in the Adirondack streams and, to a lesser extent, in the Catskill and Pennsylvania streams. In all three study areas, SO_4^{2-} or NO_3^- pulses during episodes augment the natural processes to create episodes with lower pH and ANC and higher Al concentrations than would have occurred from natural processes alone. Furthermore, the large baseline concentrations of SO_4^{2-} and NO_3^- reduce episodic minimum ANC, even when these ions do not change during episodes.

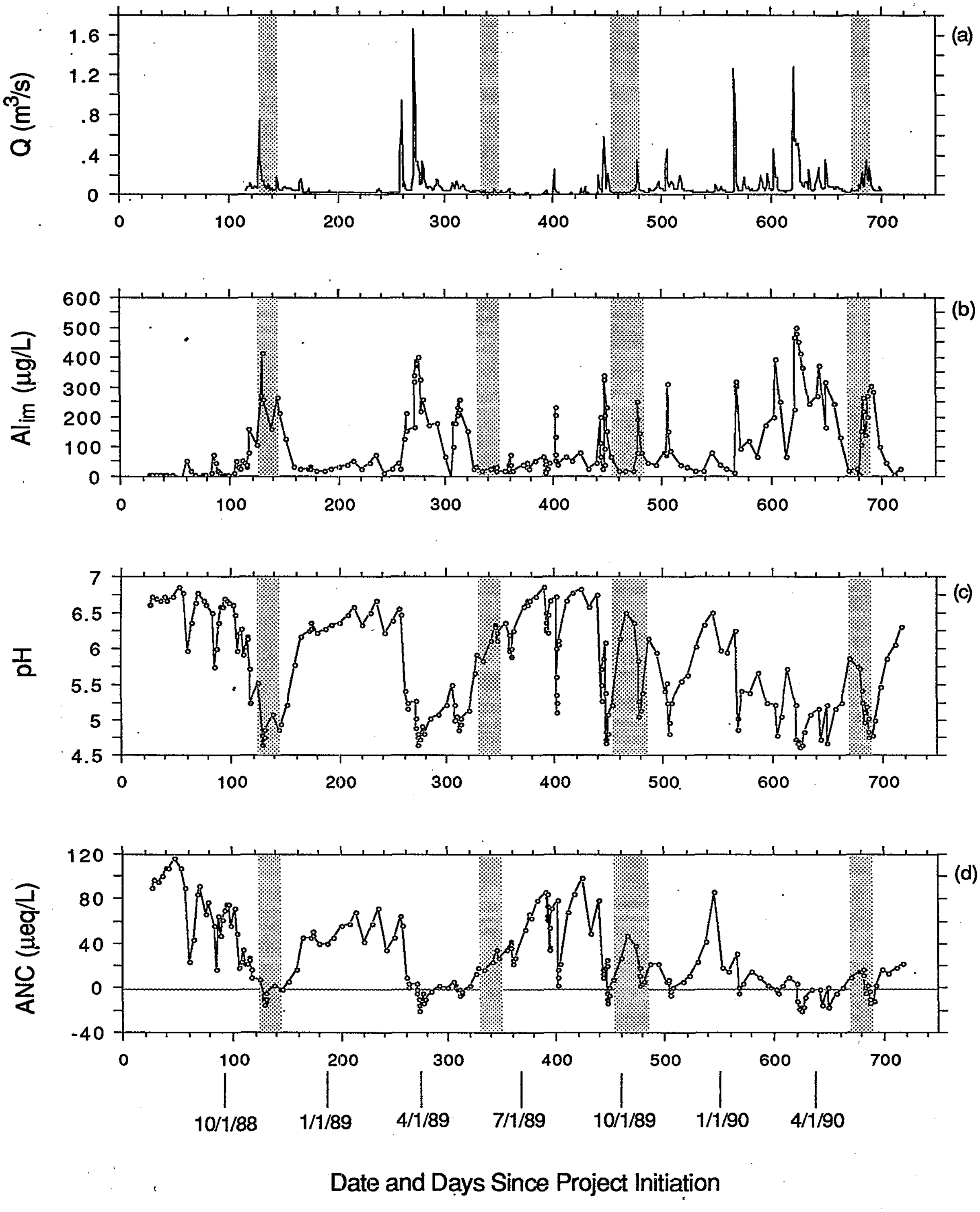


Figure 5-1. (a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Bald Mountain Brook, Adirondacks. Shaded areas designate periods when brook trout bioassays were conducted.

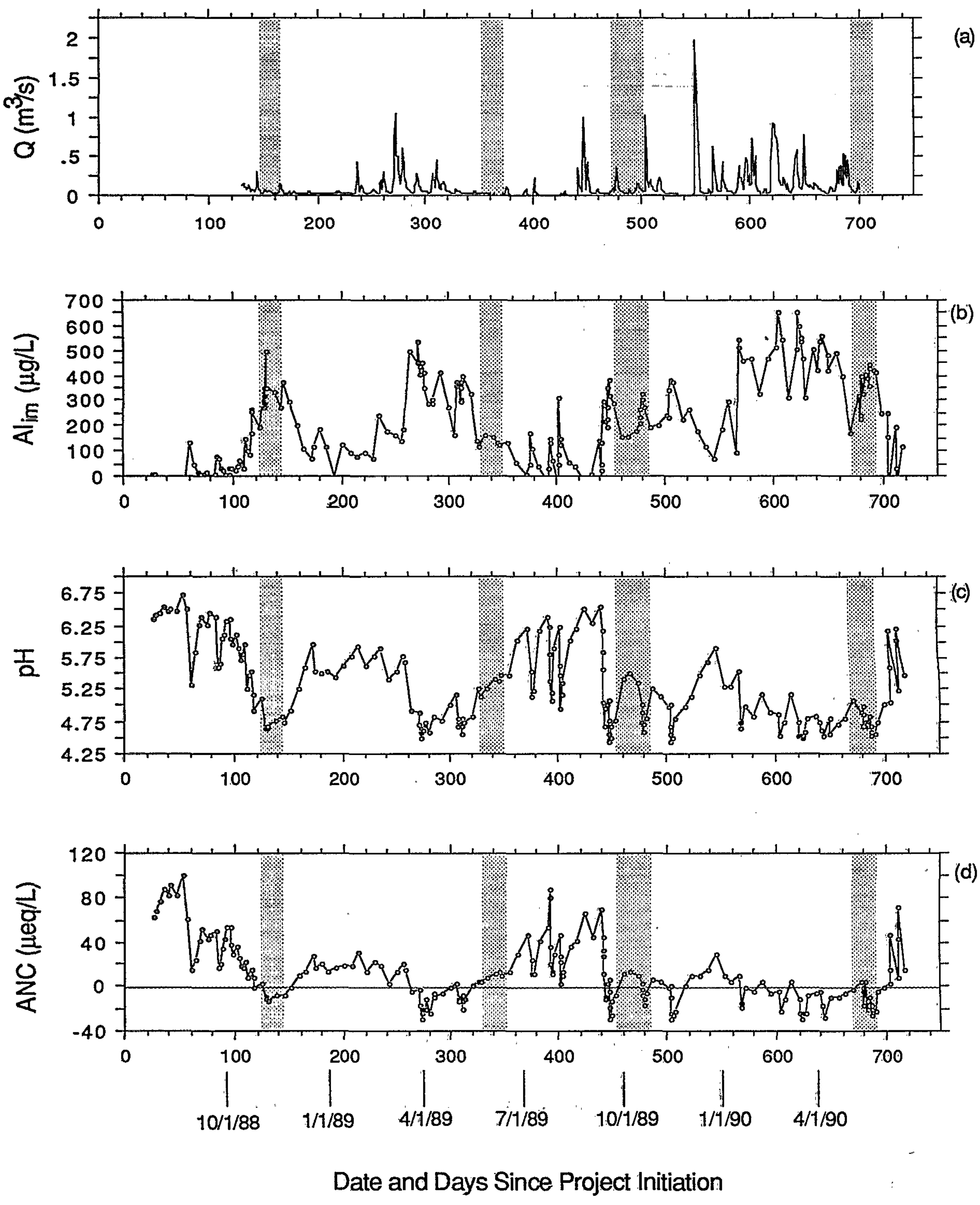


Figure 5-2. **(a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Buck Creek, Adirondacks. Shaded areas designate periods when brook trout bioassays were conducted.**

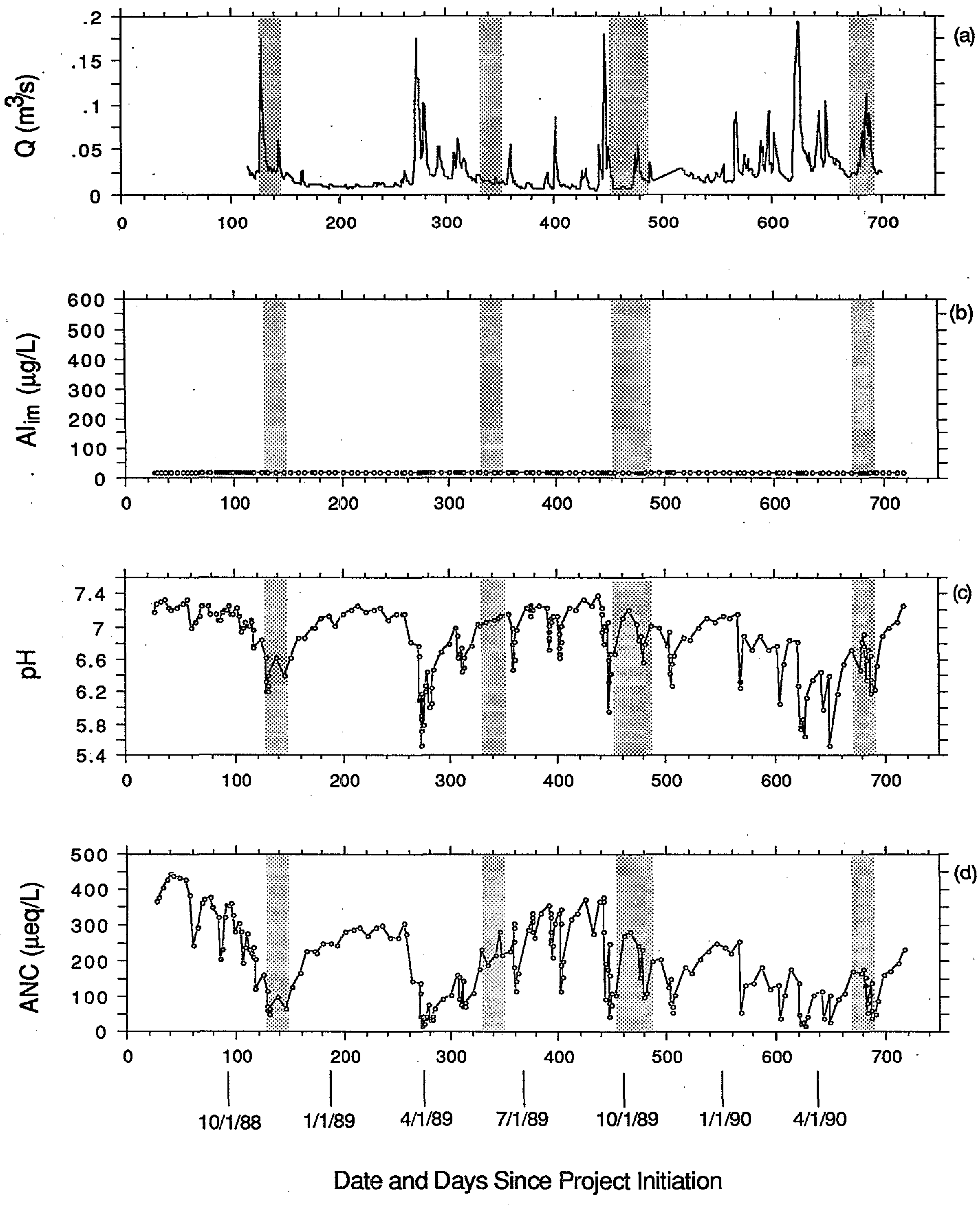


Figure 5-3. **(a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Fly Pond Outlet, Adirondacks. Shaded areas designate periods when brook trout bioassays were conducted.**

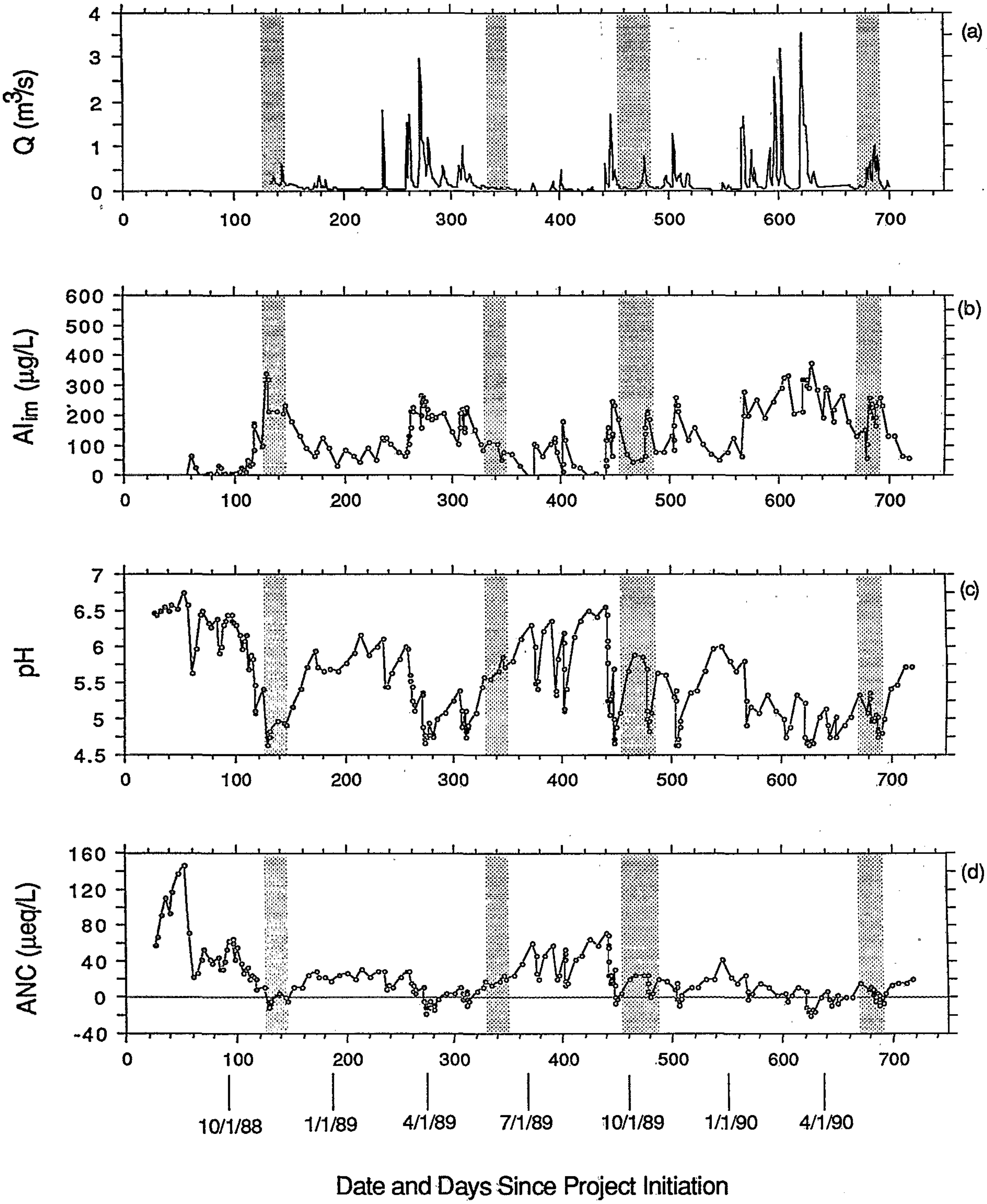


Figure 5-4. **(a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Seventh Lake Inlet, Adirondacks. Shaded areas designate periods when brook trout bioassays were conducted.**

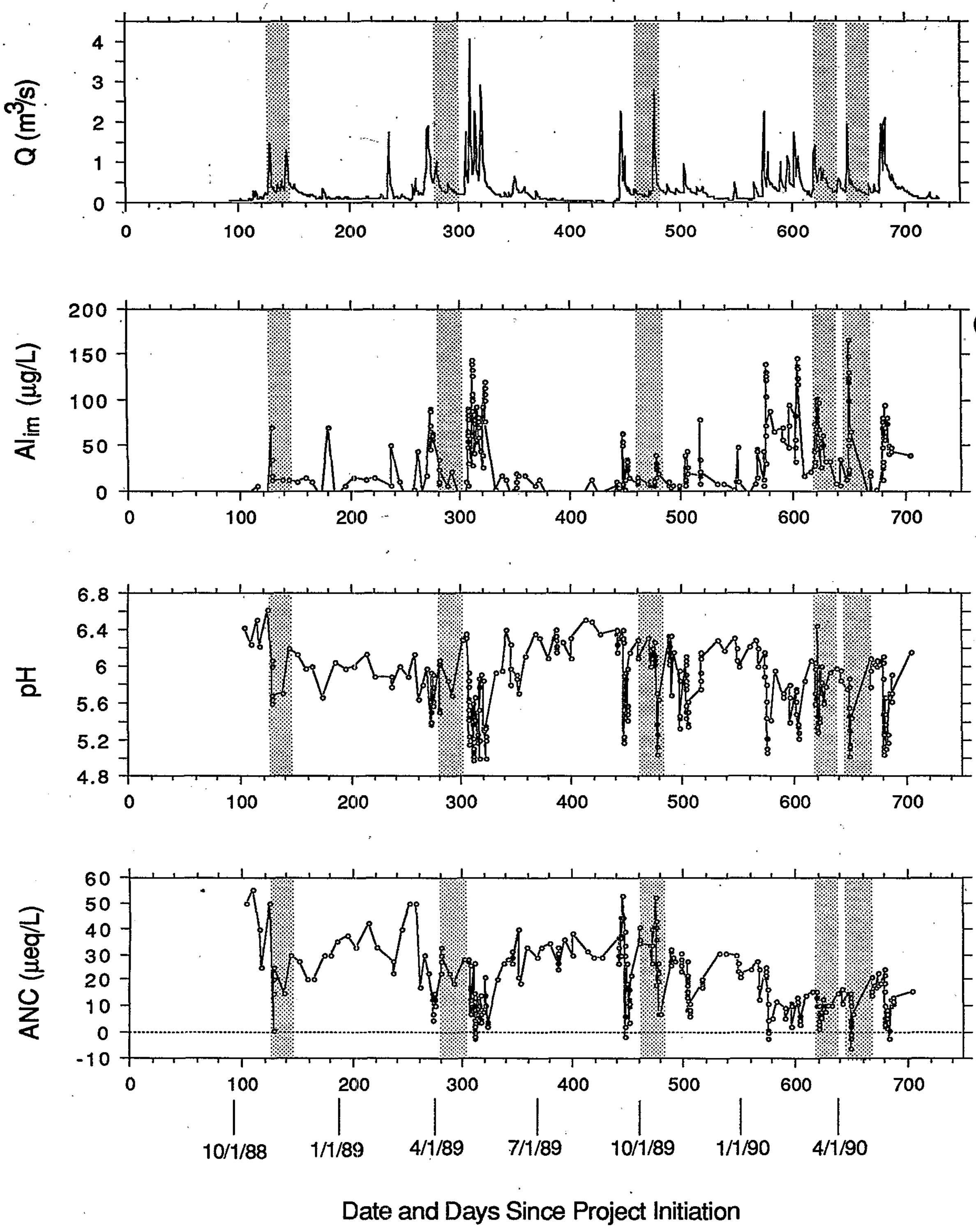


Figure 5-5. **(a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Biscuit Brook, Catskills. Shaded areas designate periods when brook trout bioassays were conducted.**

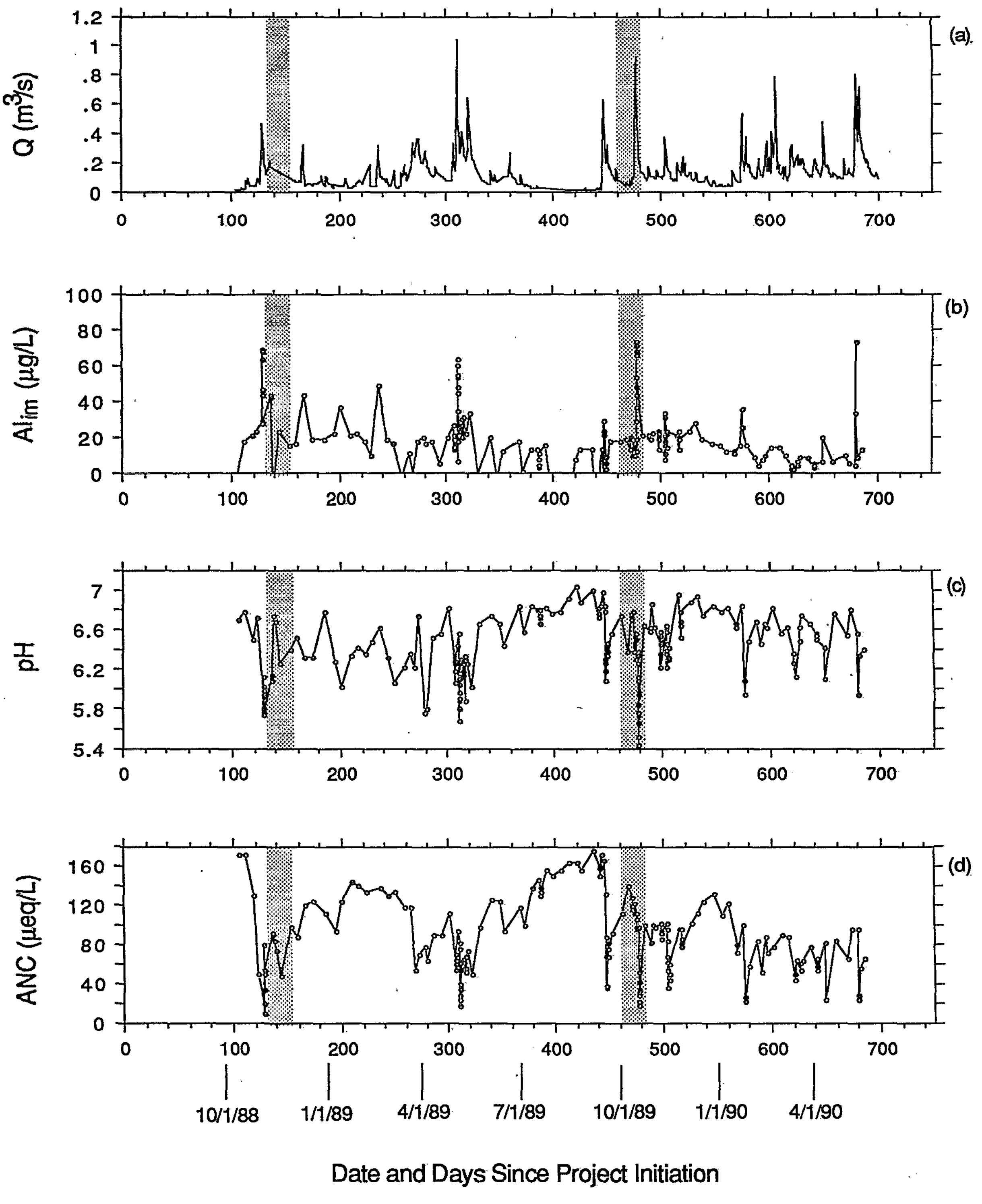


Figure 5-6. (a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Black Brook, Catskills. Shaded areas designate periods when brook trout bioassays were conducted.

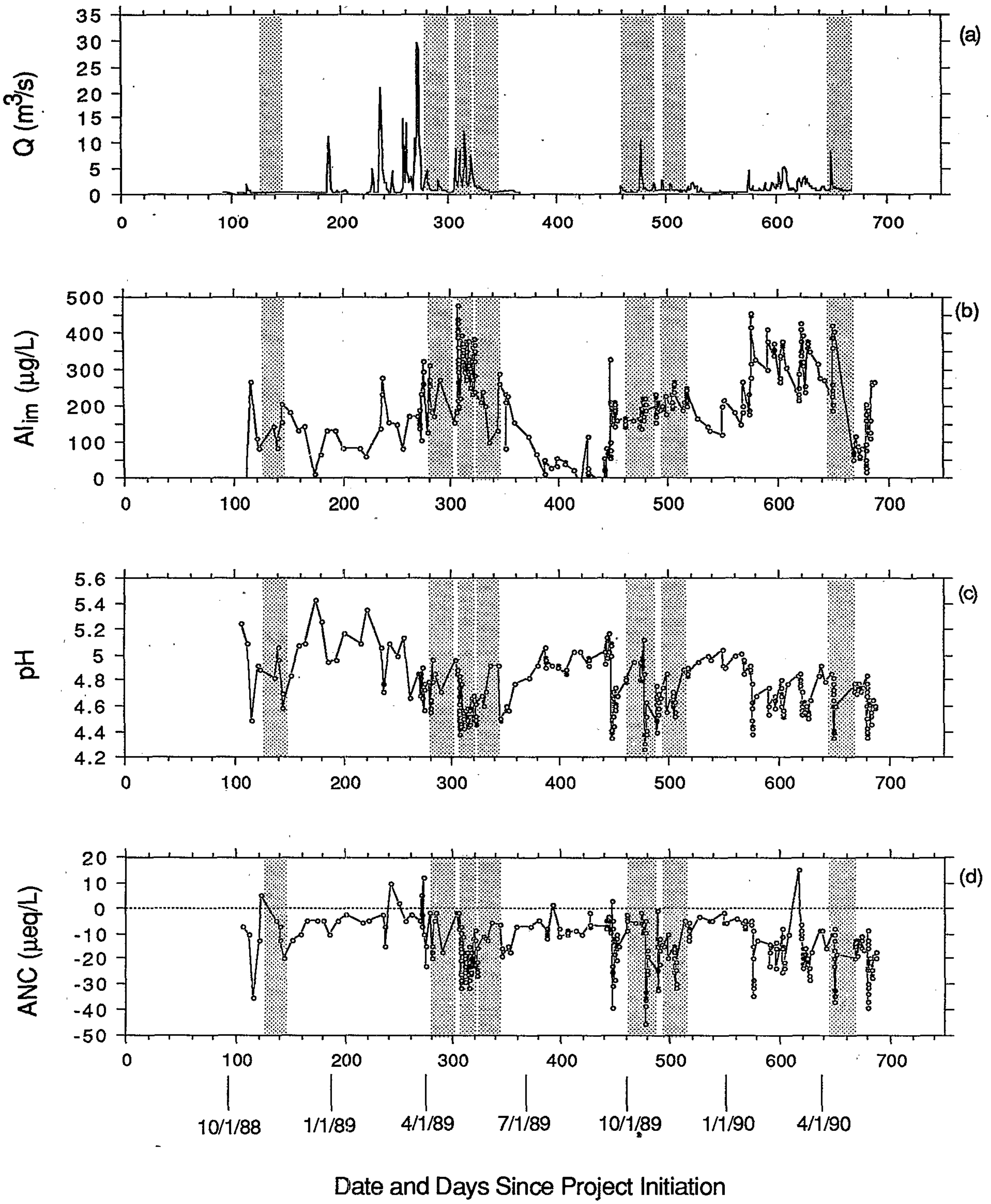


Figure 5-7. (a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for East Branch Neversink River, Catskills. Shaded areas designate periods when brook trout bioassays were conducted.

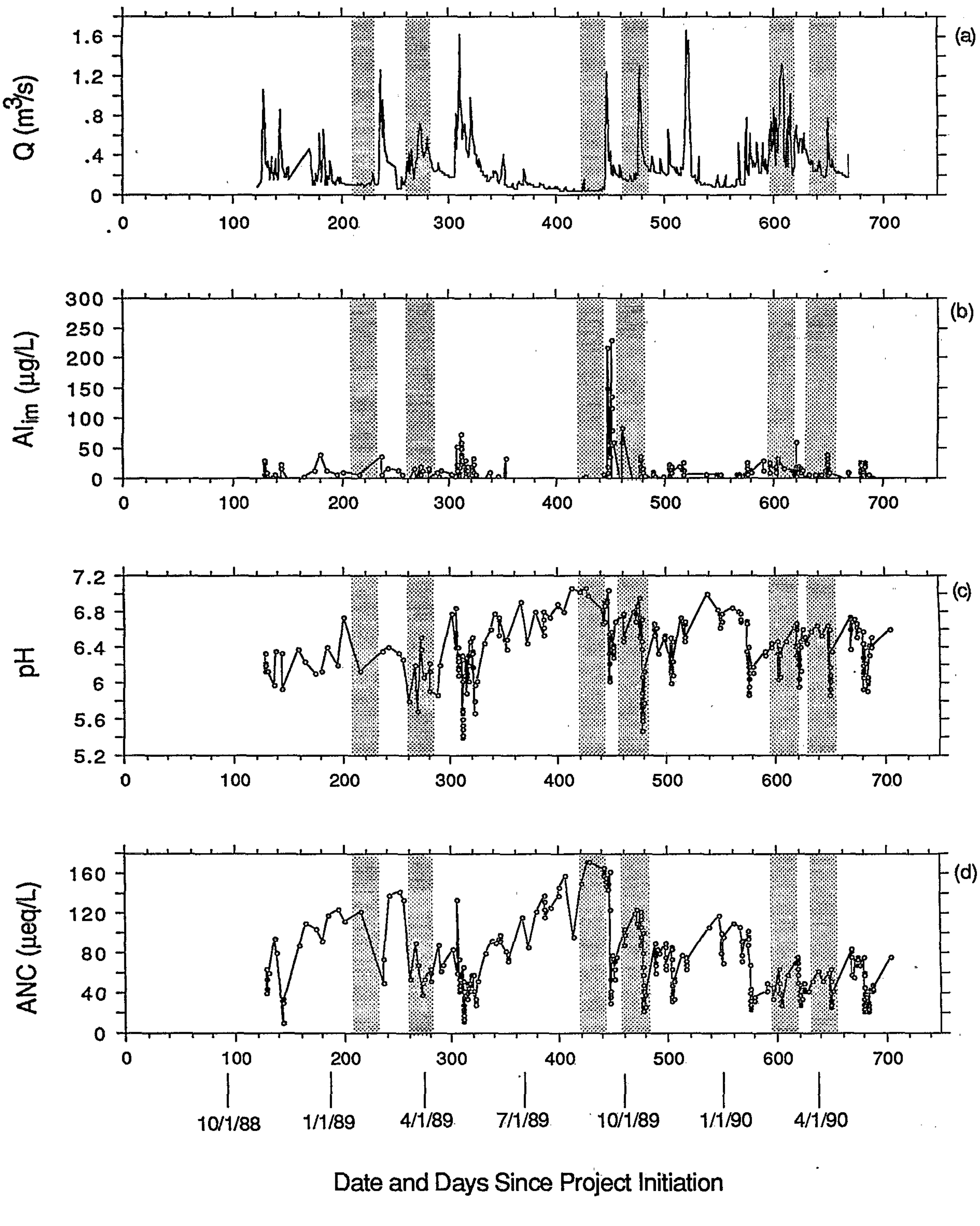


Figure 5-8. **(a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for High Falls Brook, Catskills. Shaded areas designate periods when brook trout bioassays were conducted.**

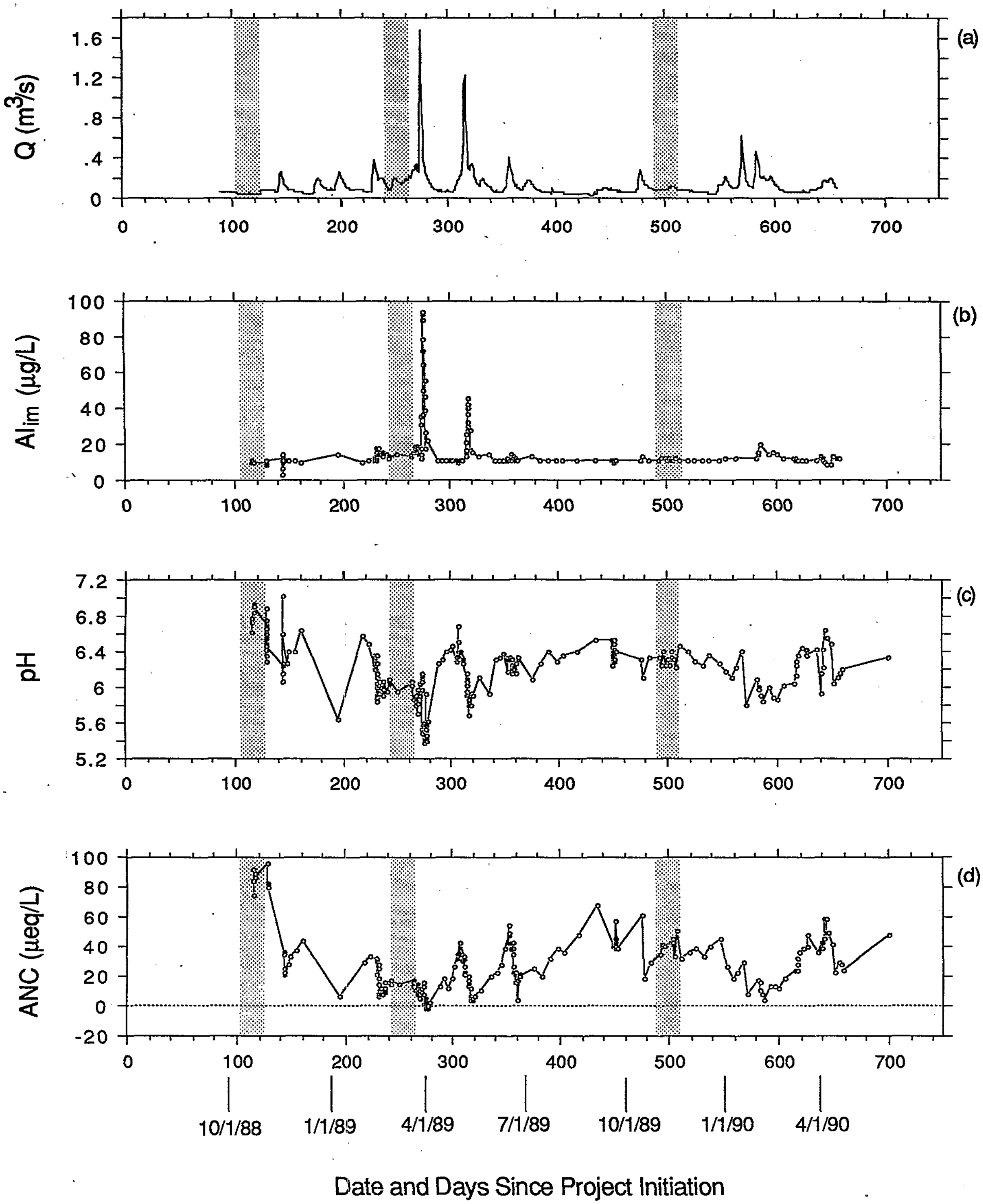


Figure 5-9. **(a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Baldwin Creek, Pennsylvania. Shaded areas designate periods when brook trout bioassays were conducted.**

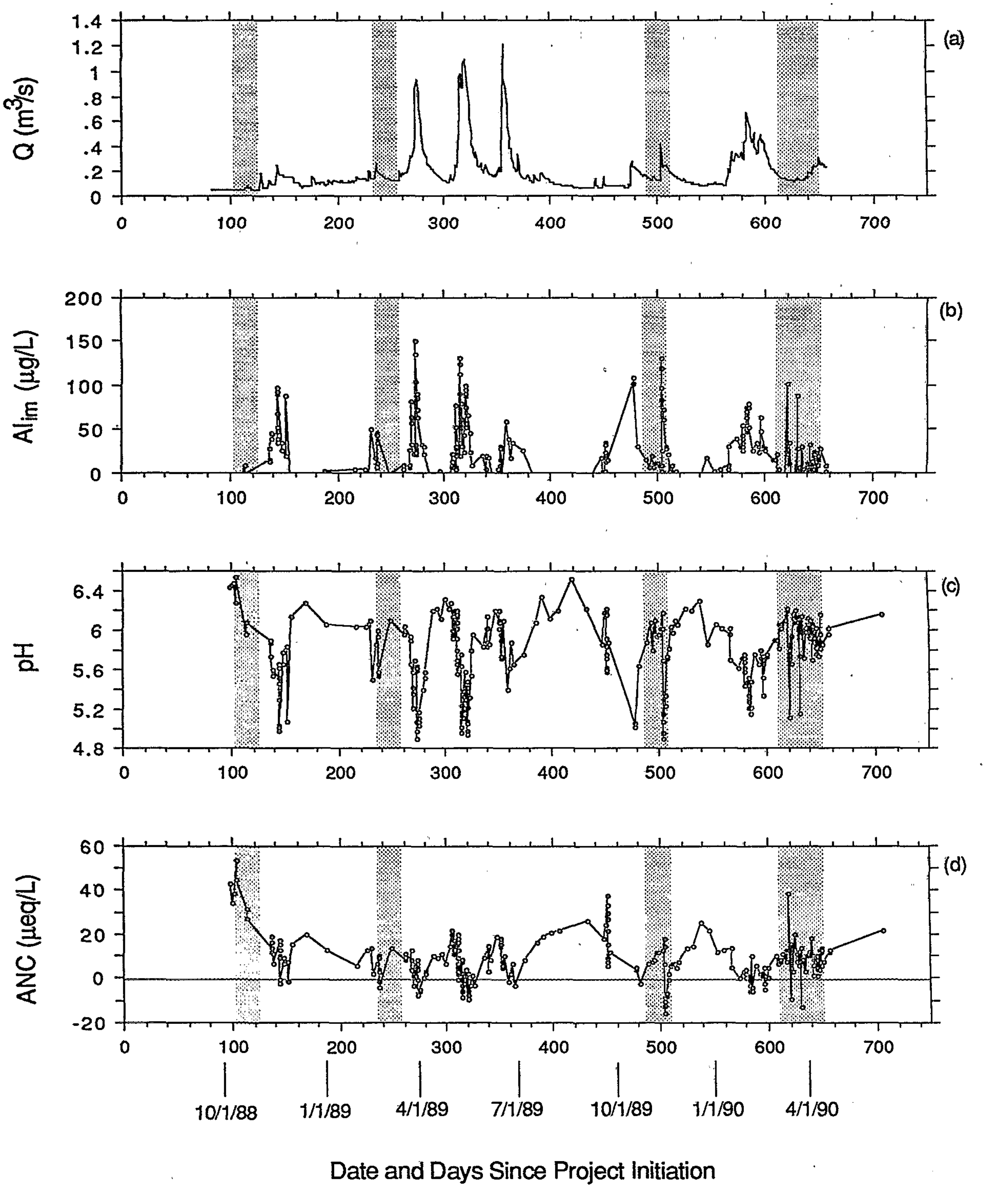


Figure 5-10. **(a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Benner Run, Pennsylvania. Shaded areas designate periods when brook trout bioassays were conducted.**

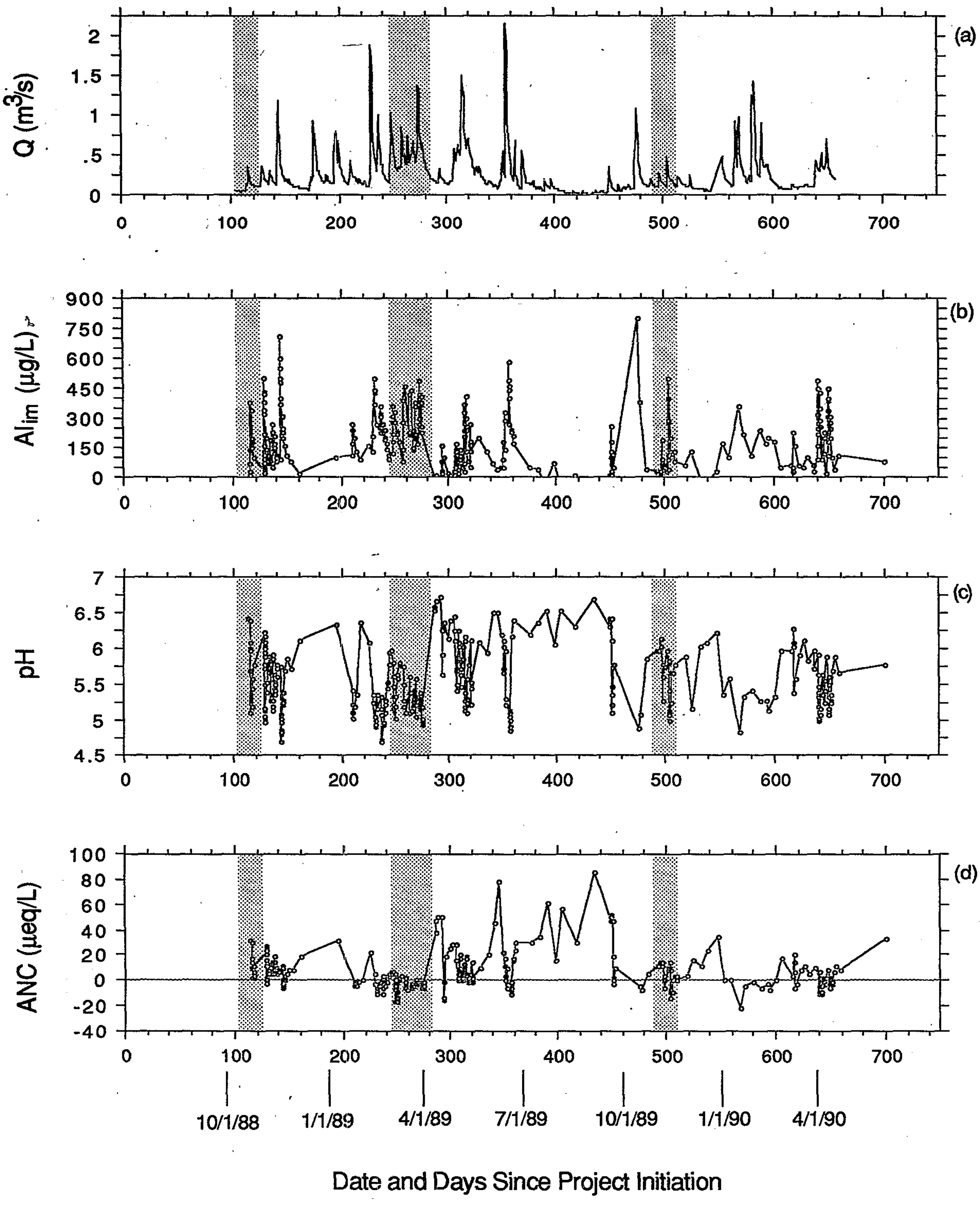


Figure 5-11. **(a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Linn Run, Pennsylvania. Shaded areas designate periods when brook trout bioassays were conducted.**

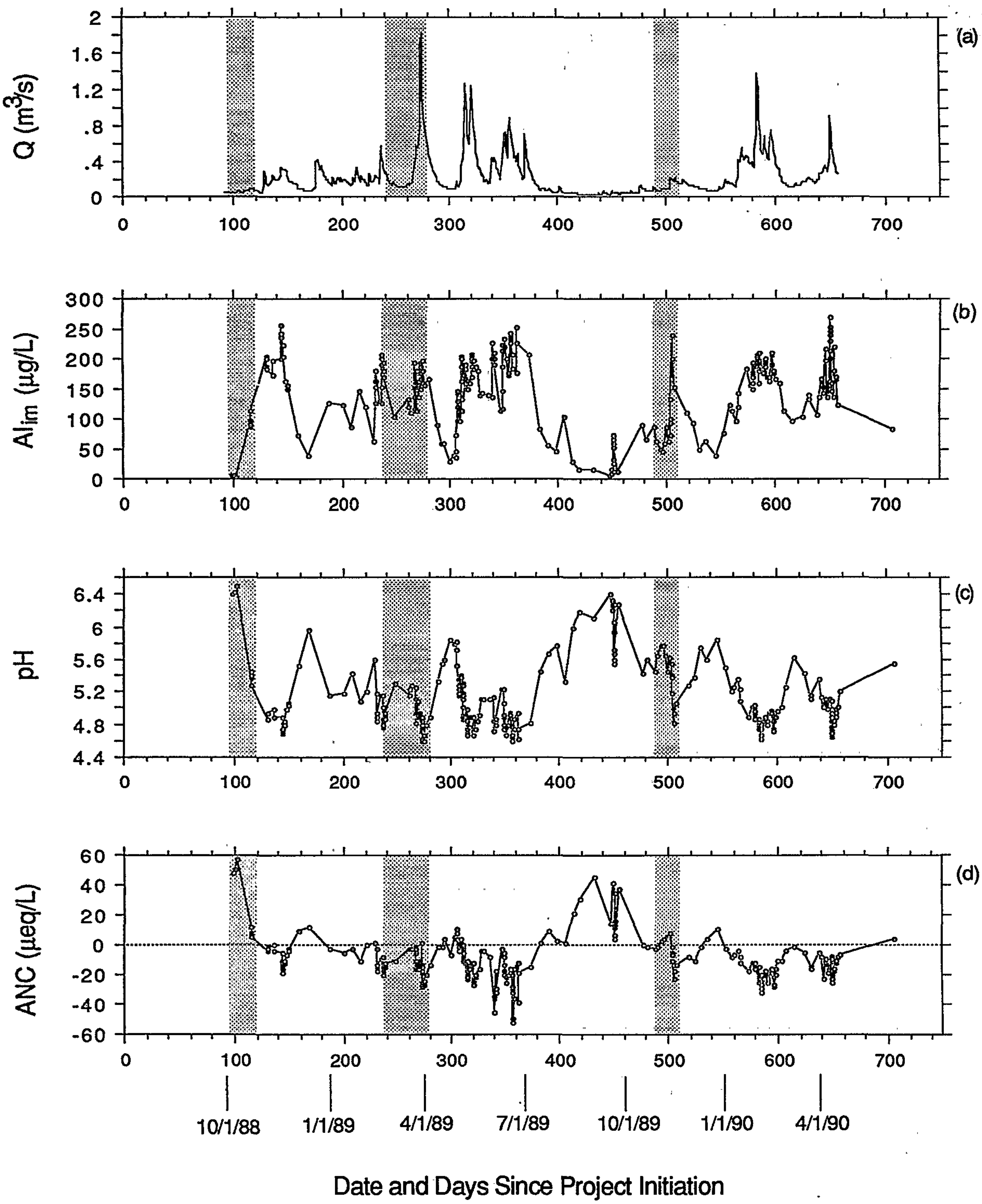


Figure 5-12. (a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Roberts Run, Pennsylvania. Shaded areas designate periods when brook trout bioassays were conducted.

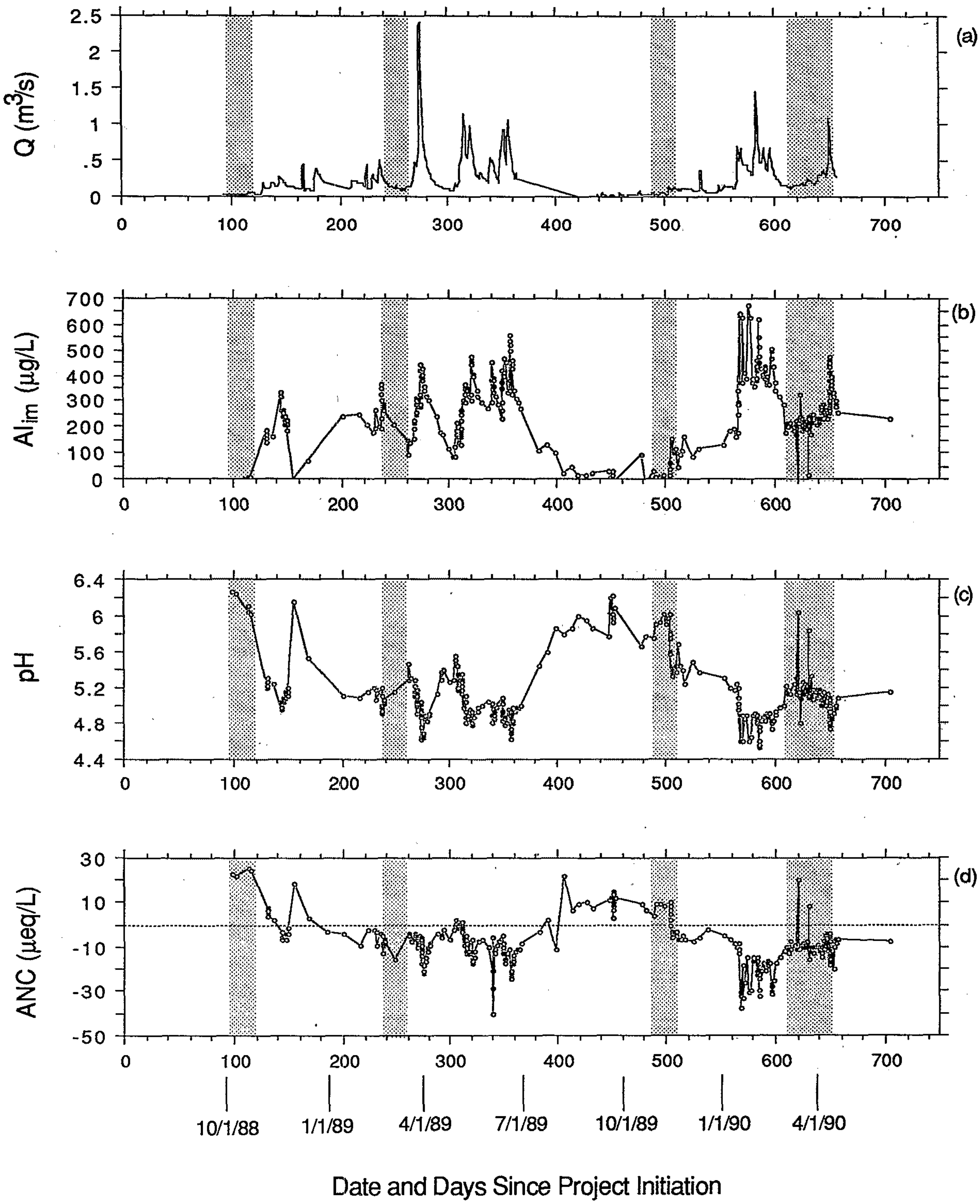


Figure 5-13. (a) Mean daily discharge, (b) estimated Al_{im}, (c) pH, and (d) ANC for Stone Run, Pennsylvania. Shaded areas designate periods when brook trout bioassays were conducted.

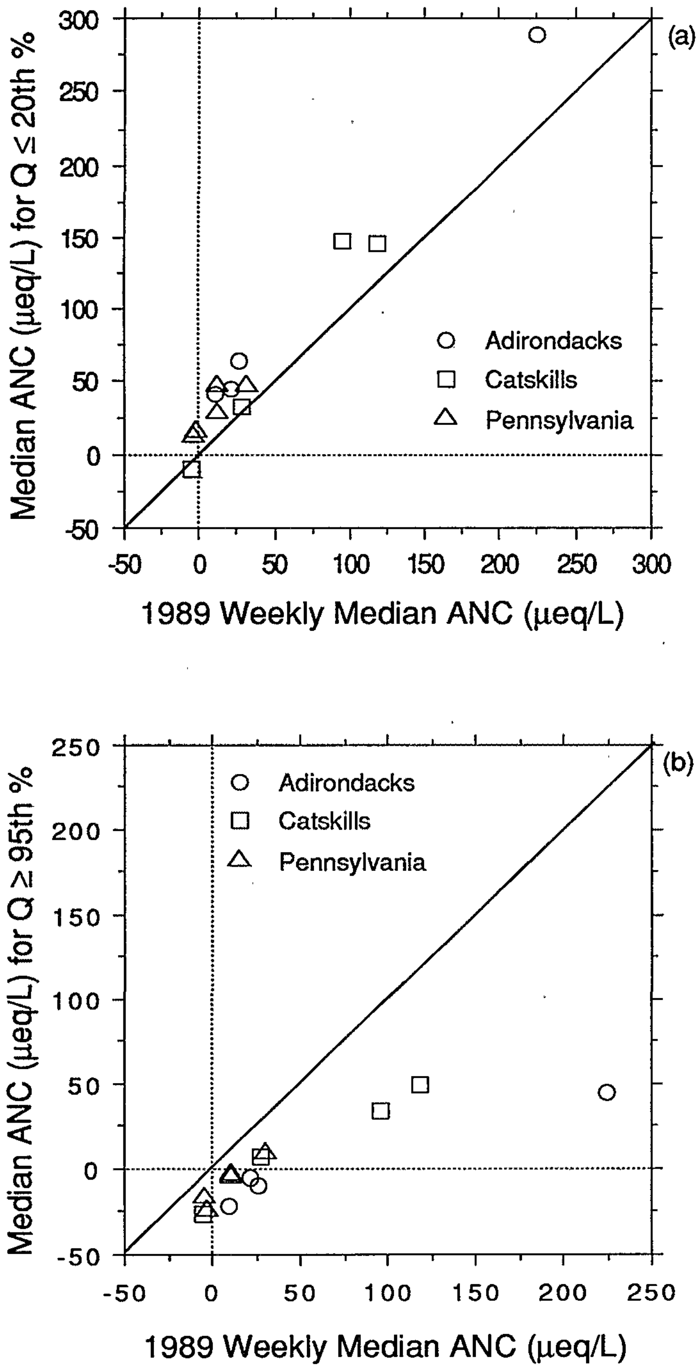
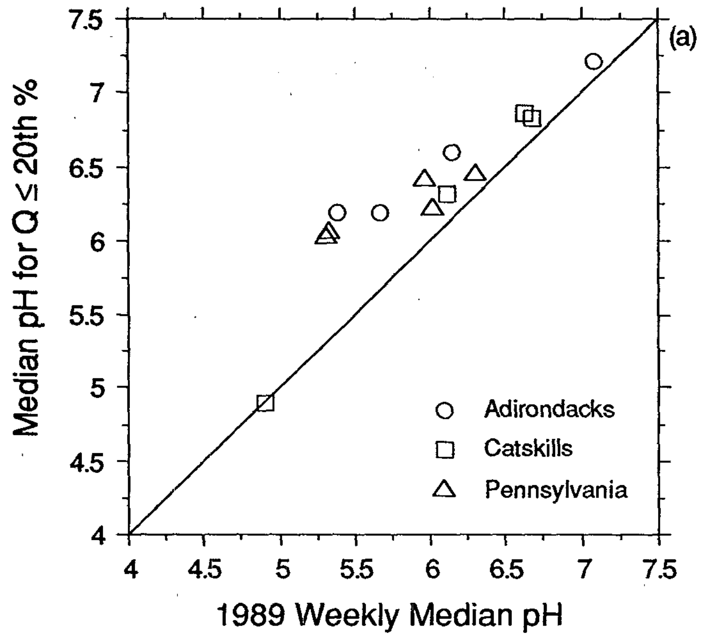


Figure 5-14. (a) Comparison of 1989 weekly median ANC (μeq/L) and median ANC for discharge ≤ 20th percentile, and (b) comparison of weekly median ANC with median ANC for discharge ≥ 95th percentile for all ERP streams.



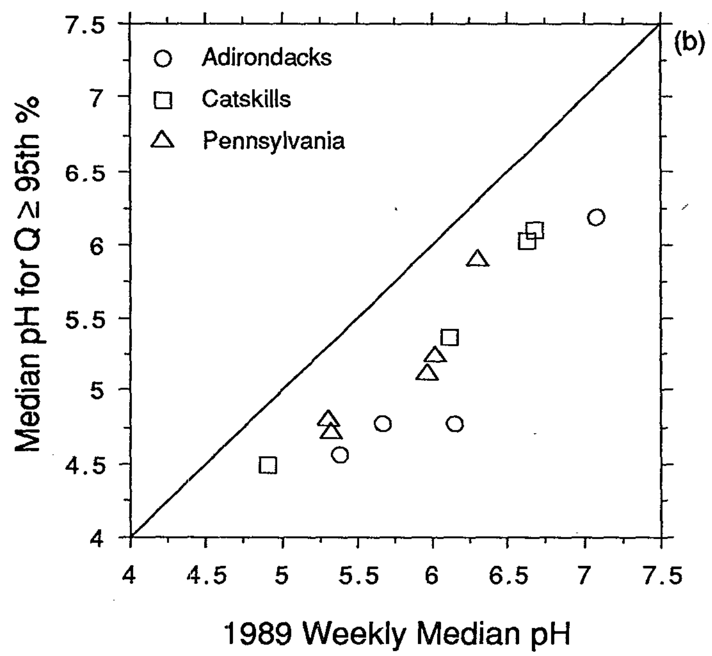


Figure 5-15. (a) Comparison of 1989 weekly median pH and median pH for discharge ≤ 20th percentile, and (b) comparison of weekly median pH with median pH for discharge ≥ 95th percentile for all ERP streams.

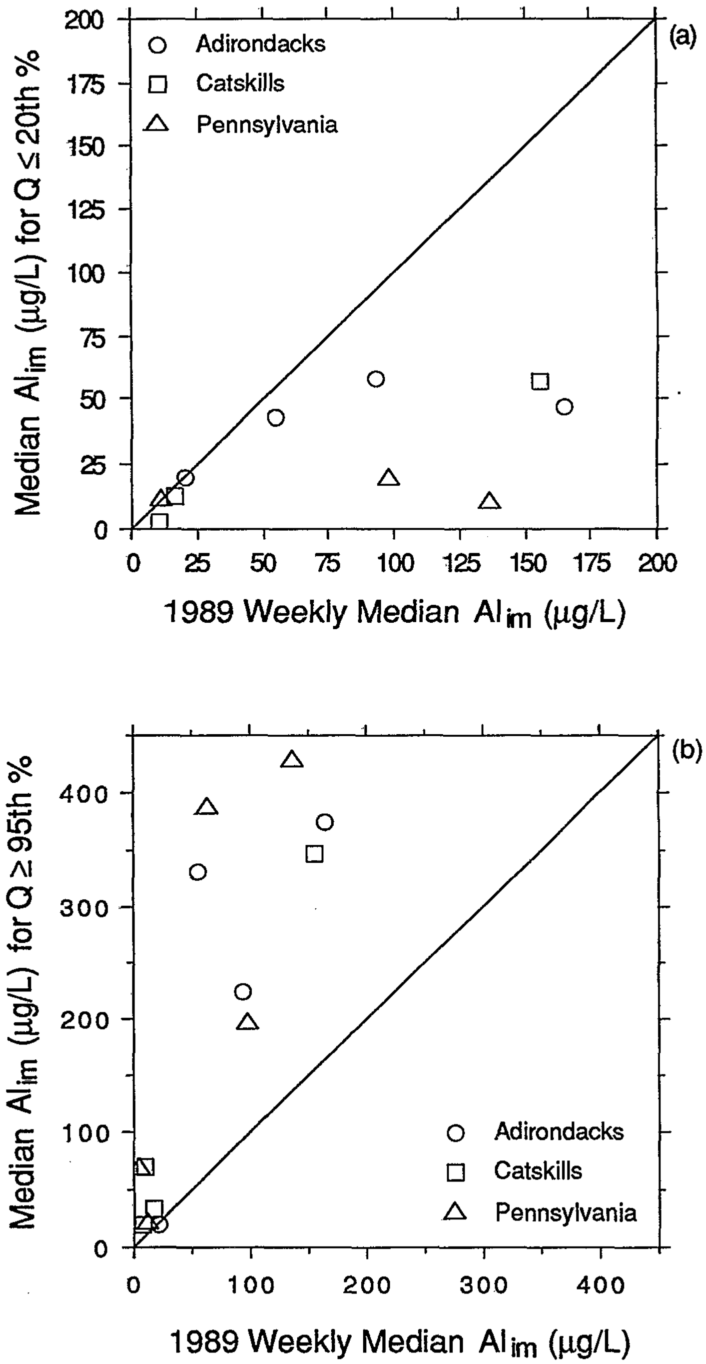


Figure 5-16. **(a) Comparison of 1989 weekly median estimated Al_{im} and median estimated Al_{im} for discharge ≤ 20th percentile, and (b) comparison of weekly median estimated Al_{im} with median estimated Al_{im} for discharge ≥ 95th percentile for all ERP streams.**

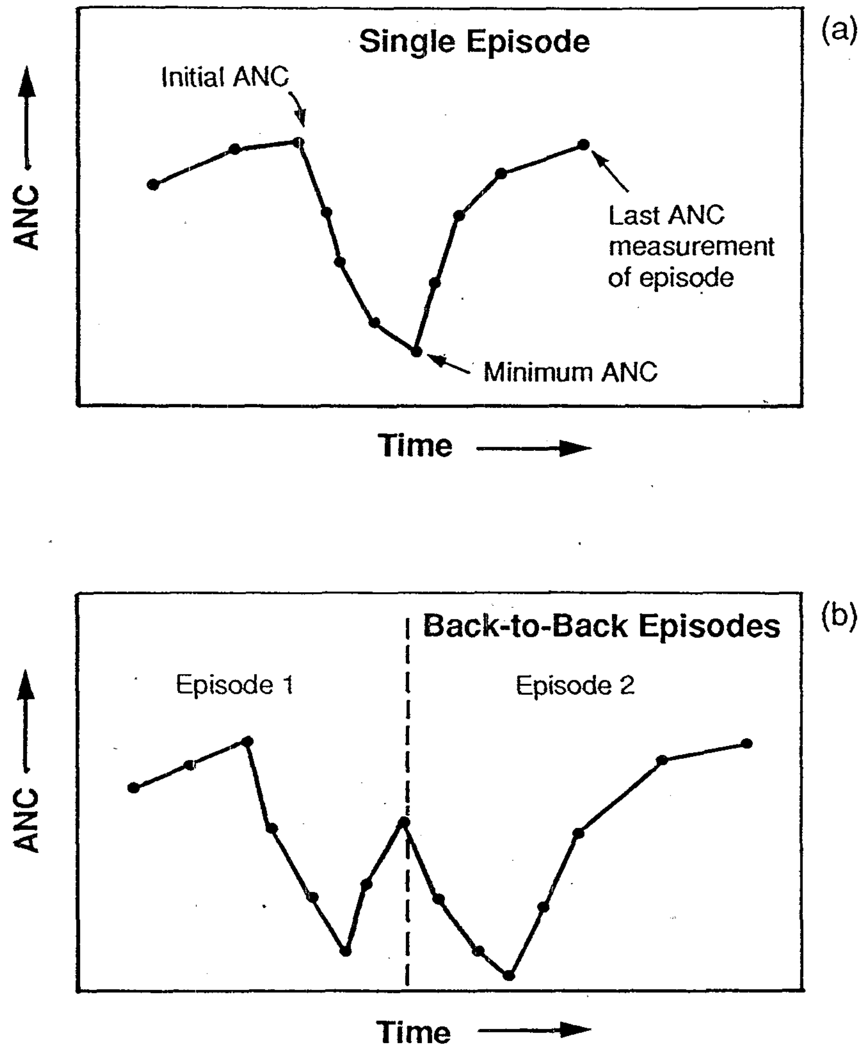


Figure 5-17. Idealized diagram of (a) a single episode and (b) back-to-back episodes to illustrate the approach used to identify episodes and their characteristics.

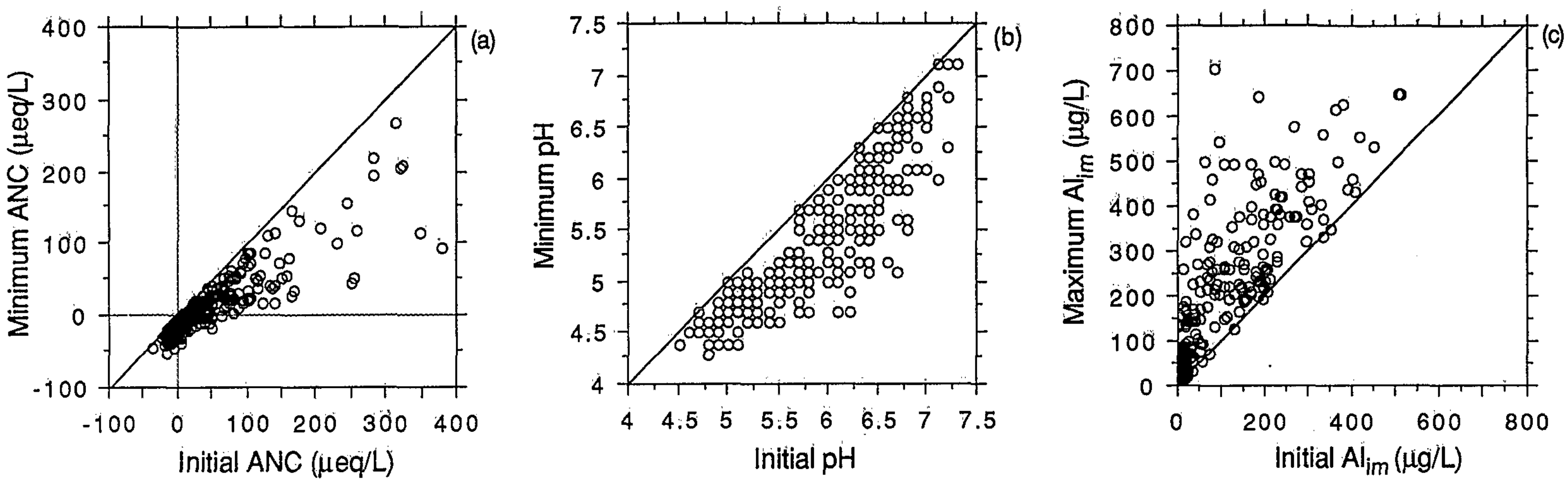


Figure 5-18. **(a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} for episodes in all ERP streams.**

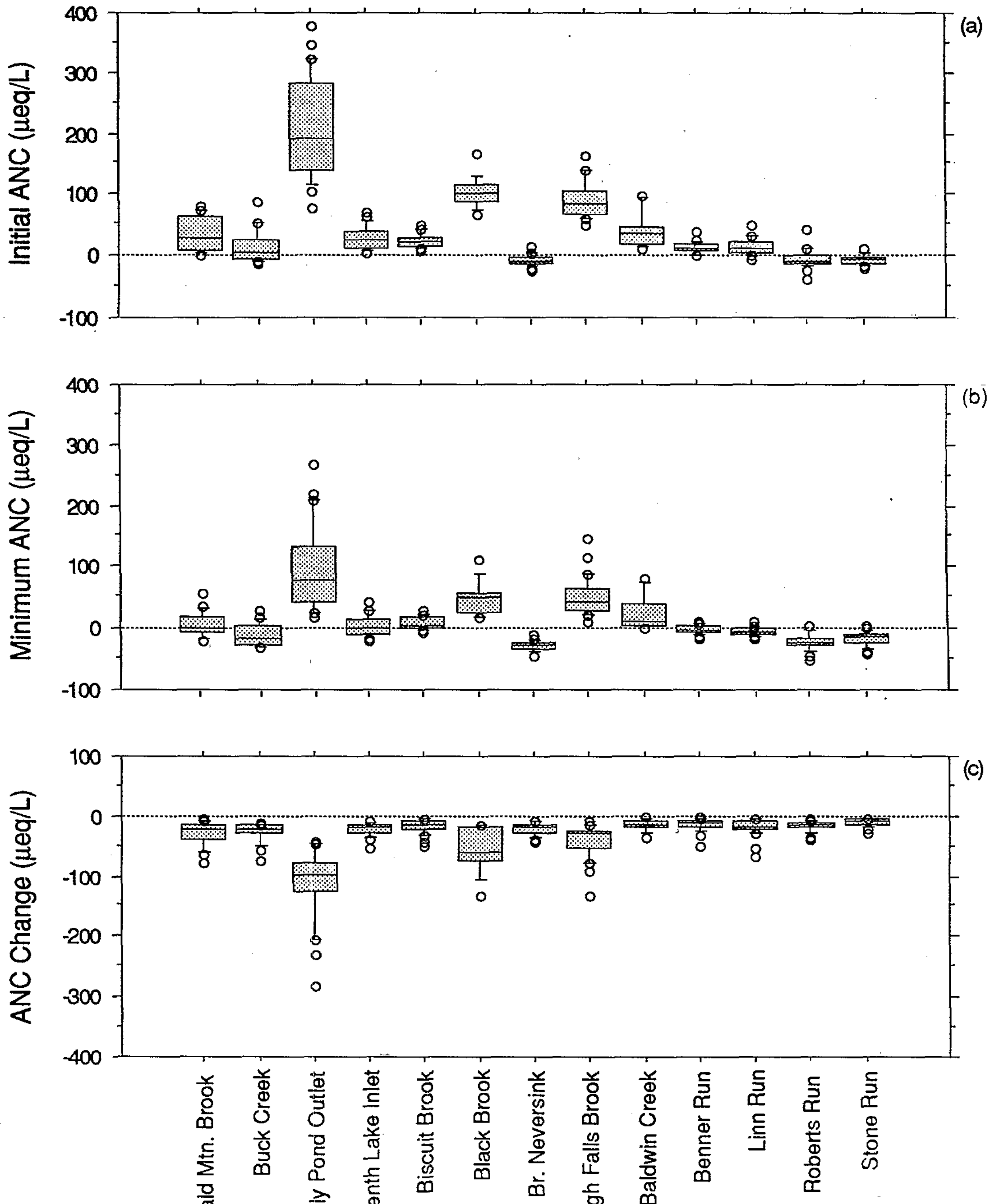


Figure 5-19. **Box plots of (a) initial ANC, (b) minimum ANC, and (c) ANC change, for episodes in ERP streams. Line in box indicates median; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.**

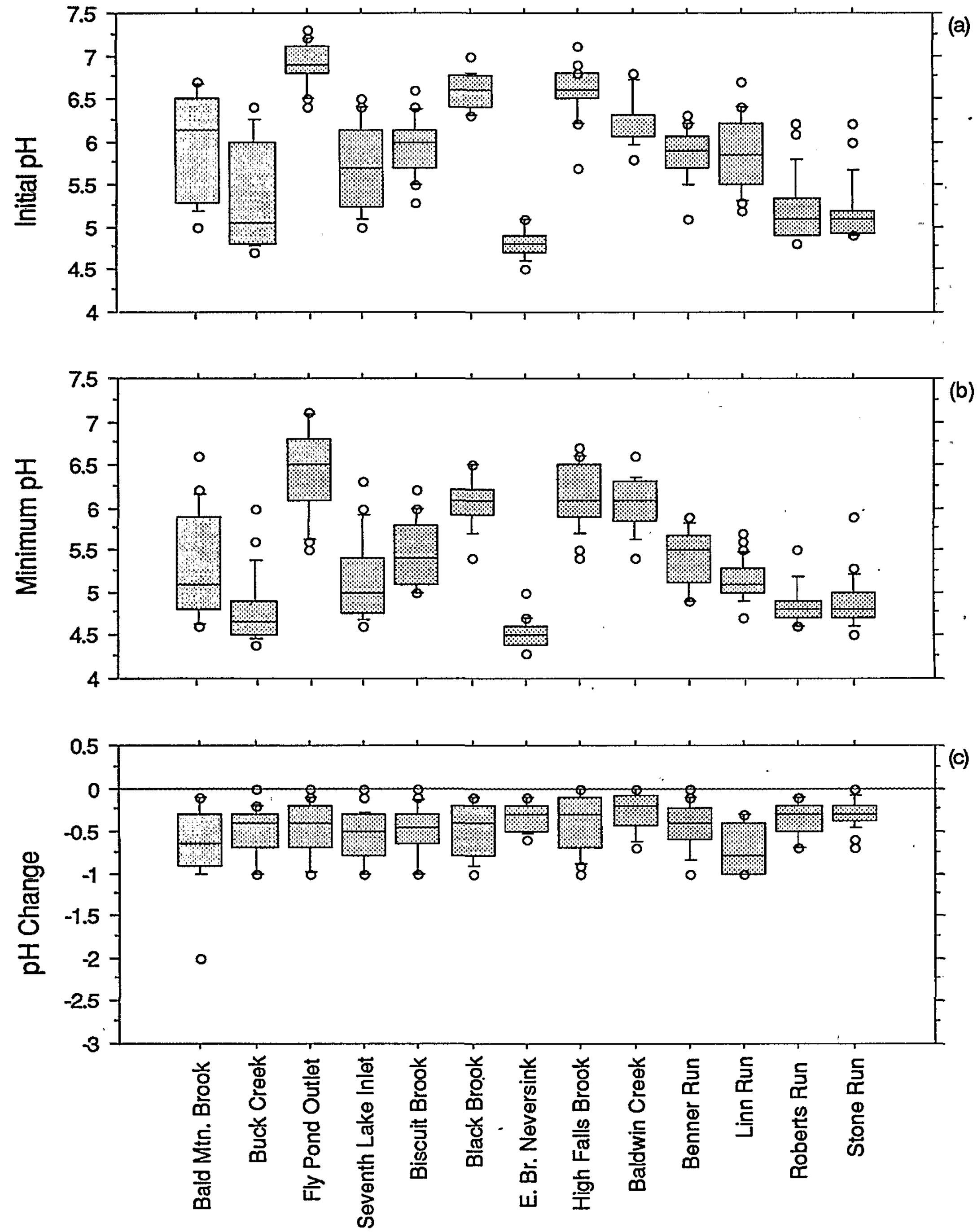


Figure 5-20. **Box plots of (a) initial pH, (b) minimum pH, and (c) pH change, for episodes in ERP streams. Line in box indicates median; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.**

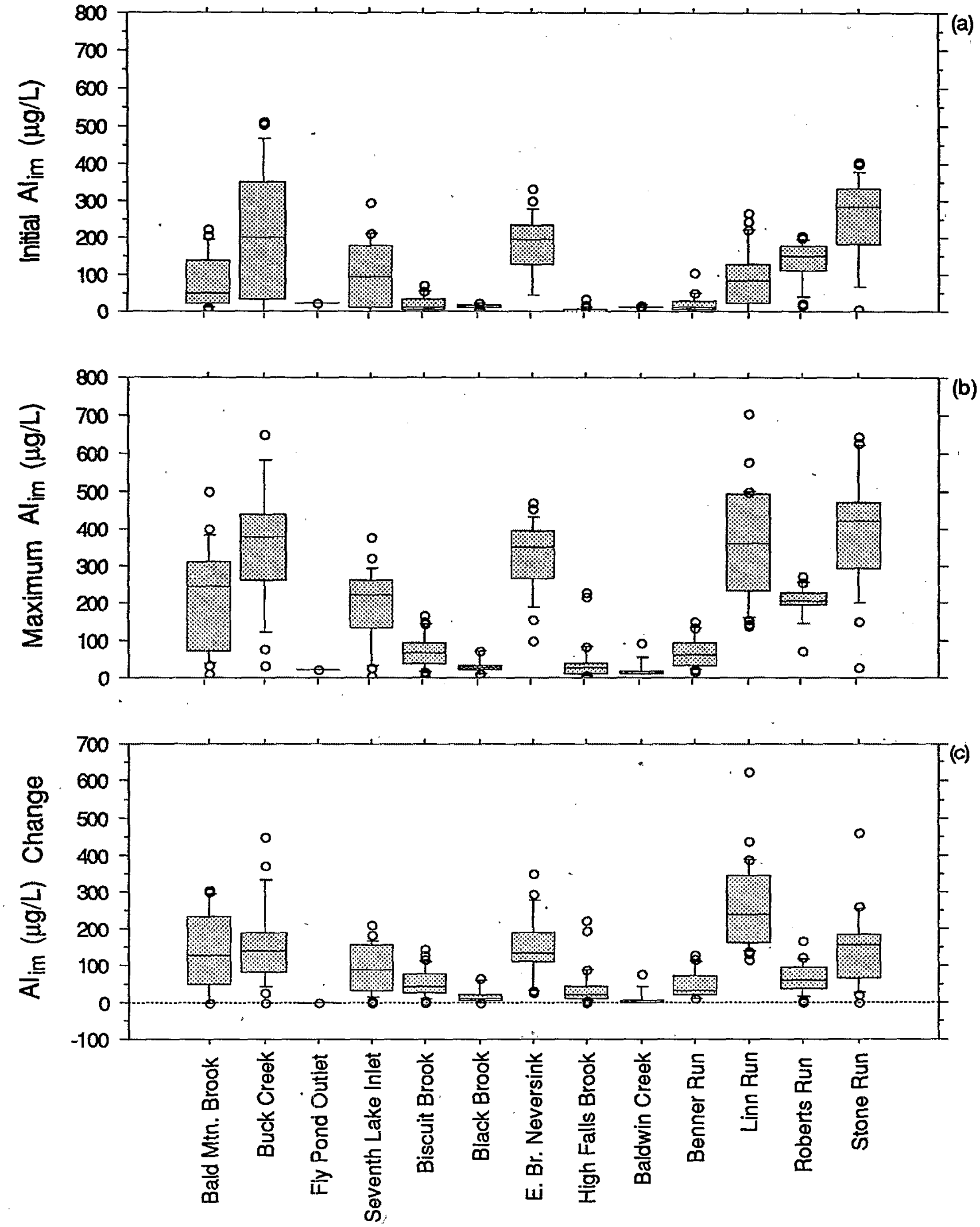


Figure 5-21. **Box plots of (a) initial estimated Al_{im}, (b) maximum estimated Al_{im}, and (c) estimated Al_{im} change, for episodes in ERP streams. Line in box indicates median; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.**

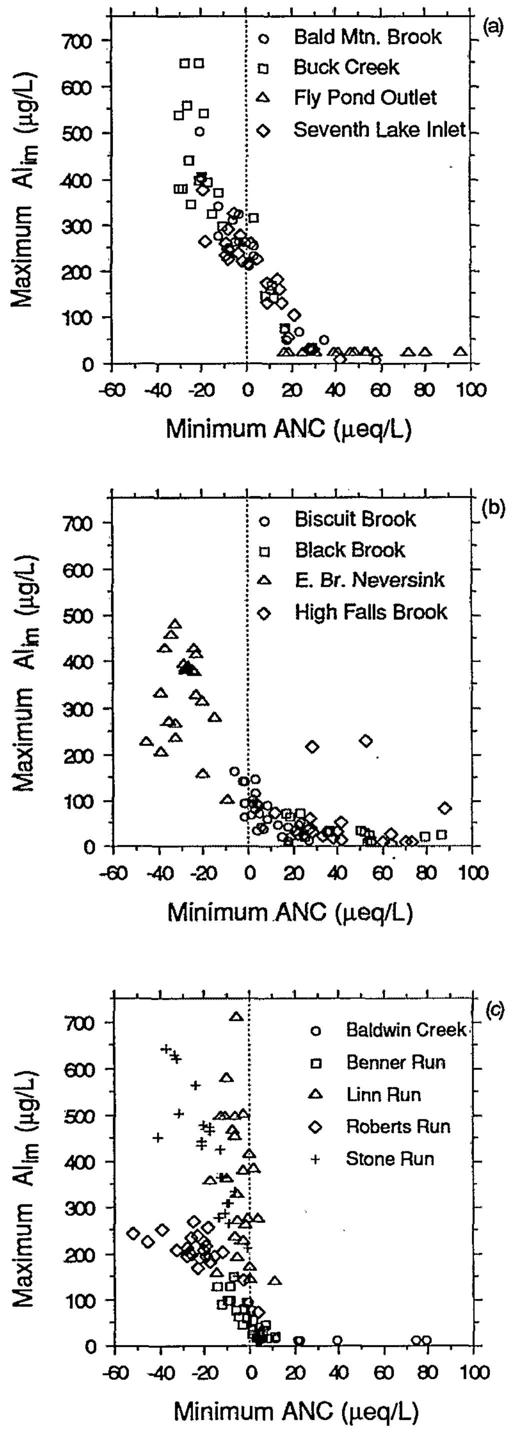


Figure 5-22. **Estimated Al_{lm} concentrations at times of minimum ANC during episodes in (a) Adirondack streams, (b) Catskill streams, and (c) Pennsylvania streams.**

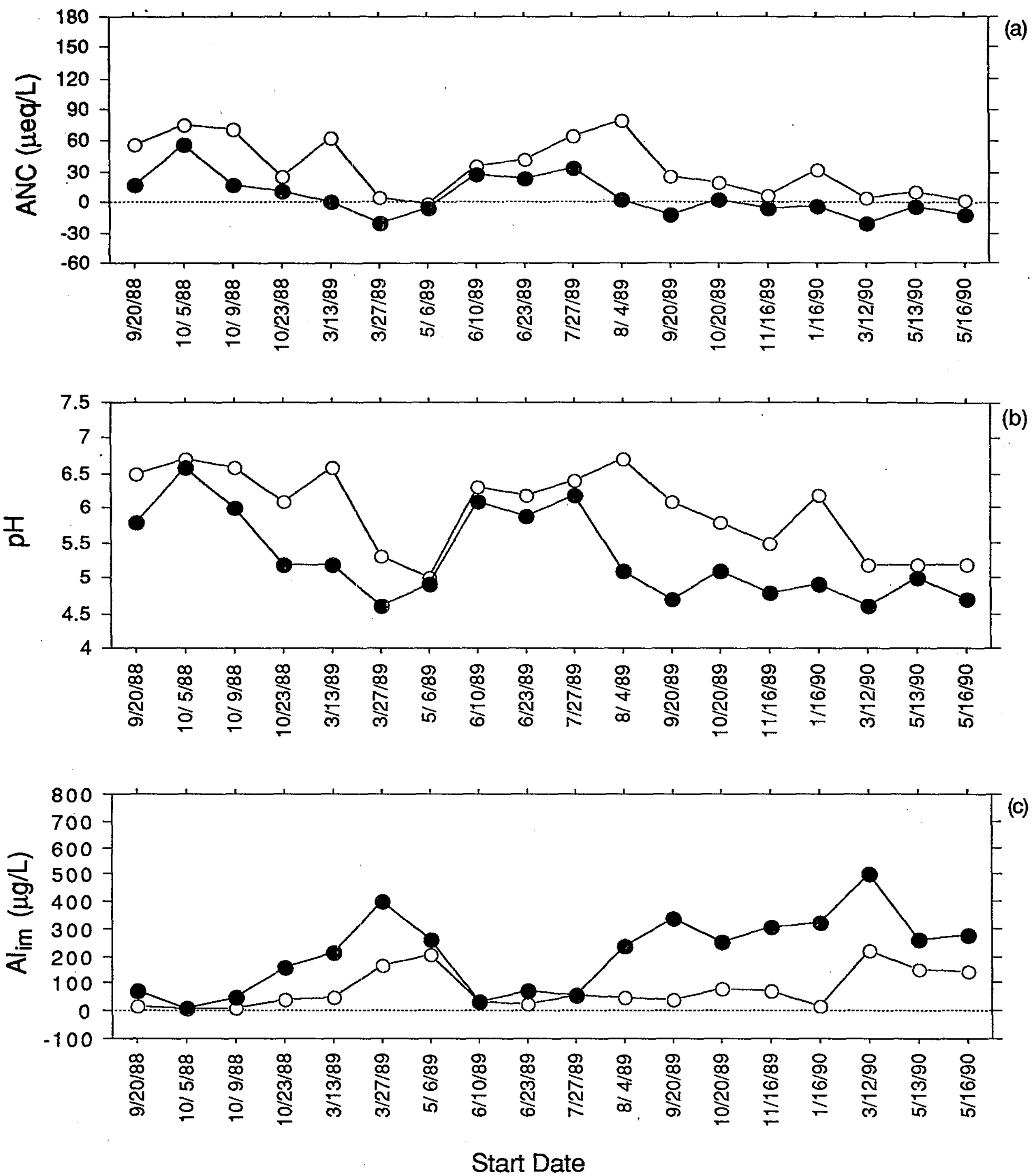


Figure 5-23. (a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Bald Mountain Brook, Adirondacks. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.

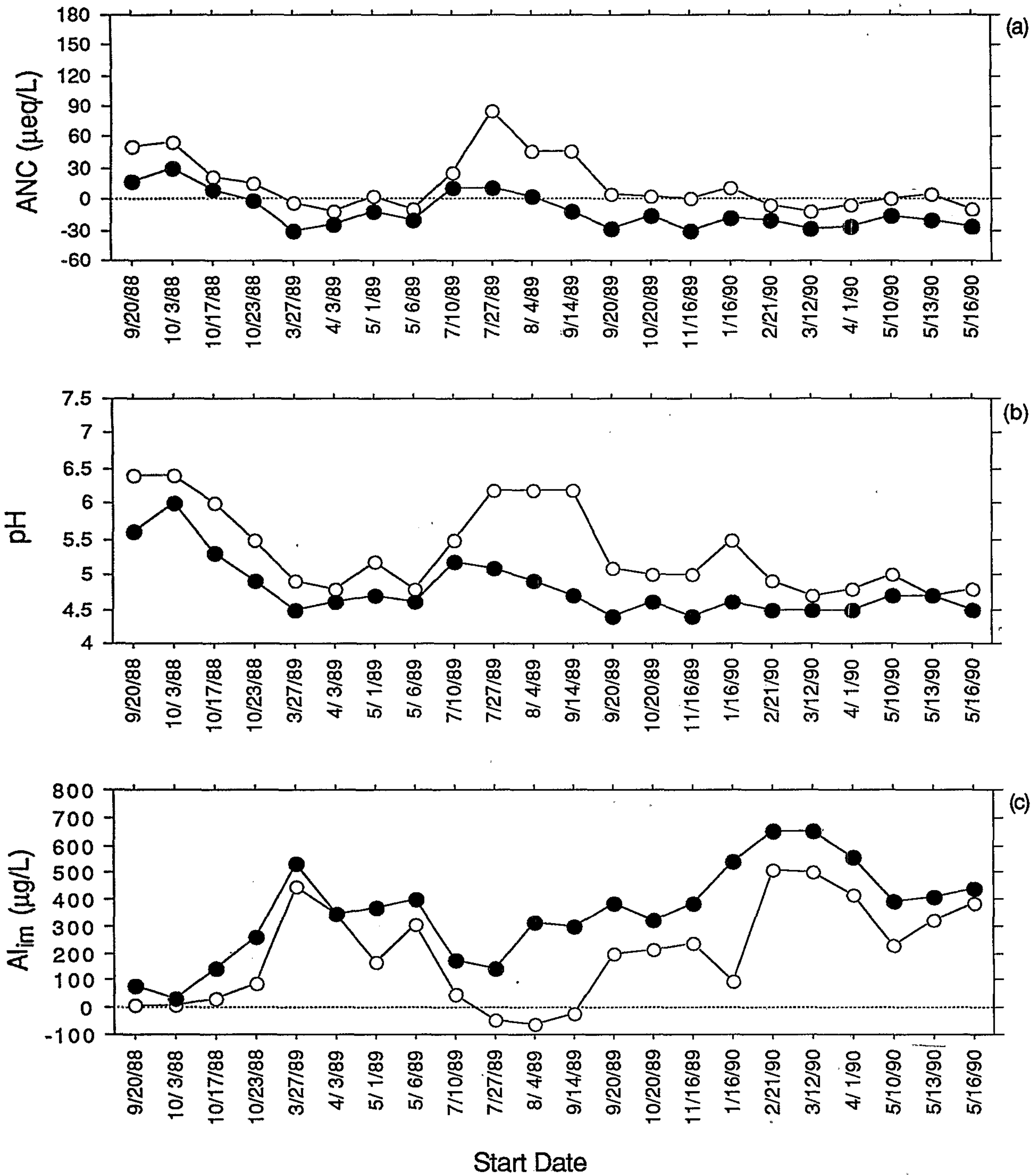


Figure 5-24. **(a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Buck Creek, Adirondacks. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.**

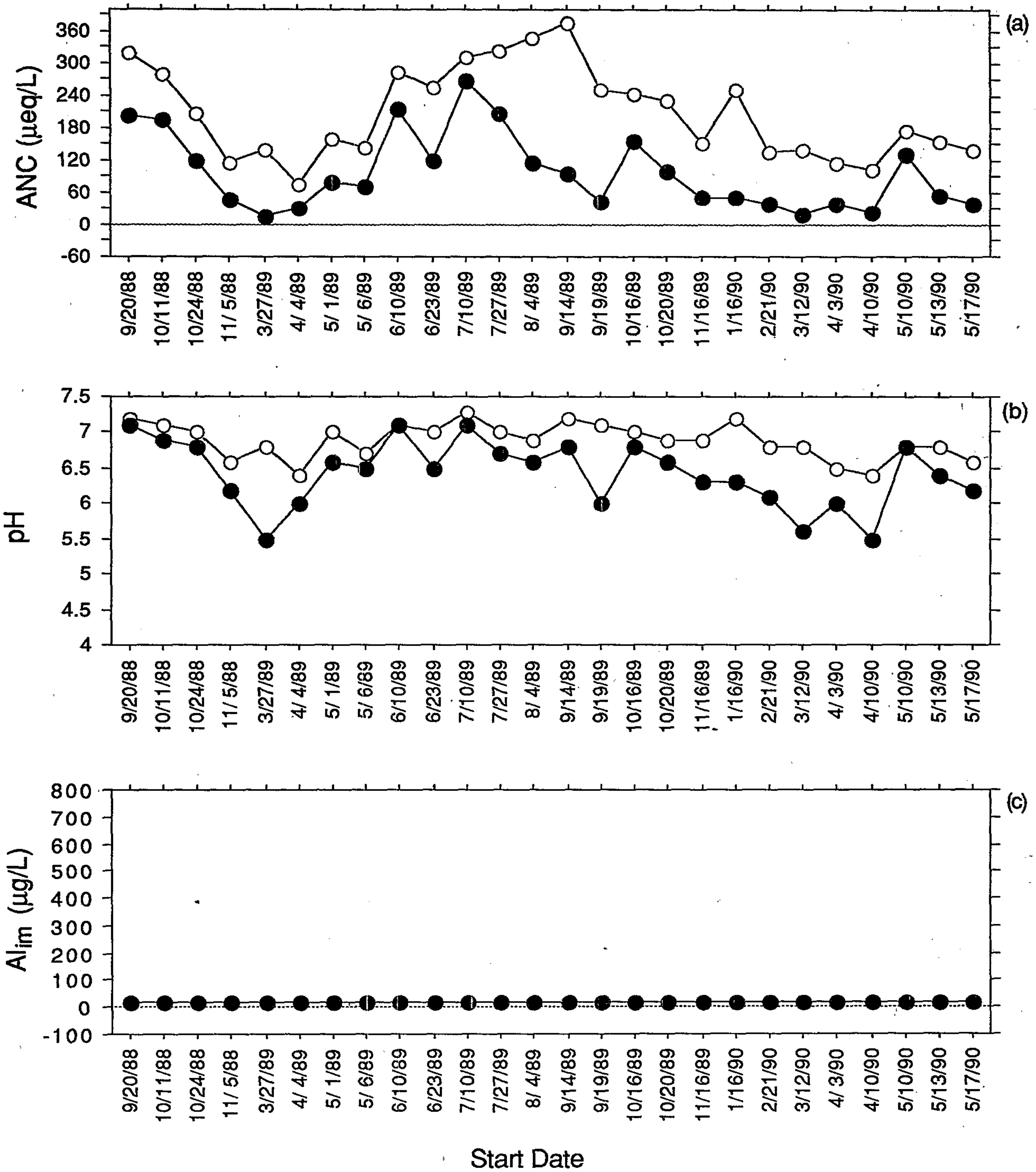


Figure 5-25. **(a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Fly Pond Outlet, Adirondacks. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.**

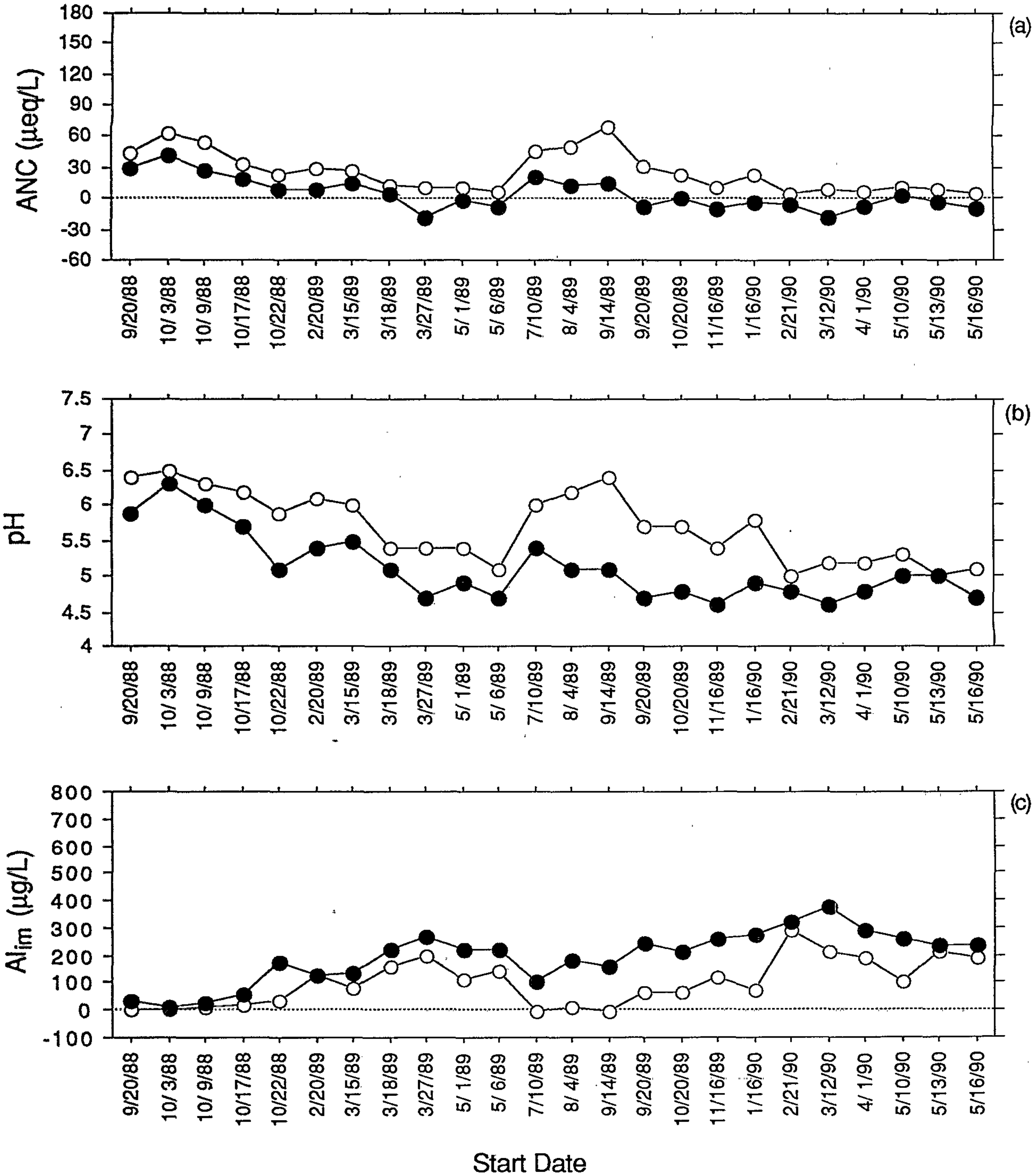


Figure 5-26. **(a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Seventh Lake Inlet, Adirondacks. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.**

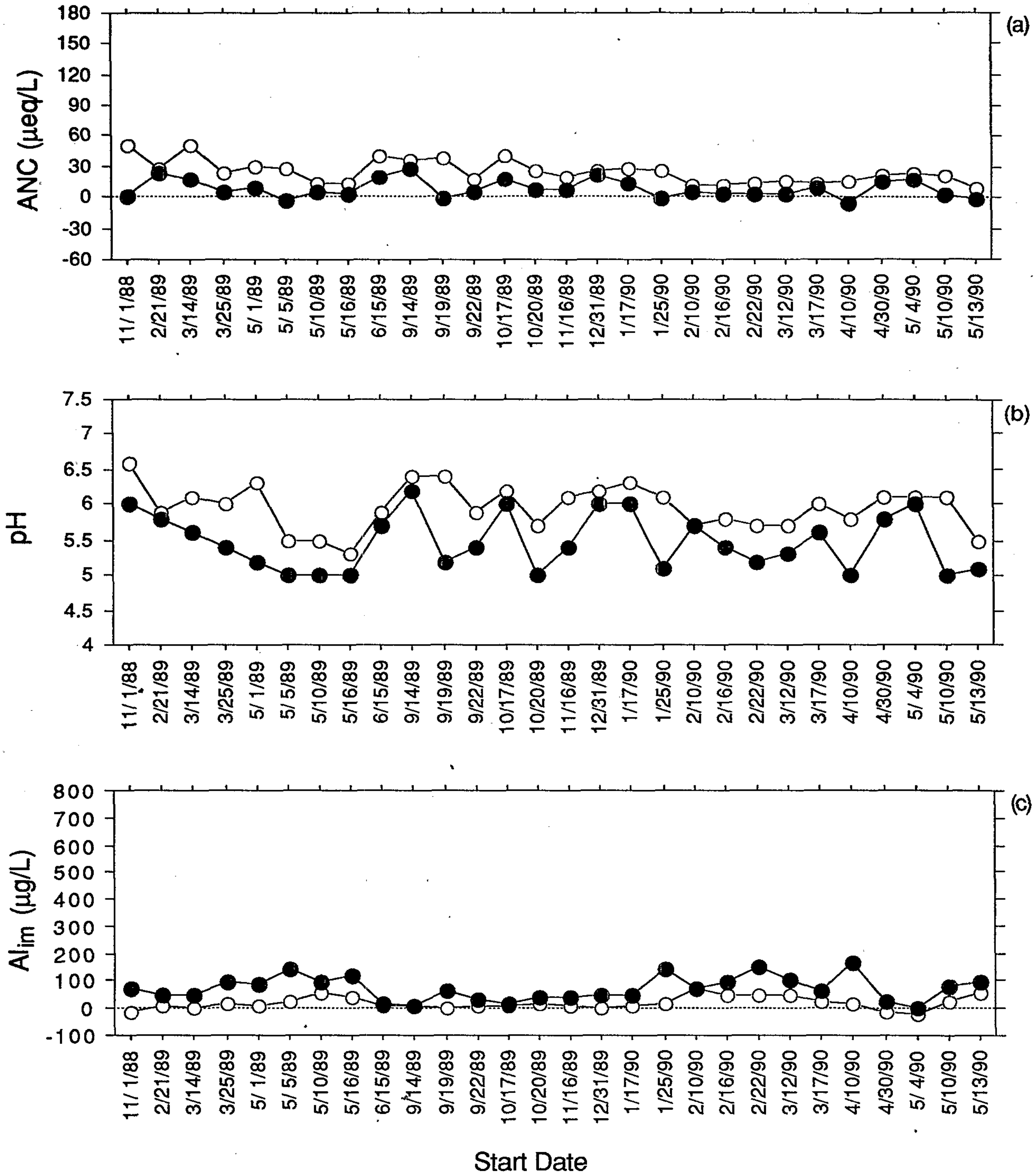


Figure 5-27. (a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Biscuit Brook, Catskills. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.

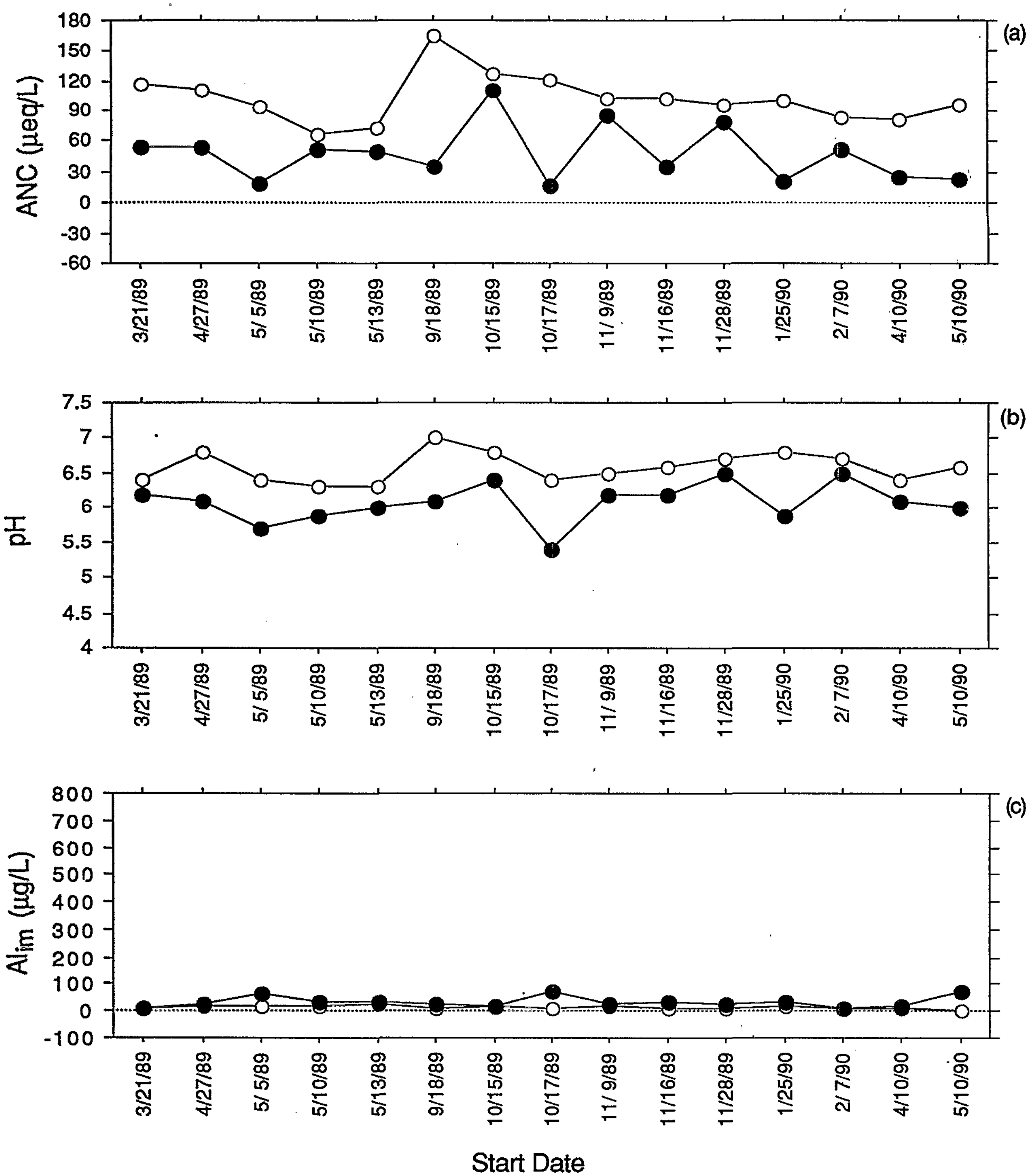


Figure 5-28. (a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Black Brook, Catskills. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.

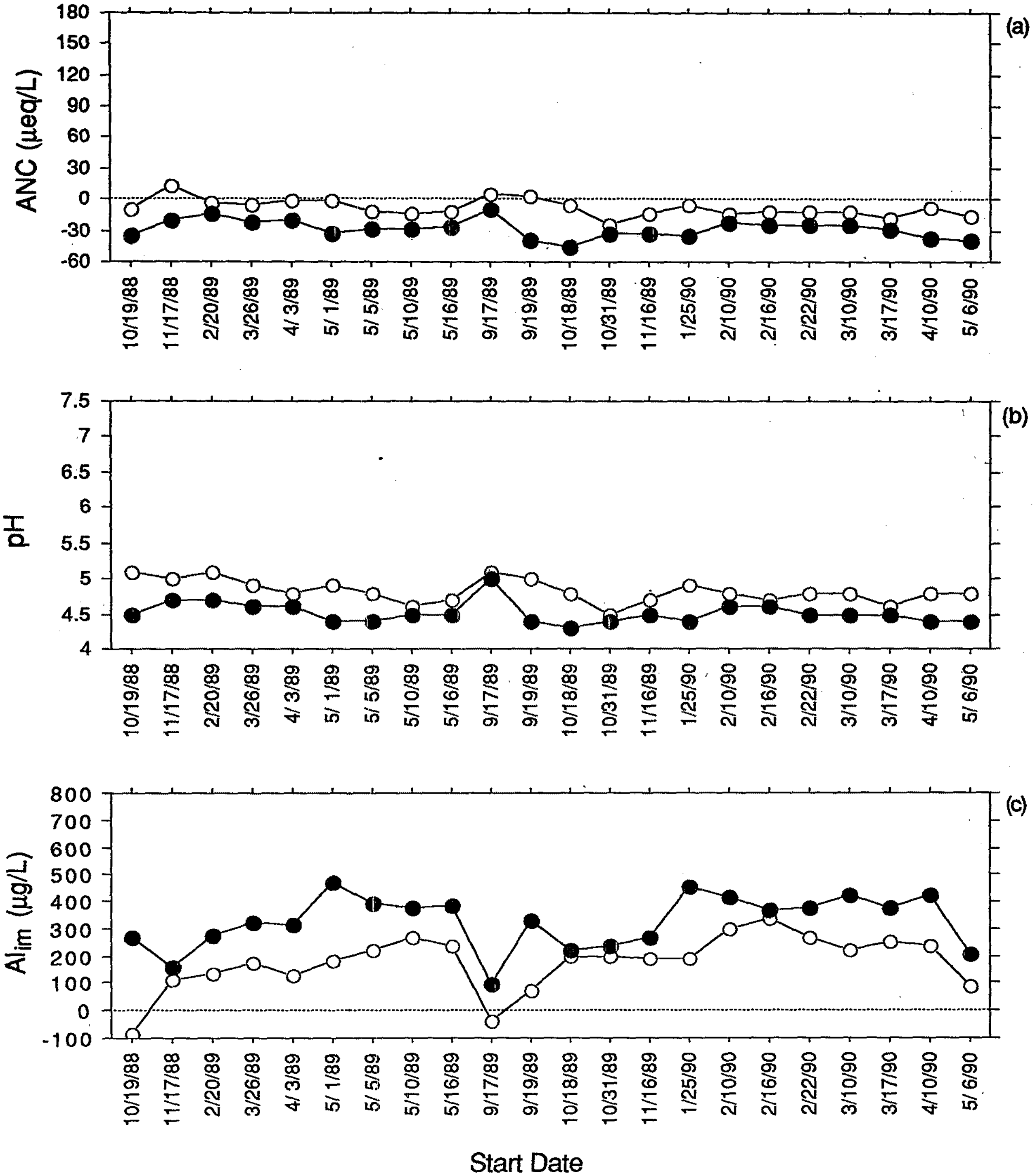


Figure 5-29. (a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in East Branch Neversink River, Catskills. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.

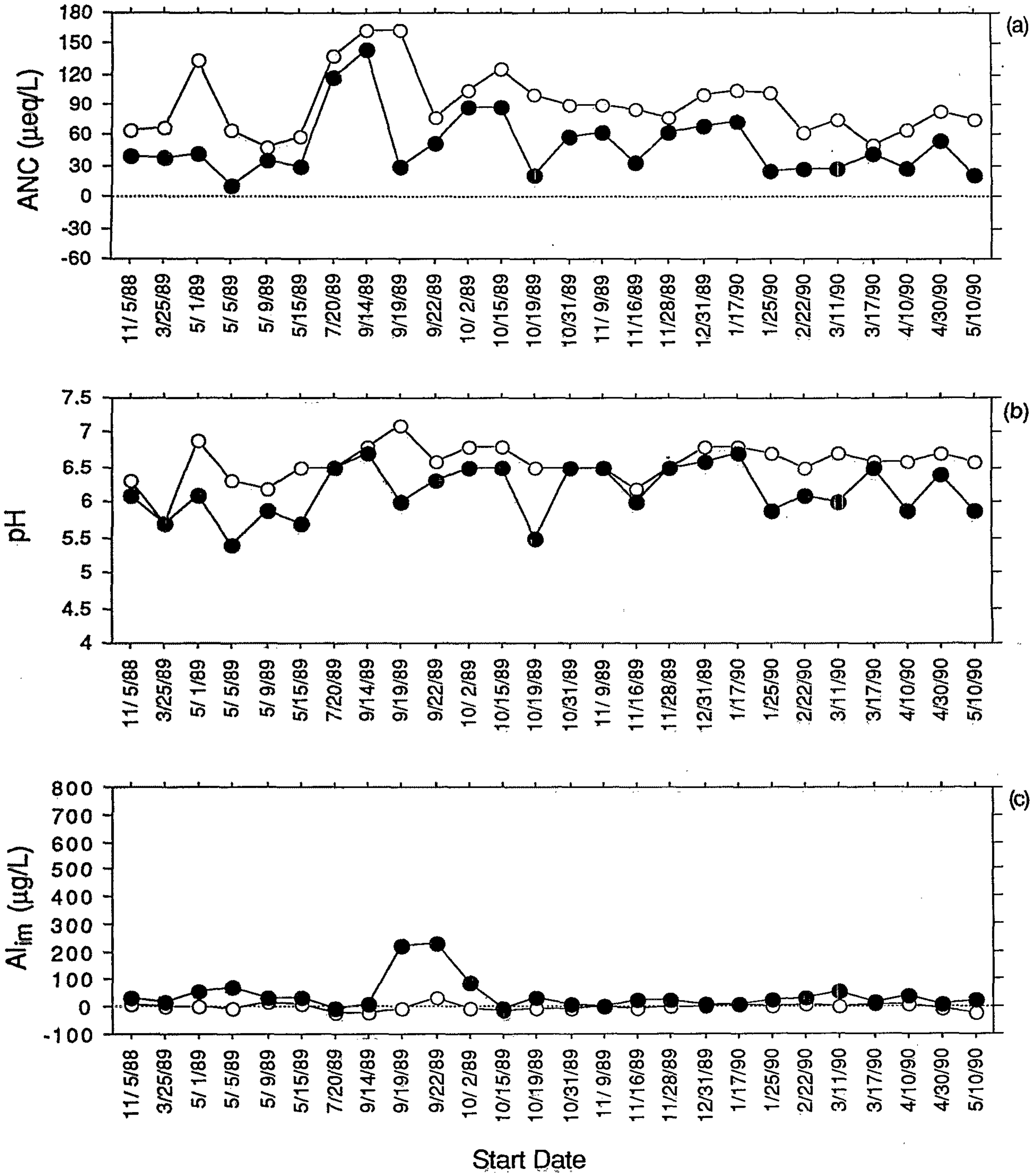


Figure 5-30. (a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in High Falls Brook, Catskills. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.

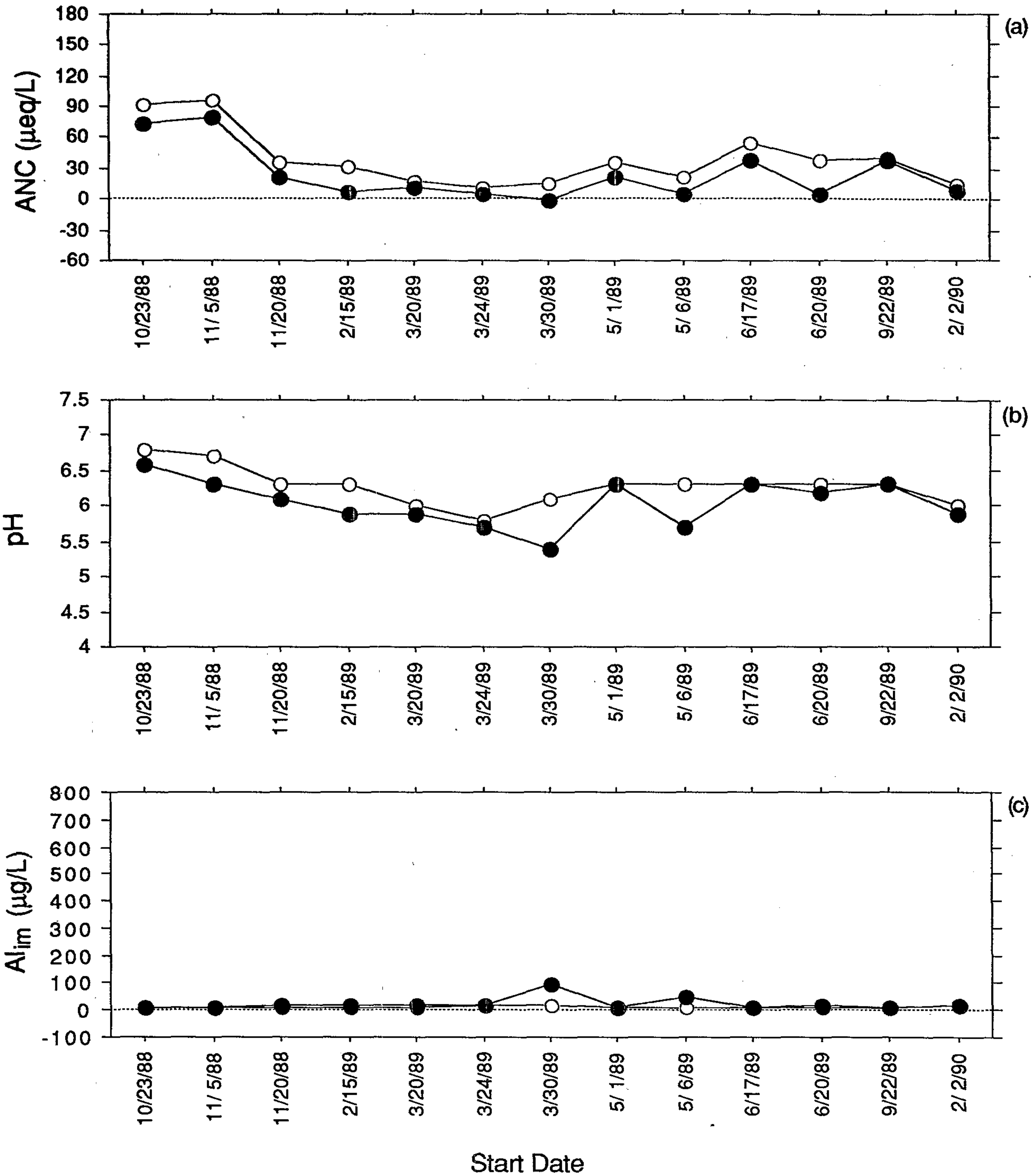


Figure 5-31. (a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Baldwin Creek, Pennsylvania. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.

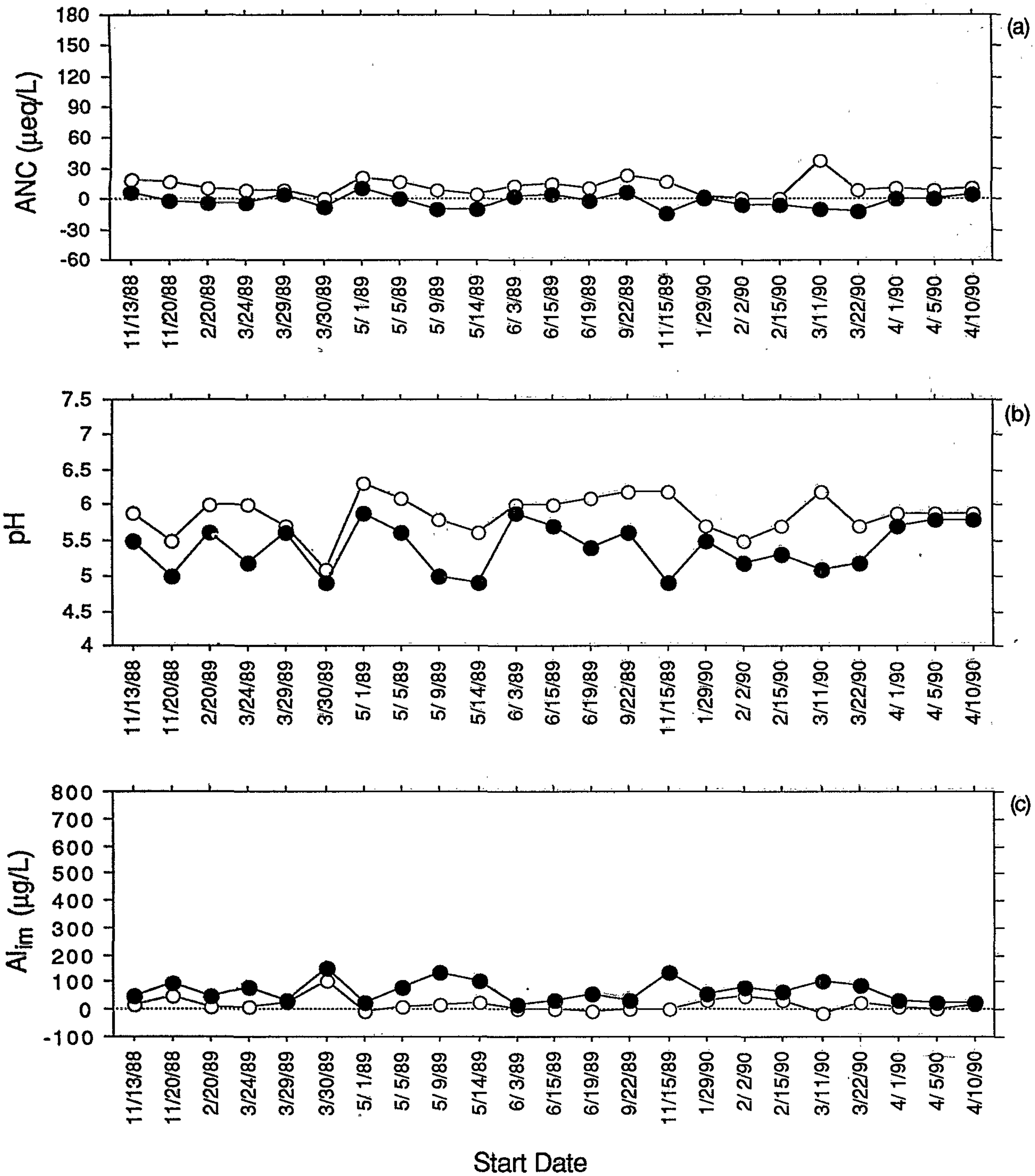


Figure 5-32. (a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Benner Run, Pennsylvania. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.

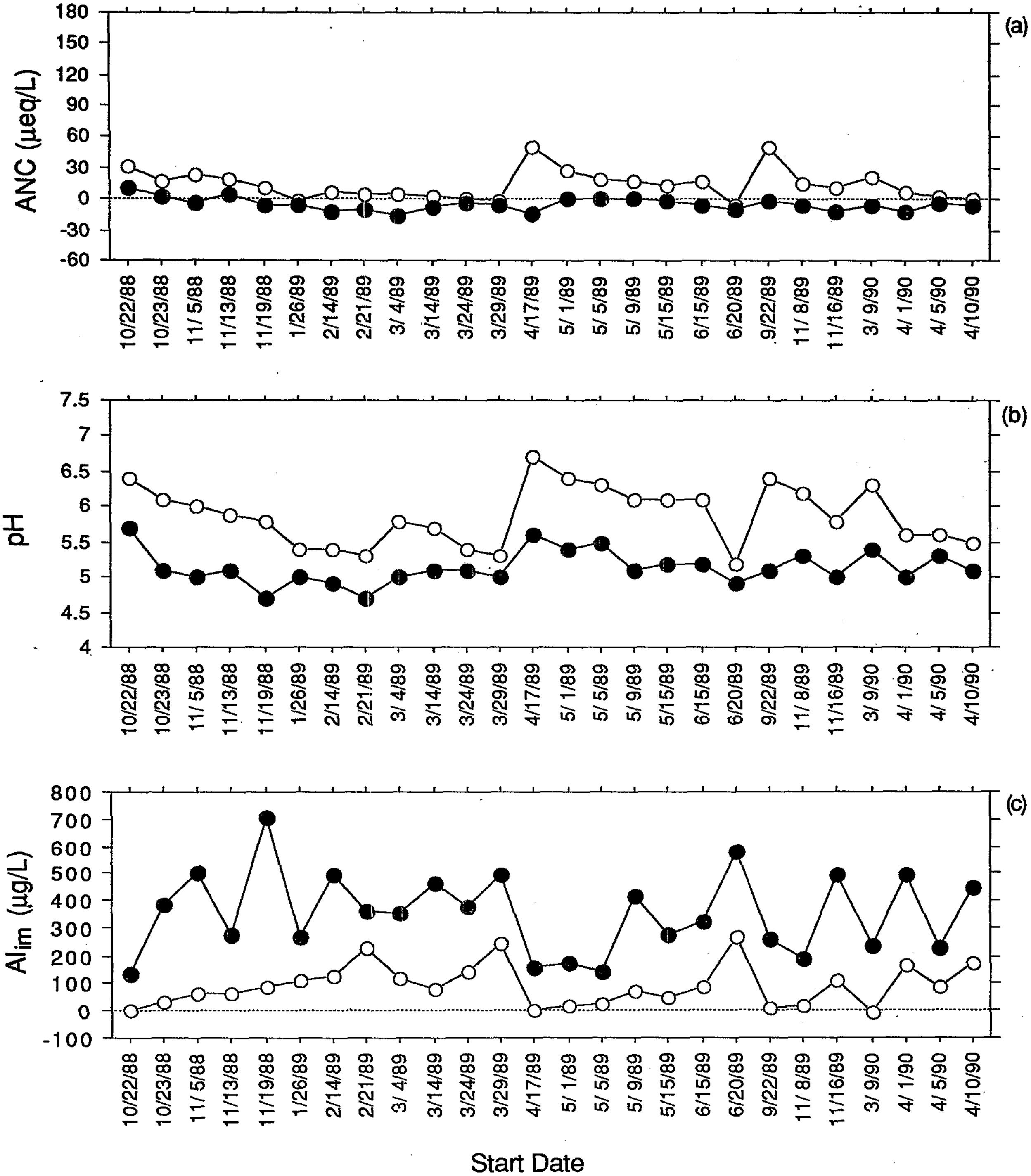


Figure 5-33. (a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Linn Run, Pennsylvania. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.

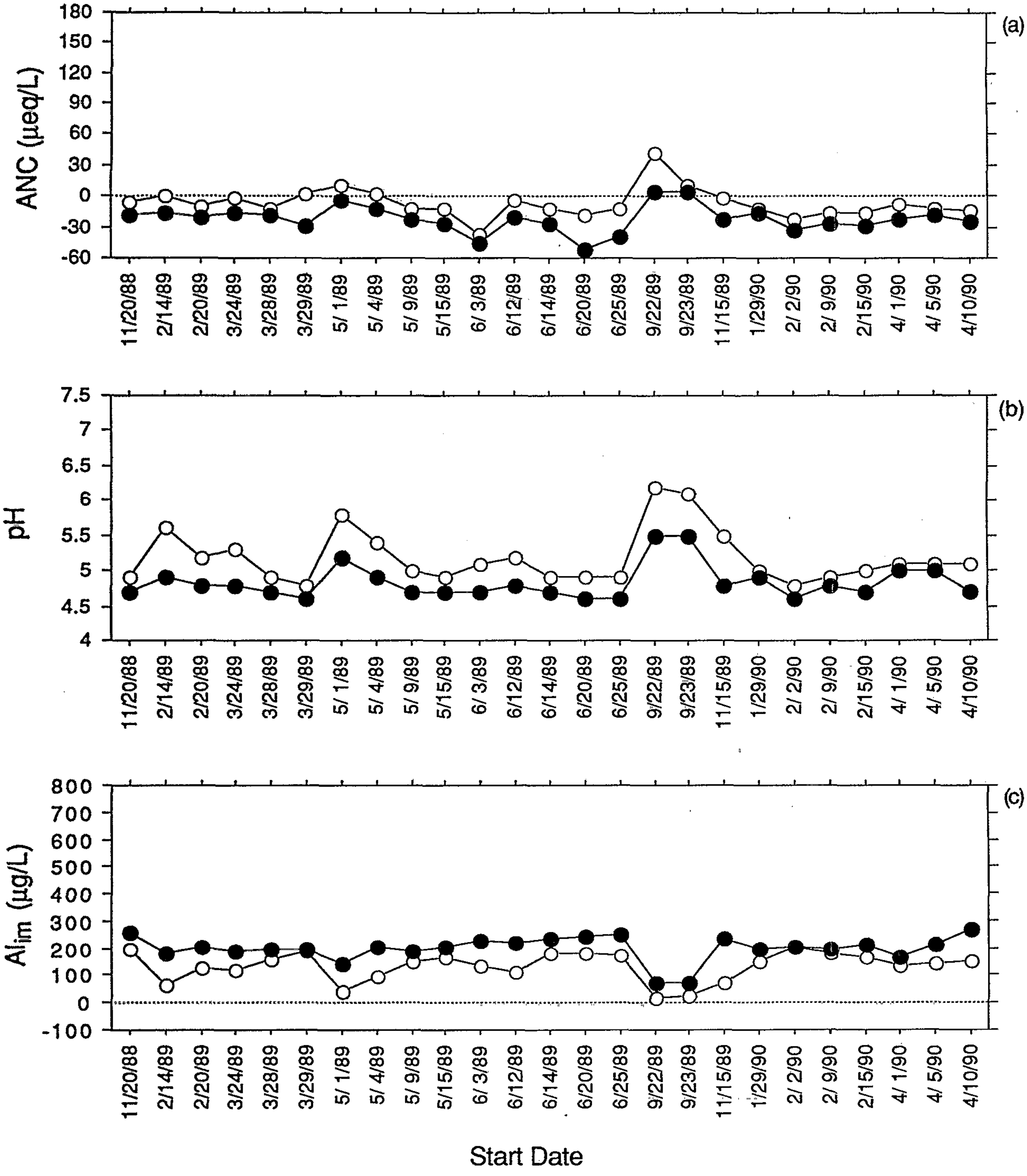


Figure 5-34. (a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Roberts Run, Pennsylvania. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.

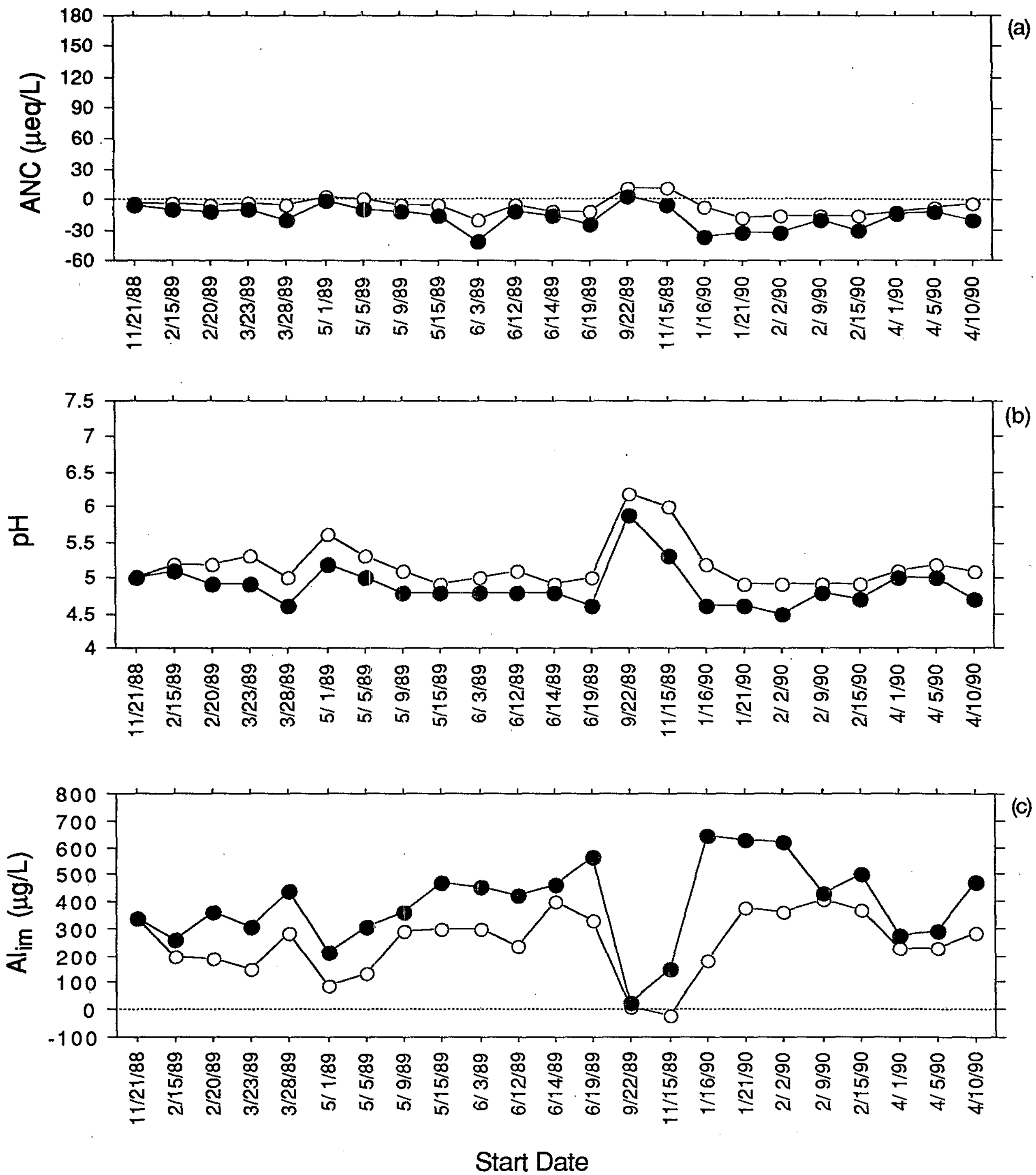


Figure 5-35. (a) Initial and minimum ANC, (b) initial and minimum pH, and (c) initial and maximum estimated Al_{im} during episodes in Stone Run, Pennsylvania. Distances between episode start dates on the x-axis are not linear. Open circles designate initial values, and closed circles designate minimum or maximum values.

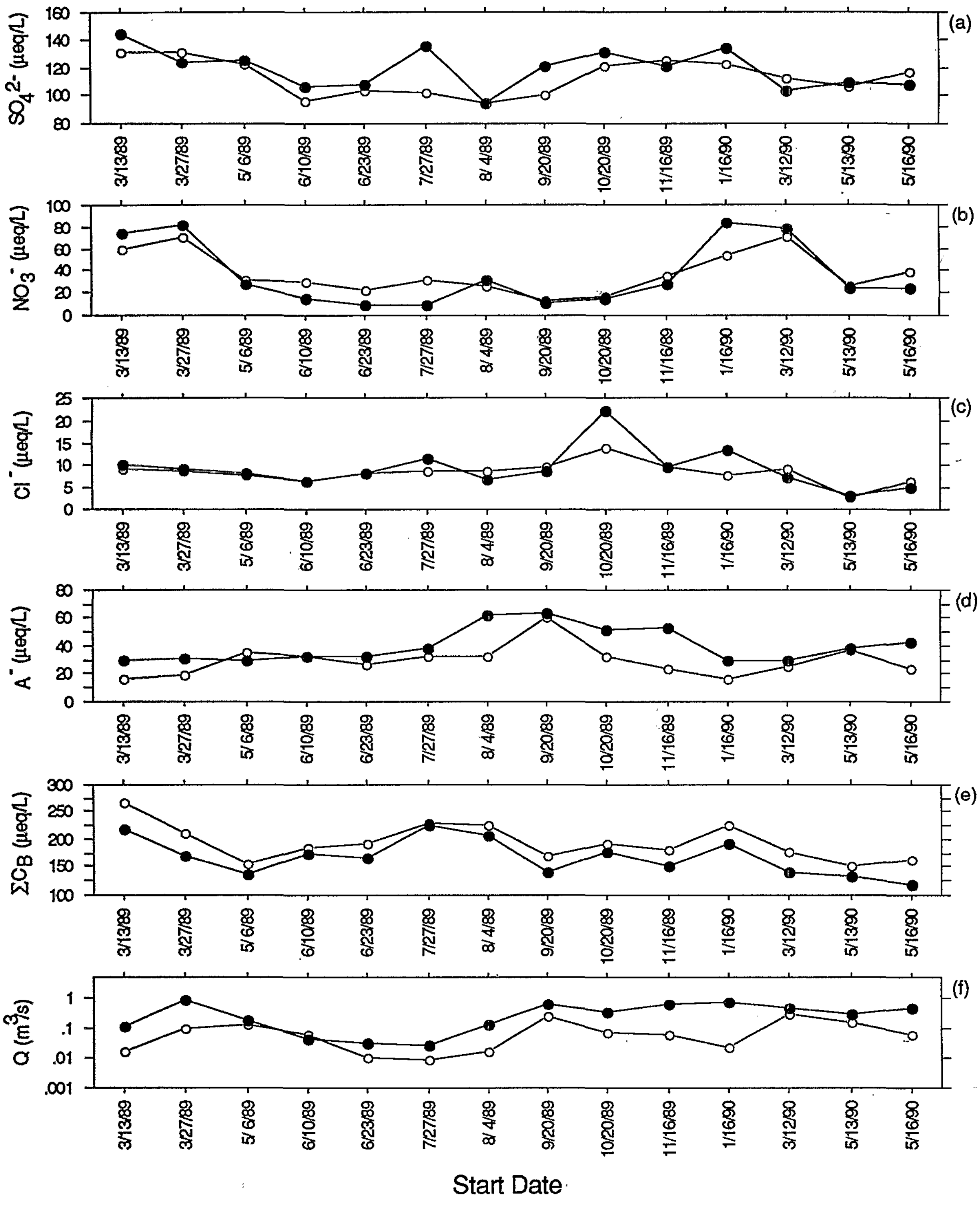


Figure 5-36. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Bald Mountain Brook, Adirondacks. Distances between episode start dates on the x-axis are not linear.

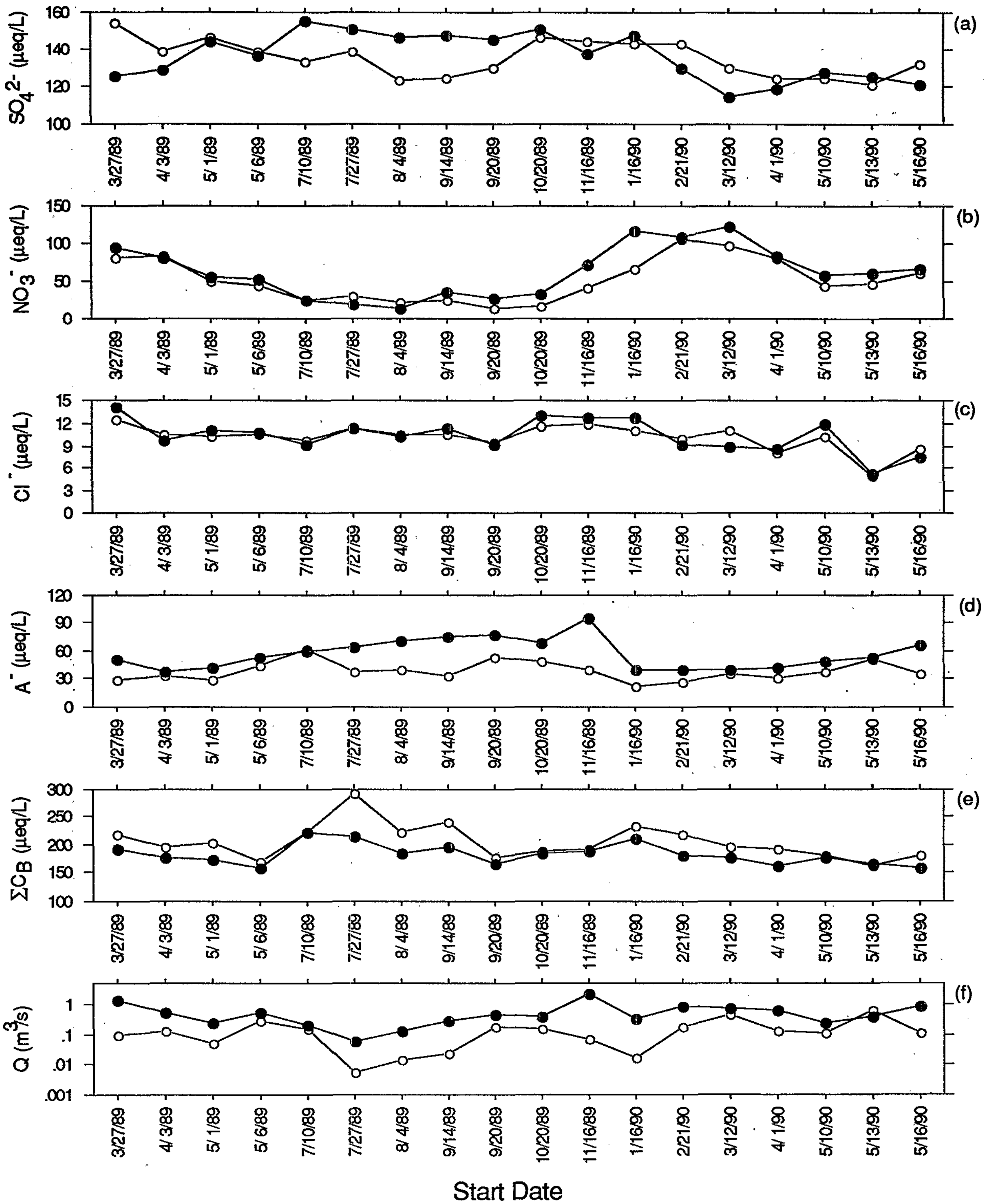


Figure 5-37. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Buck Creek, Adirondacks. Distances between episode start dates on the x-axis are not linear.

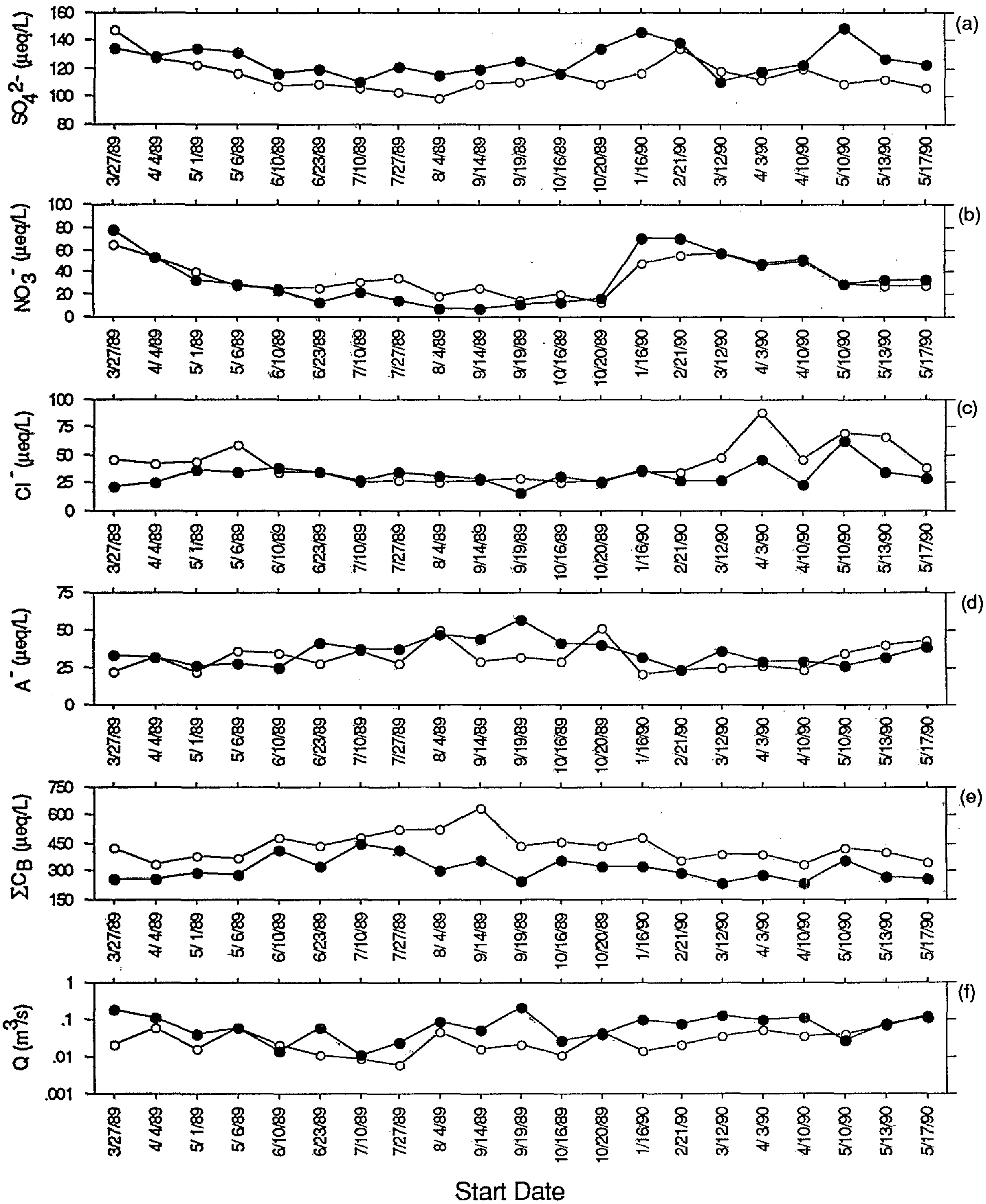


Figure 5-38. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Fly Pond Outlet, Adirondacks. Distances between episode start dates on the x-axis are not linear.

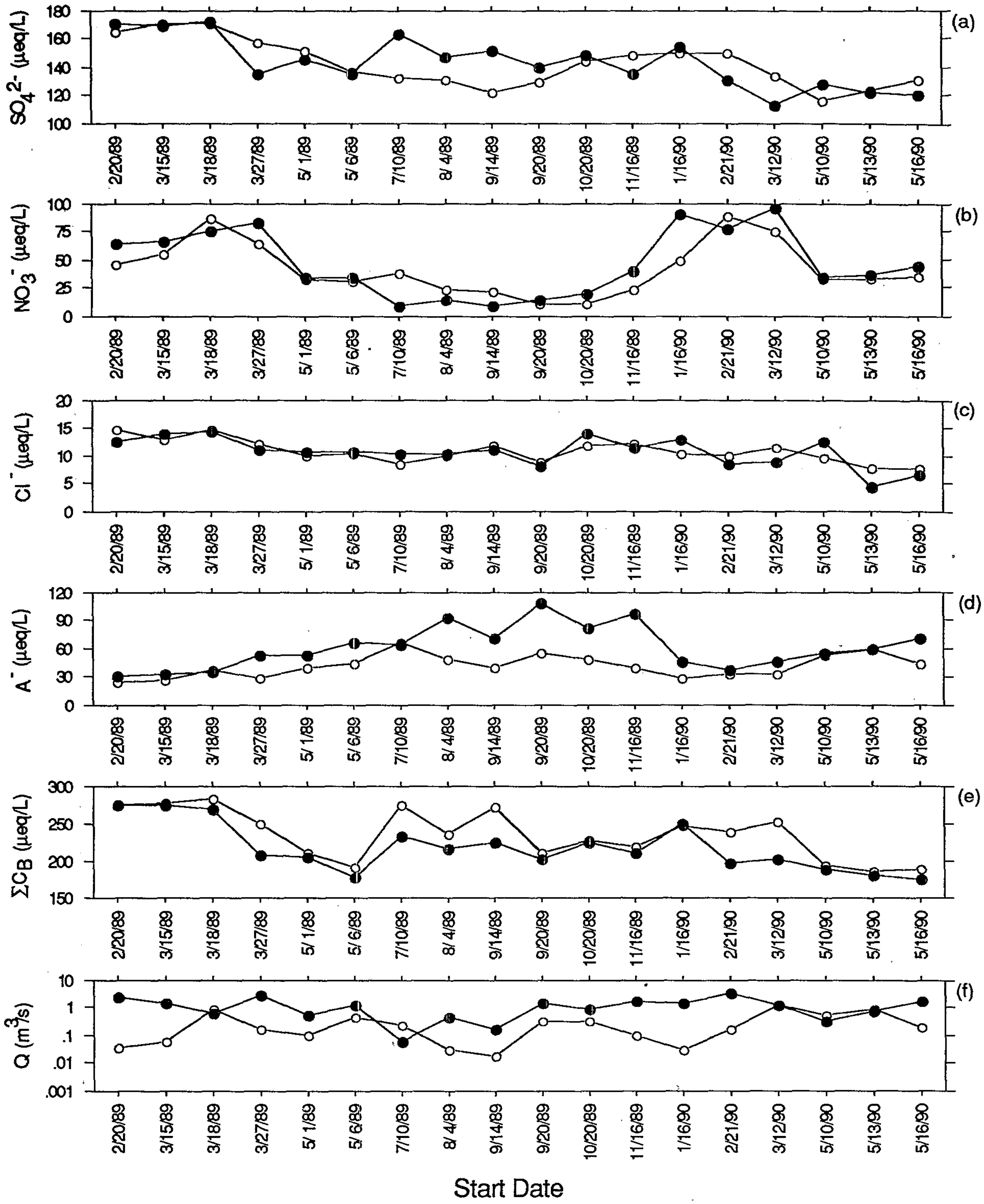


Figure 5-39. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Seventh Lake Inlet, Adirondacks. Distances between episode start dates on the x-axis are not linear.

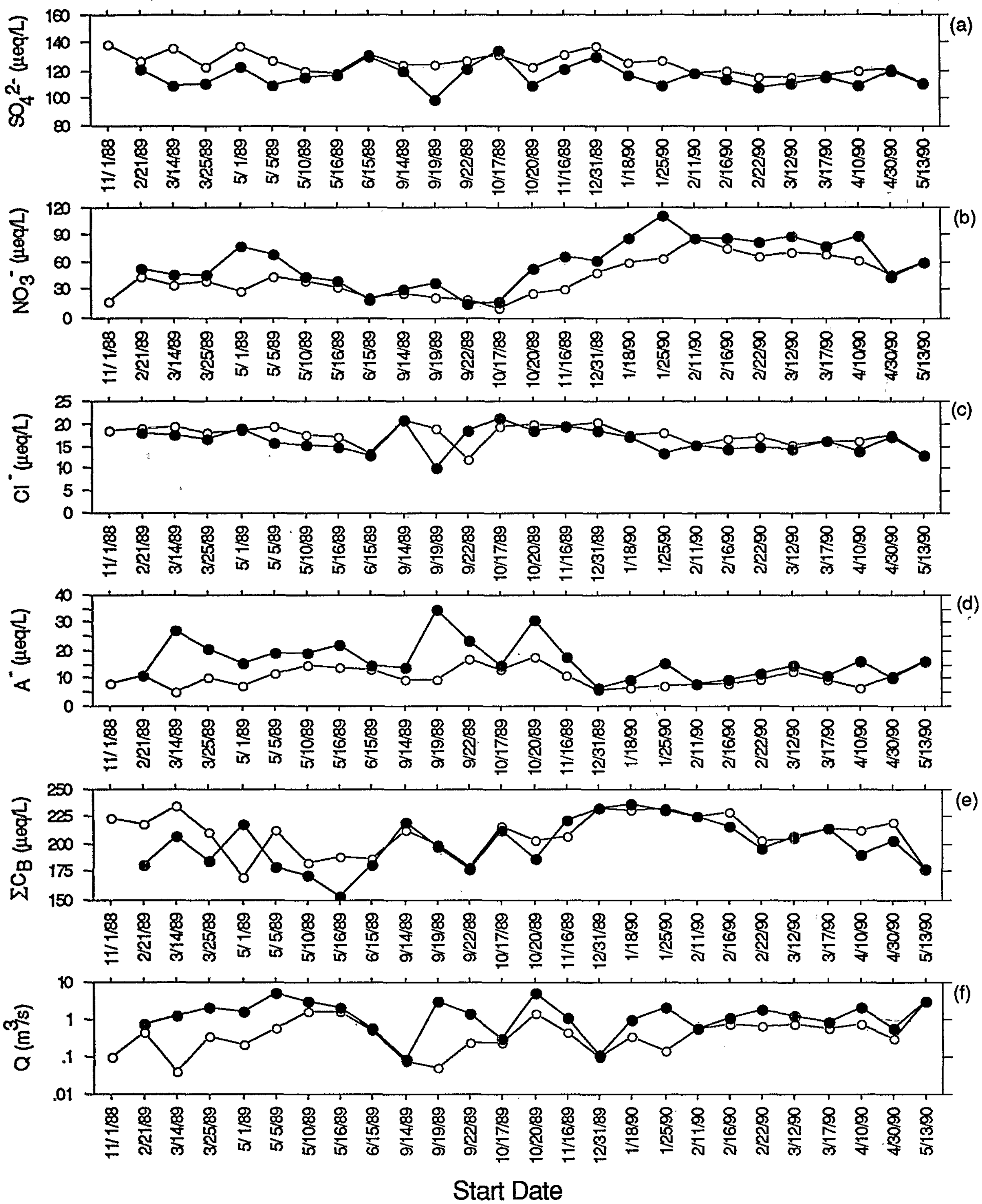


Figure 5-40. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Biscuit Brook, Catskills. Distances between episode start dates on the x-axis are not linear.

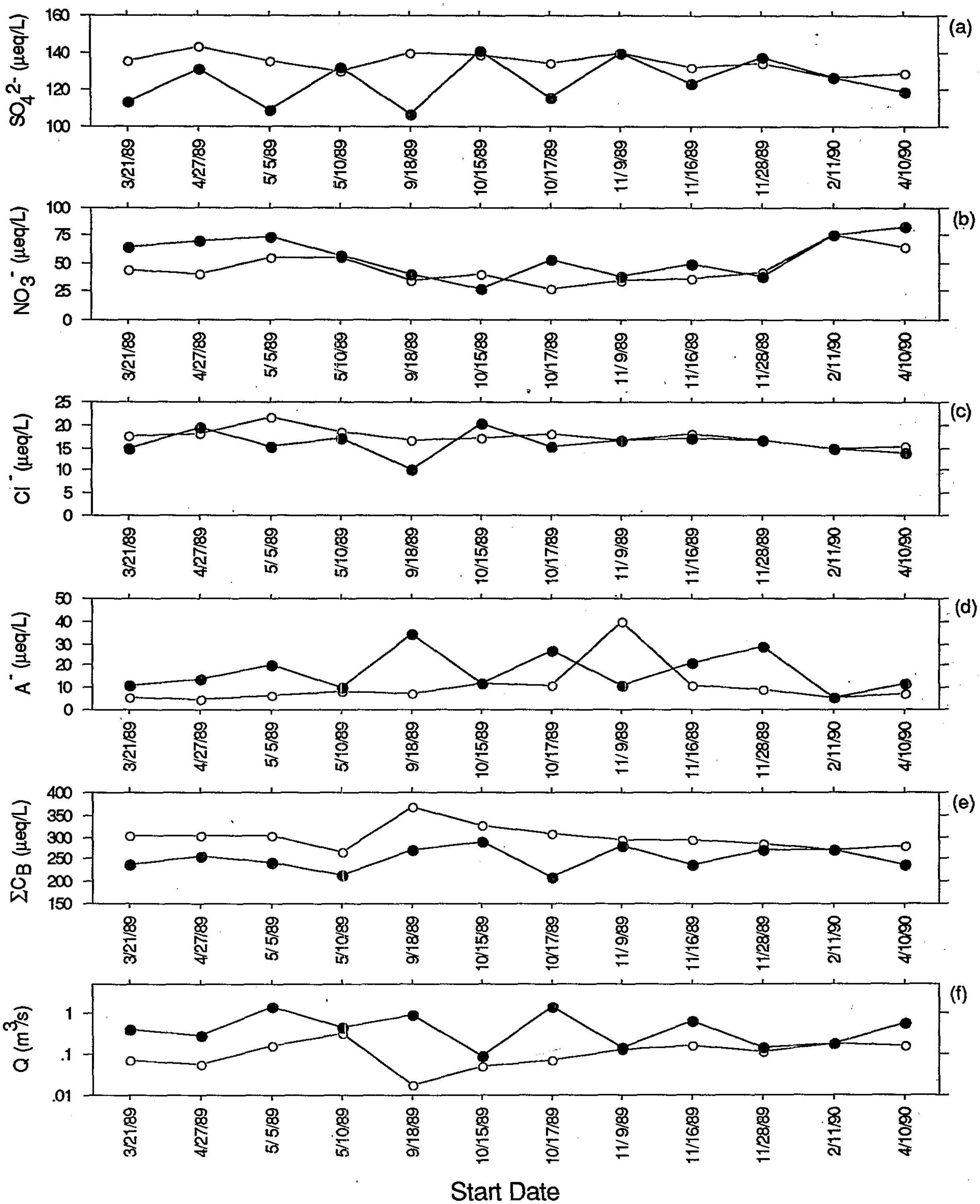


Figure 5-41. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Black Brook, Catskills. Distances between episode start dates on the x-axis are not linear.

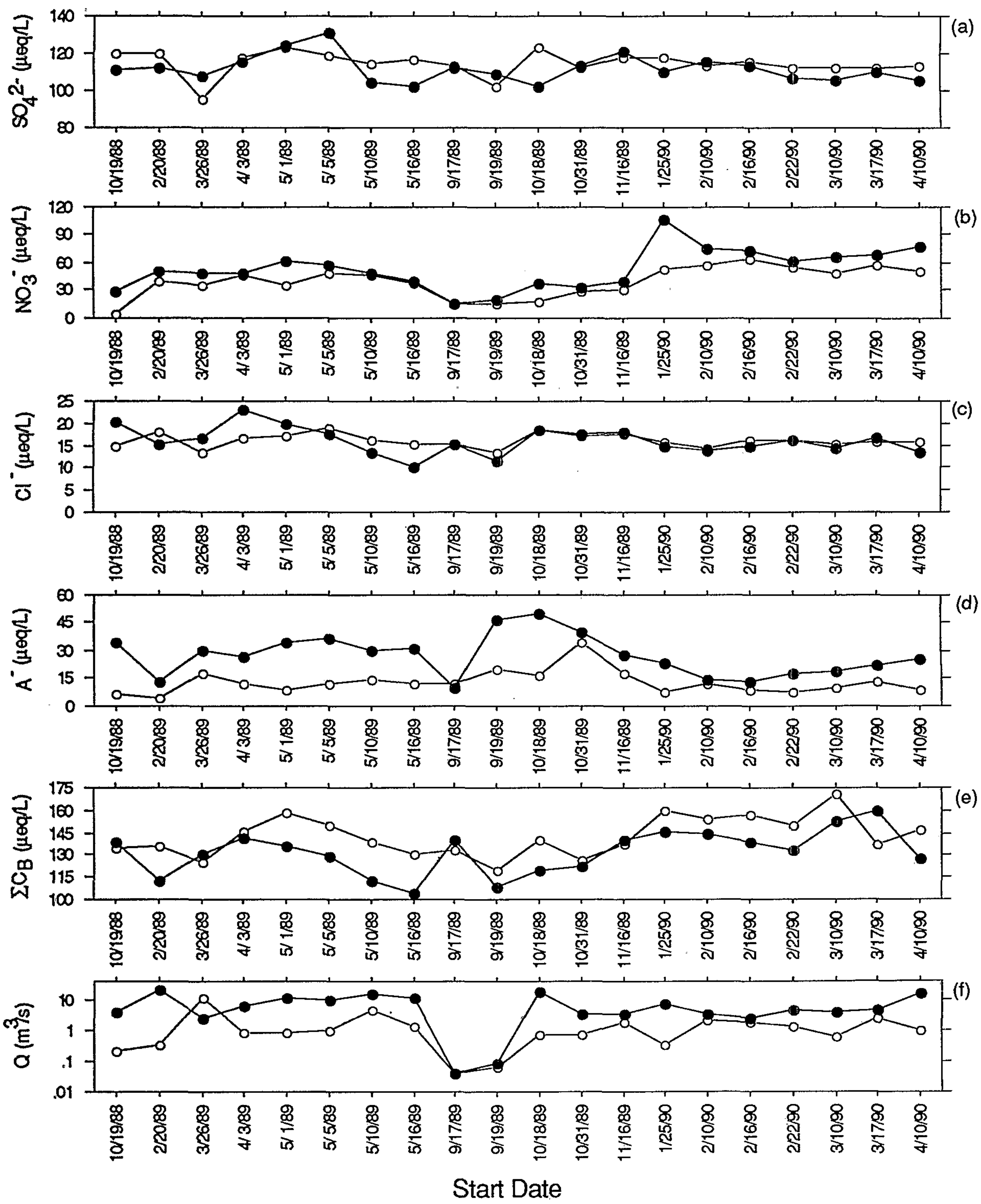


Figure 5-42. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in East Branch Neversink River, Catskills. Distances between episode start dates on the x-axis are not linear.

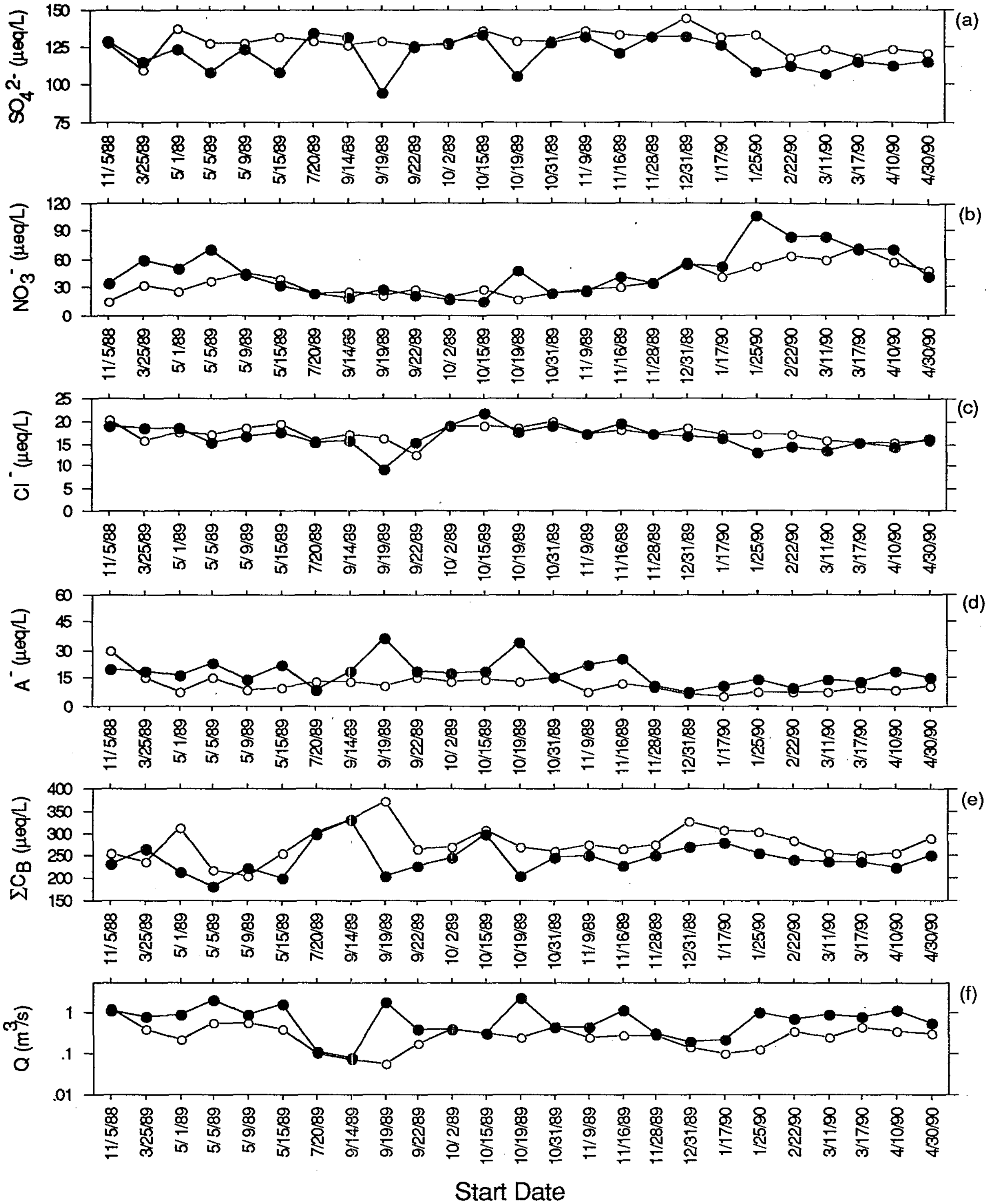


Figure 5-43. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in High Falls Brook, Catskills. Distances between episode start dates on the x-axis are not linear.

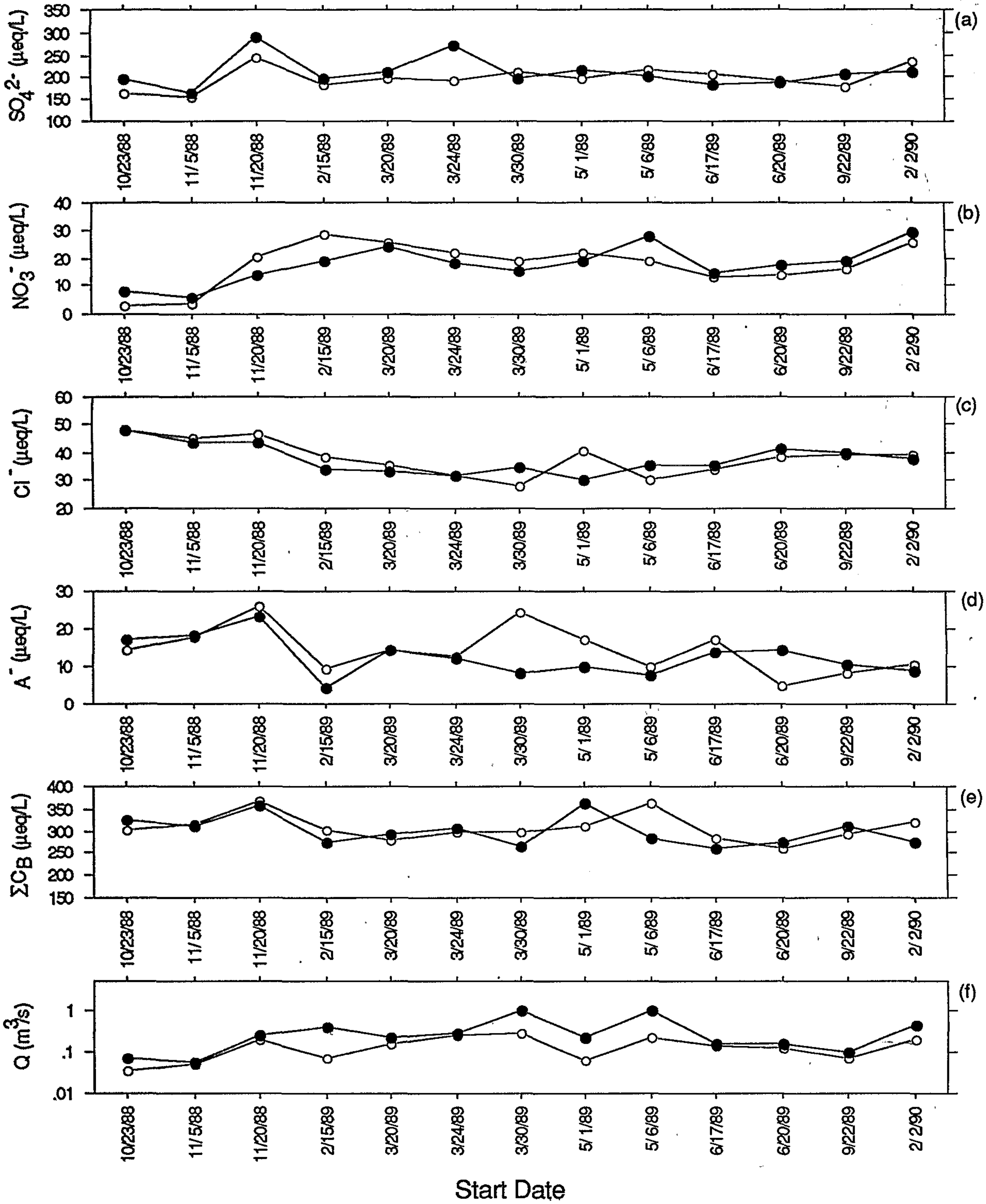


Figure 5-44. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Baldwin Creek, Pennsylvania. Distances between episode start dates on the x-axis are not linear.

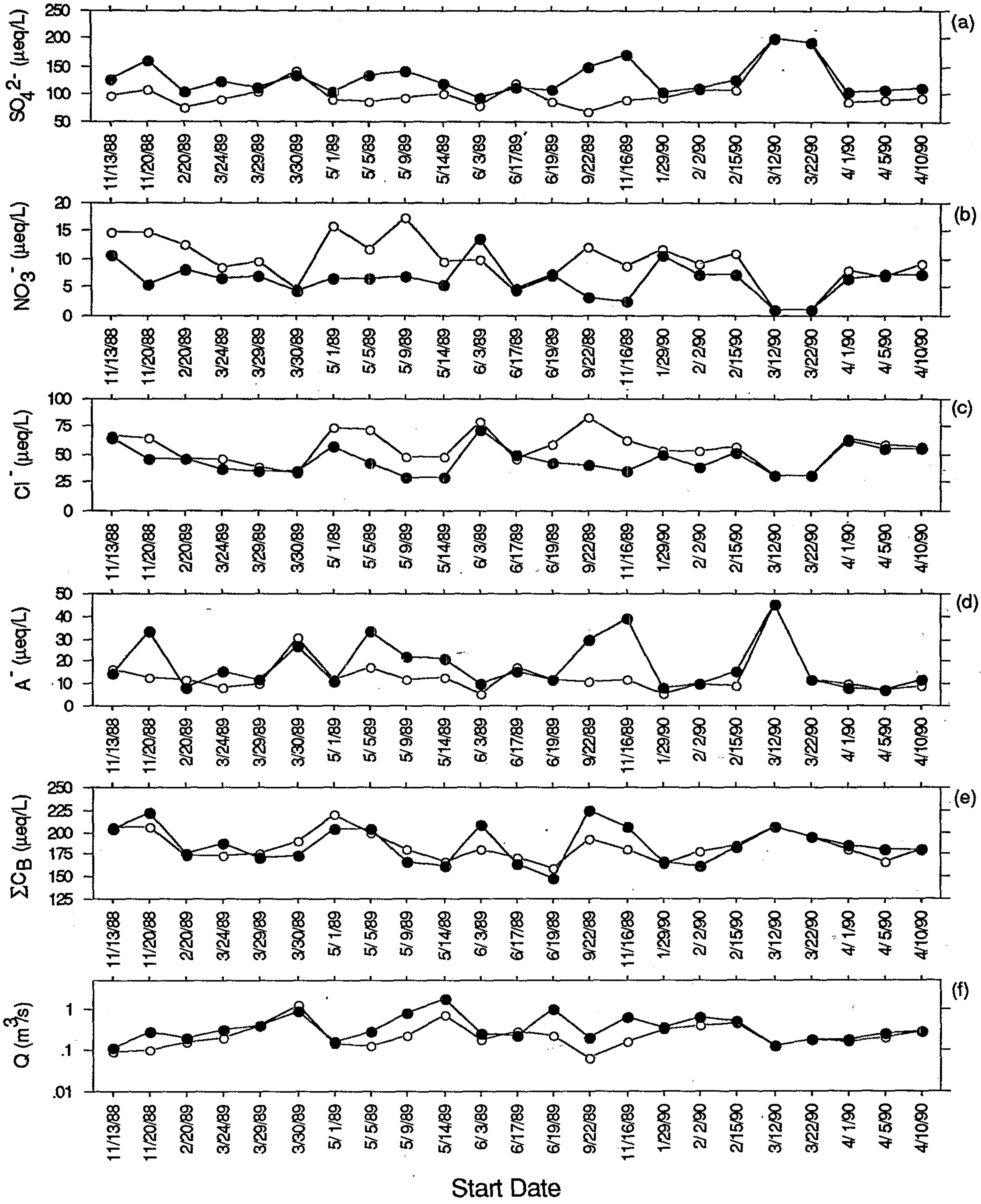


Figure 5-45. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Benner Run, Pennsylvania. Distances between episode start dates on the x-axis are not linear.

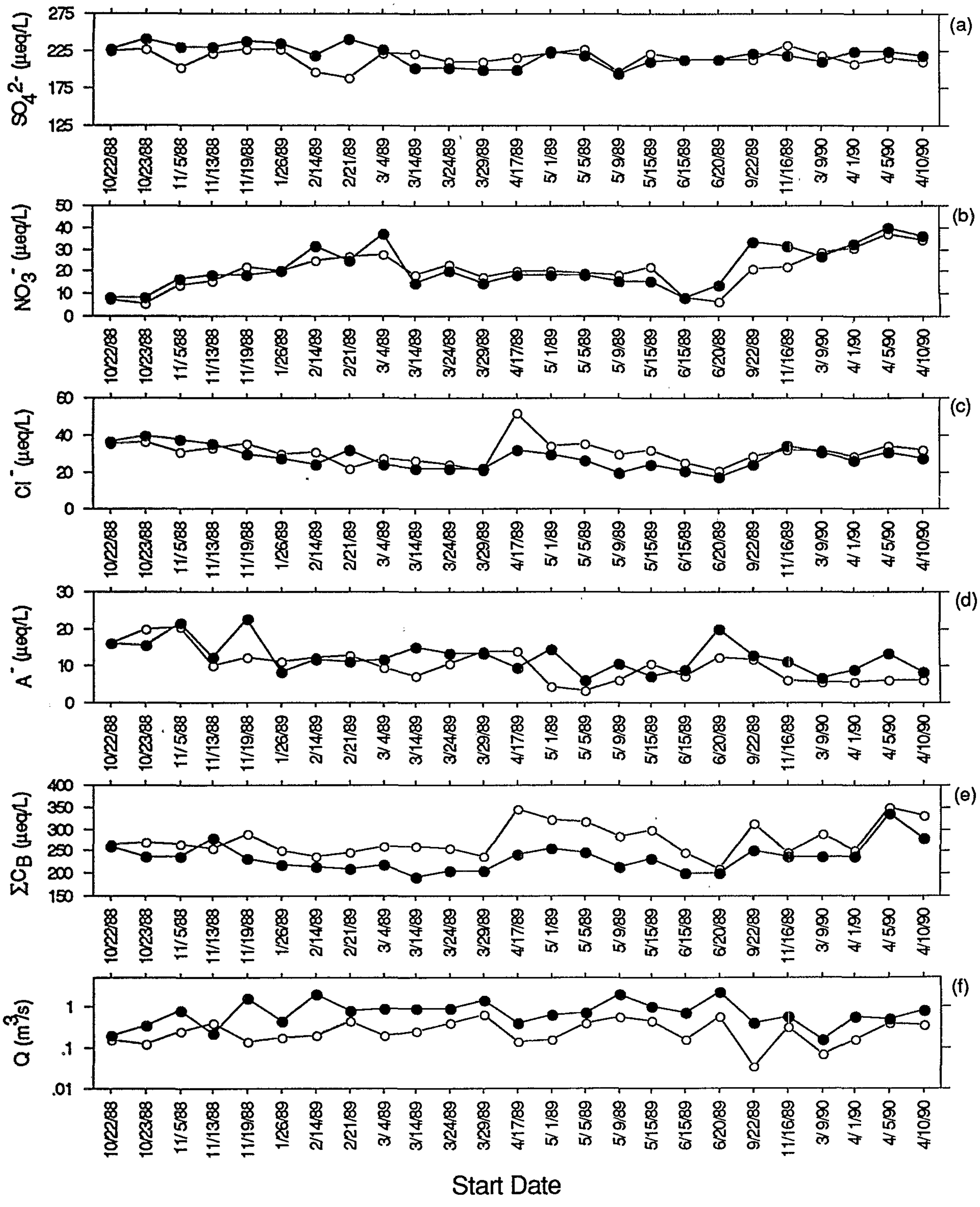


Figure 5-46. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Linn Run, Pennsylvania. Distances between episode start dates on the x-axis are not linear.

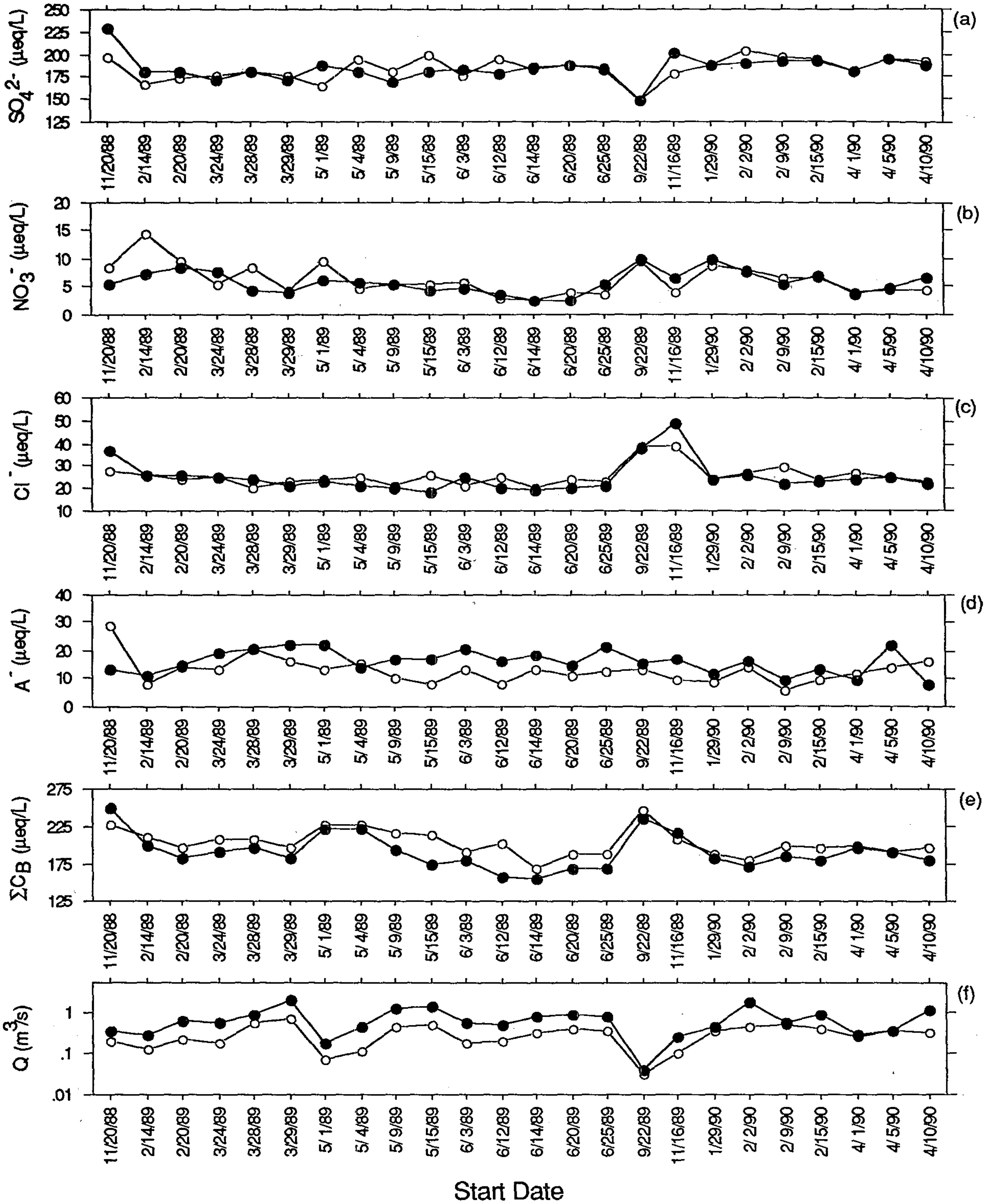


Figure 5-47. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Roberts Run, Pennsylvania. Distances between episode start dates on the x-axis are not linear.

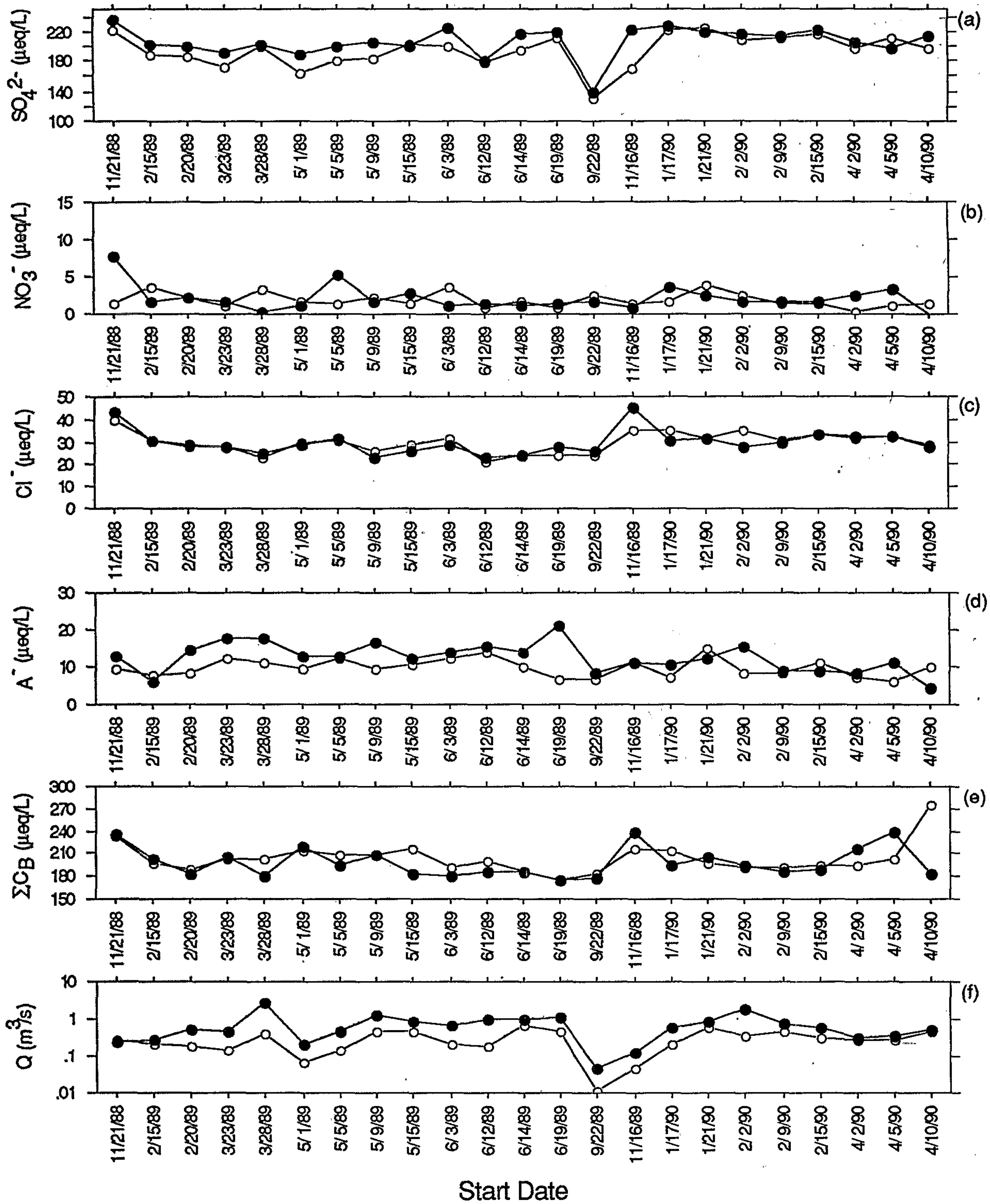


Figure 5-48. (a) SO_4^{2-}, (b) NO_3^-, (c) Cl^-, (d) estimated A^-, (e) ΣC_B, and (f) discharge at the beginning of episodes (open circles) and at the time of minimum ANC (closed circles) during episodes in Stone Run, Pennsylvania. Distances between episode start dates on the x-axis are not linear.

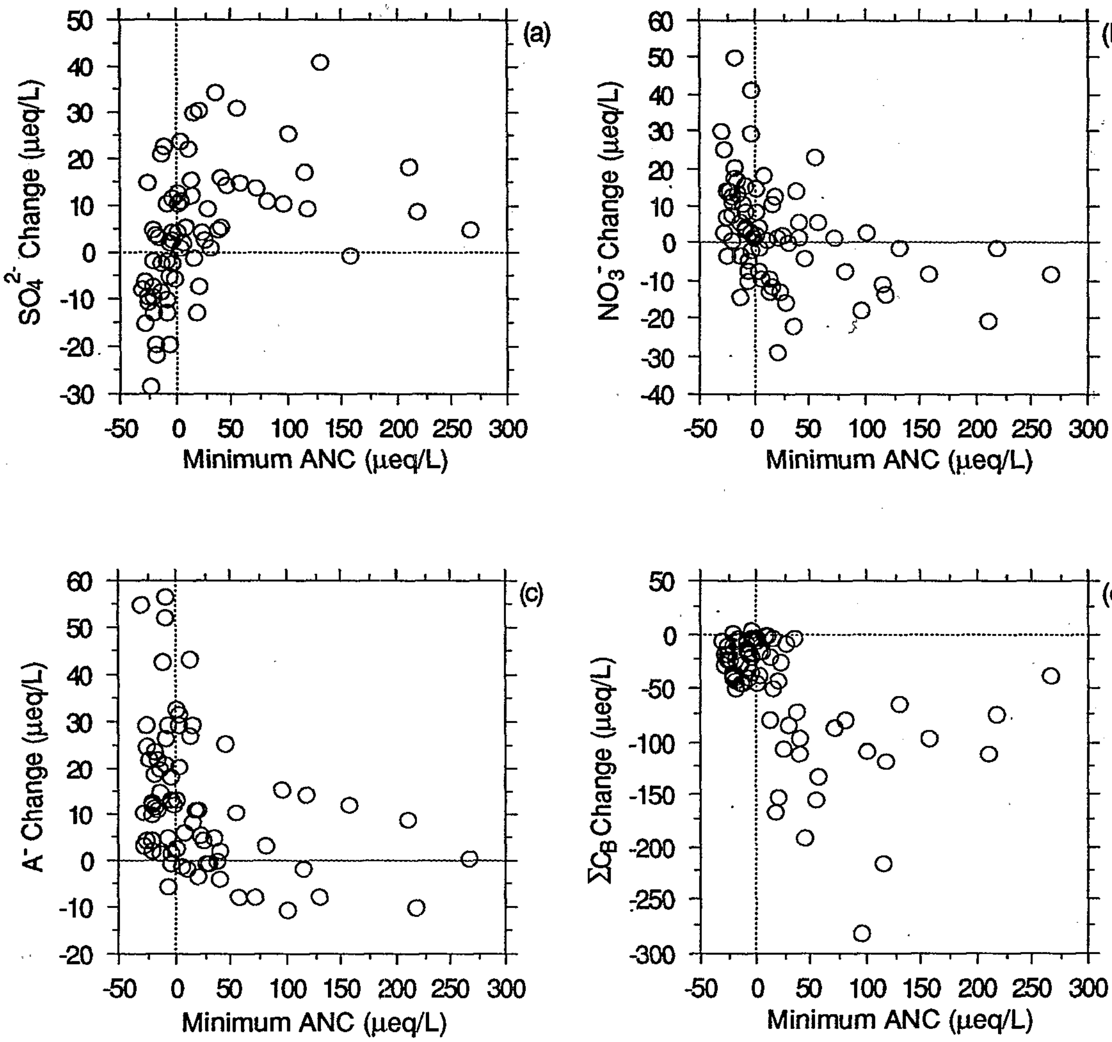


Figure 5-49. **Relationship of (a) SO_4^{2-}, (b) NO_3^-, (c) estimated A^-, and (d) ΣC_B changes during episodes to minimum ANC, Adirondacks.**

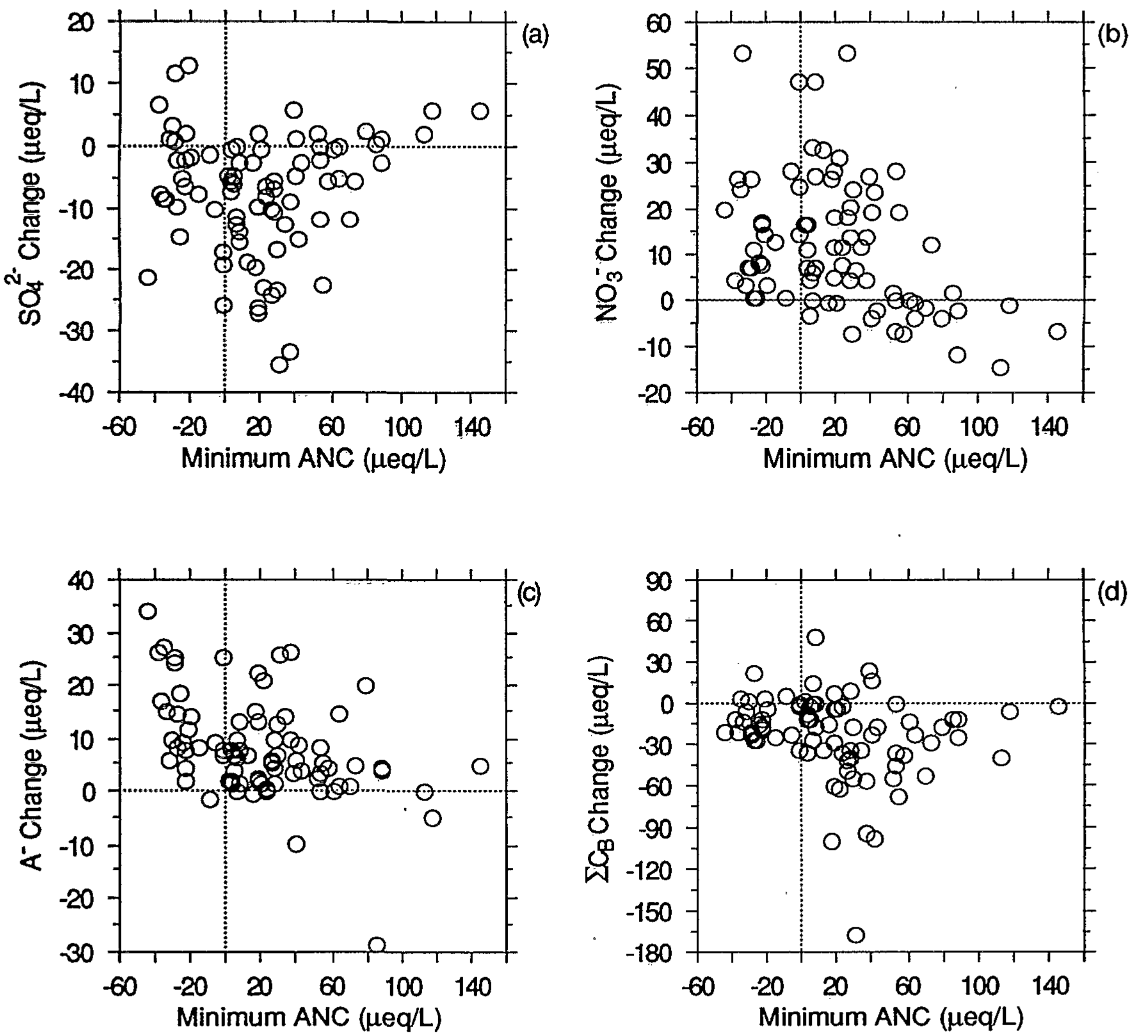


Figure 5-50. **Relationship of (a) SO_4^{2-}, (b) NO_3^-, (c) estimated A^-, and (d) ΣC_B changes during episodes to minimum ANC, Catskills.**

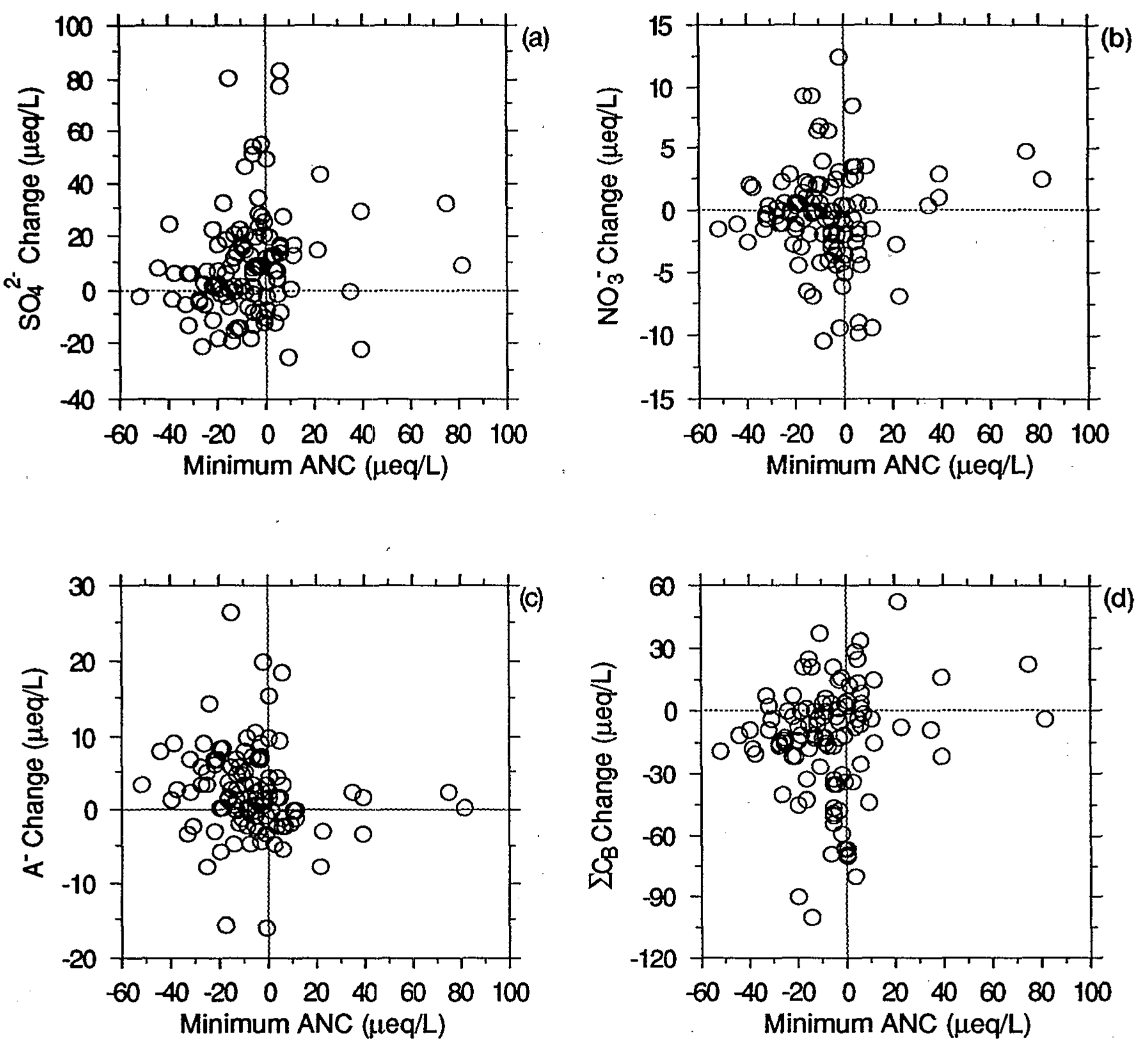


Figure 5-51. **Relationship of (a) SO_4^{2-}, (b) NO_3^-, (c) estimated A^-, and (d) ΣC_B changes during episodes to minimum ANC, Pennsylvania.**

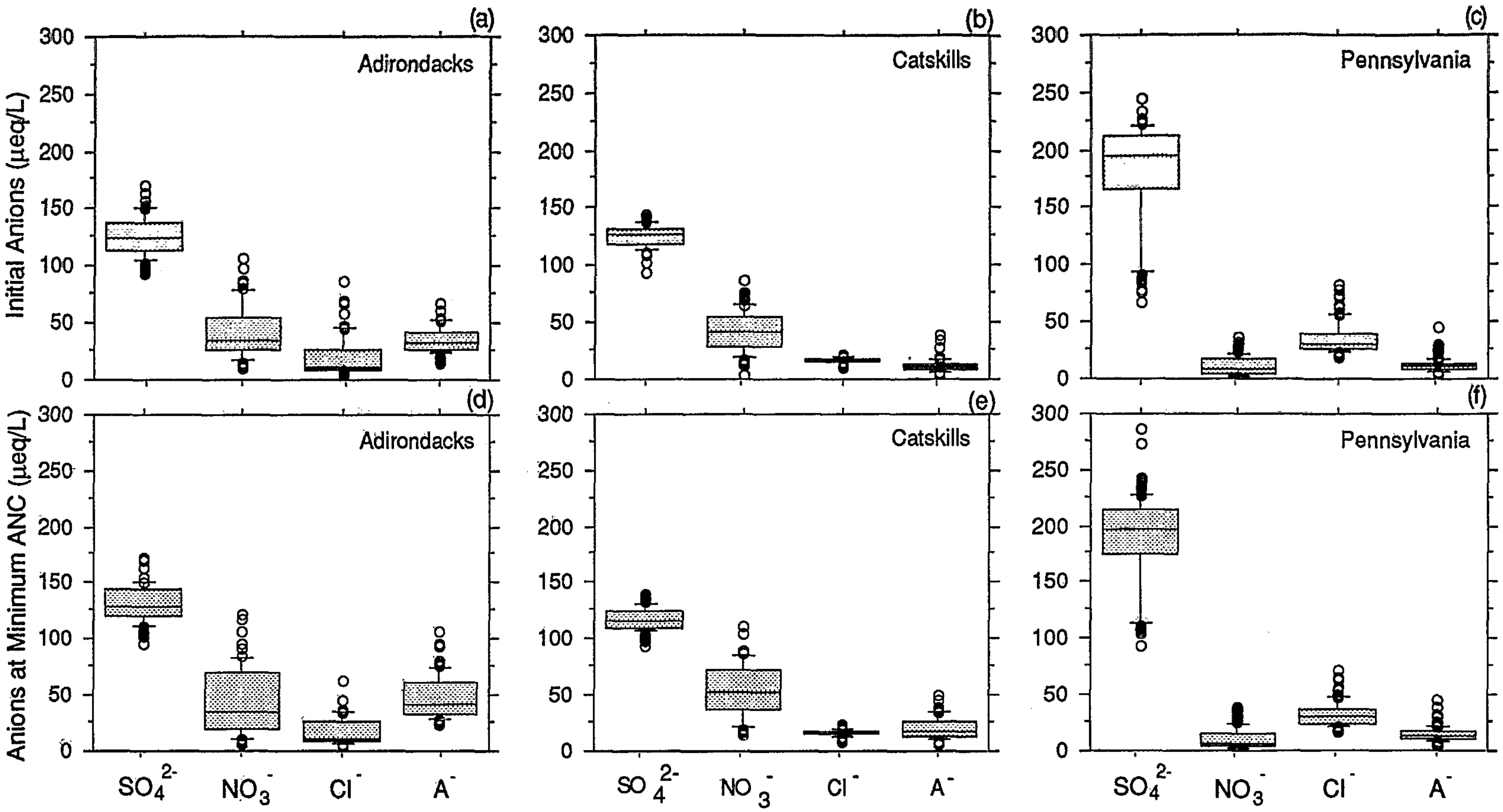


Figure 5-52. **Anion concentrations for (a) Adirondack, (b) Catskill, and (c) Pennsylvania streams at the beginning of episodes, and anion concentrations for (d) Adirondack, (e) Catskill, and (f) Pennsylvania streams at the time of minimum ANC. A^- concentrations are estimates. Line in box indicates median; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.**

Table 5-1. Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Bald Mountain Brook, Adirondacks (unless specified, units are μeq/L)

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} (μg/L)	Al_{im}[a] (μg/L)
Overall minimum	0.01	4.60	–21	88	3	3	1.7	71	20	16	4	37	0
Overall maximum	2.86	6.87	117	146	86	22	11.1	157	65	69	25	730	571
1989 weekly minimum[b]	0.01	4.80	–10	93	11	7	1.7	92	28	22	4	72	0
1989 weekly 25th percentile	0.02	5.42	7	112	25	8	2.6	101	36	34	8	129	25
1989 weekly 50th percentile	0.02	6.15	26	124	34	9	3.2	111	42	42	8	176	55
1989 weekly 75th percentile	0.05	6.53	56	131	54	9	3.7	120	50	53	9	300	95
1989 weekly maximum	2.86	6.87	99	146	77	13	6.9	142	65	70	12	609	338
n for weekly statistics	51	52	52	52	52	52	51	52	52	52	52	52	52

[a] Measured or estimated values.
[b] 2/1/89 through 1/31/90.

Table 5-2. Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Buck Creek, Adirondacks (unless specified, units are µeq/L)

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} (µg/L)	Al_{im}[a] (µg/L)
Overall minimum	< 0.01	4.43	–30	108	11	5	2.6	92	25	16	4	160	0
Overall maximum	4.13	6.72	101	167	123	19	14.9	164	52	68	28	954	690
1989 weekly minimum[b]	< 0.01	4.71	–22	129	12	9	2.6	103	27	25	4	160	0
1989 weekly 25th percentile	0.02	4.98	0	142	20	11	3.9	117	34	31	9	291	94
1989 weekly 50th percentile	0.03	5.38	10	147	37	11	4.7	124	37	37	10	396	165
1989 weekly 75th percentile	0.08	5.84	21	152	58	12	5.4	134	44	47	11	522	279
1989 weekly maximum	0.58	6.54	71	167	100	14	9	151	52	68	13	823	536
n for weekly statistics	51	52	52	52	52	52	52	52	52	52	52	52	52

[a] Measured or estimated values.
[2] 2/1/89 through 1/31/90.

Table 5-3. **Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Fly Pond Outlet, Adirondacks (unless specified, units are $\mu eq/L$)**

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} ($\mu g/L$)	Al_{im}[a] ($\mu g/L$)
Overall minimum	0.01	5.51	17	80	7	12	2.2	143	35	32	7	60	0
Overall maximum	0.26	7.38	442	154	93	88	18.2	422	111	116	29	485	142
1989 weekly minimum[b]	0.01	6.12	46	97	11	18	2.2	175	48	49	7	60	0
1989 weekly 25th percentile	0.01	6.85	151	115	25	25	3.0	227	62	77	12	98	20
1989 weekly 50th percentile	0.01	7.08	225	121	32	32	3.9	258	76	92	13	127	20
1989 weekly 75th percentile	0.02	7.19	282	128	48	36	4.8	285	88	100	14	169	20
1989 weekly maximum	0.08	7.38	375	154	86	69	7.8	314	109	116	17	369	107
n for weekly statistics	47	52	52	52	52	52	52	52	52	52	52	52	52

[a] Measured or estimated values.
[b] 2/1/89 through 1/31/90.

Table 5-4. Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Seventh Lake Inlet, Adirondacks (unless specified, units are μeq/L)

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} (μg/L)	Al_{im}[a] (μg/L)
Overall minimum	< 0.01	4.63	−20	107	7	4	2.6	107	32	18	4	118	0
Overall maximum	4.12	6.74	146	184	106	16	17.8	202	64	52	27	846	485
1989 weekly minimum[b]	0.01	4.89	−5	140	7	9	3.7	116	34	22	4	190	0
1989 weekly 25th percentile	0.03	5.28	7	140	14	10	4.8	130	39	28	8	290	64
1989 weekly 50th percentile	0.06	5.67	21	148	26	11	6.2	139	43	33	9	333	93
1989 weekly 75th percentile	0.16	5.99	30	154	45	12	6.9	150	50	41	10	407	158
1989 weekly maximum	2.60	6.56	70	184	78	15	11.5	174	63	52	14	572	264
n for weekly statistics	51	52	52	52	52	52	52	52	52	51	52	52	52

[a] Measured or estimated values.
[b] 2/1/89 through 1/31/90.

Table 5-5. **Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Biscuit Brook, Catskills (unless specified, units are $\mu eq/L$)**

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} ($\mu g/L$)	Al_{im}[a] ($\mu g/L$)
Overall minimum	< 0.01	4.97	–6	98	1	10	0.3	98	31	6	4	13	0
Overall maximum	9.57	6.63	55	149	129	27	7.5	198	63	38	21	332	159
1989 weekly minimum[b]	0.03	5.34	7	111	11	13	1.0	108	36	9	5	13	0
1989 weekly 25th percentile	0.08	5.89	22	128	23	18	1.0	127	48	14	5	24	1
1989 weekly 50th percentile	0.20	6.11	28	132	33	19	1.8	137	50	16	6	41	10
1989 weekly 75th percentile	0.46	6.29	33	134	45	19	2.2	144	53	17	6	55	15
1989 weekly maximum	2.84	6.50	50	144	68	21	4.8	166	58	22	11	166	92
n for weekly statistics	52	51	51	51	49	51	51	51	51	51	51	49	51

[a] Measured or estimated values.
[b] 2/1/89 through 1/31/90.

Table 5-6. Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Black Brook, Catskills (unless specified, units are $\mu eq/L$)

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} ($\mu g/L$)	Al_{im}[a] ($\mu g/L$)
Overall minimum	0.01	5.44	10	100	10	5	0.7	136	31	6	4	2	9
Overall maximum	1.6	7.04	176	146	108	23	8.1	294	66	39	27	539	72
1989 weekly minimum[b]	0.01	5.77	50	106	28	15	0.7	182	40	10	5	2	0
1989 weekly 25th percentile	0.05	6.44	94	135	37	16	1.0	223	48	10	5	11	10
1989 weekly 50th percentile	0.08	6.67	118	139	41	17	1.3	235	52	11	6	18	17
1989 weekly 75th percentile	0.17	6.82	137	141	45	18	2.0	256	55	12	7	35	20
1989 weekly maximum	0.52	7.04	176	146	72	23	7.9	288	63	26	16	306	49
n for weekly statistics	42	52	50	51	51	51	49	51	51	51	51	49	52

[a] Measured or estimated values.

[b] 2/1/89 through 1/31/90.

Table 5-7. **Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for East Branch Neversink River, Catskills (unless specified, units are μeq/L)**

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} (μg/L)	Al_{im}[a] (μg/L)
Overall minimum	0.01	4.27	–45	68	4	10	0.3	37	28	7	4	94	36
Overall maximum	41.7	5.43	21	143	106	28	11.7	124	67	87	20	737	505
1989 weekly minimum[b]	0.03	4.45	–31	84	13	11	1.0	51	30	8	4	101	0
1989 weekly 25th percentile	0.06	4.78	–9	115	15	15	1.6	62	45	13	5	148	99
1989 weekly 50th percentile	0.55	4.91	–6	118	32	16	2.0	66	49	15	6	191	156
1989 weekly 75th percentile	1.23	5.0	–3	119	39	17	2.5	75	55	17	8	240	188
1989 weekly maximum	37.4	5.35	10	124	67	19	6.3	80	61	37	13	562	380
n for weekly statistics	49	52	52	52	52	52	49	52	52	52	52	51	52

[a] Measured or estimated values.
[b] 2/1/89 through 1/31/90.

Table 5-8. **Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for High Falls Brook, Catskills (unless specified, units are $\mu eq/L$)**

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} ($\mu g/L$)	Al_{im}[a] ($\mu g/L$)
Overall minimum	0.02	5.40	10	91	14	9	0.9	119	26	8	3	10	0
Overall maximum	2.38	7.07	172	153	106	23	8.0	277	60	62	23	258	84
1989 weekly minimum[b]	0.04	5.86	38	91	17	12	0.9	119	26	10	3	6	0
1989 weekly 25th percentile	0.09	6.33	72	129	25	16	1.4	196	42	13	6	12	0
1989 weekly 50th percentile	0.20	6.61	95	133	31	17	1.8	209	46	14	6	24	6
1989 weekly 75th percentile	0.35	6.83	122	136	37	18	2.7	235	50	16	7	40	11
1989 weekly maximum	2.21	7.07	172	146	61	20	4.3	277	57	33	12	258	84
n for weekly statistics	52	49	52	52	52	52	49	51	52	51	52	50	52

[a] Measured or estimated values.
[b] 2/1/89 through 1/31/90.

Table 5-9. Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Baldwin Creek, Pennsylvania (unless specified, units are μeq/L)

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} (μg/L)	Al_{im}[a] (μg/L)
Overall minimum	0.02	5.37	−1	102	3	12	0.3	84	64	11	9	1	0
Overall maximum	1.95	7.03	97	288	39	63	6.2	244	151	31	37	102	84
1989 weekly minimum[b]	0.03	5.62	3	102	10	12	0.3	133	74	13	13	1	10
1989 weekly 25th percentile	0.07	6.11	19	185	16	34	1.0	153	81	19	15	17	11
1989 weekly 50th percentile	0.08	6.29	31	194	17	40	1.4	160	83	21	17	26	11
1989 weekly 75th percentile	0.13	6.40	40	203	22	43	2.3	174	87	22	20	35	12
1989 weekly maximum	0.32	6.70	68	253	34	50	4.0	199	102	24	25	87	22
n for weekly statistics[c]	49	52	52	40	40	40	40	40	40	40	40	52	49

[a] Measured or estimated values.
[b] 2/1/89 through 1/31/90.
[c] Missing values for period 11/89 through 1/31/90.

Table 5-10. **Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Benner Run, Pennsylvania (unless specified, units are μeq/L)**

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} (μg/L)	Al_{im}[a] (μg/L)
Overall minimum	0.04	4.91	–15	59	1	25	0.6	54	38	15	13	4	0
Overall maximum	2.01	6.53	54	204	25	102	9.6	168	81	54	30	232	133
1989 weekly minimum[b]	0.06	5.06	–6	59	1	32	0.7	61	44	25	13	4	0
1989 weekly 25th percentile	0.10	5.86	7	72	8	53	1.2	73	46	35	18	15	0
1989 weekly 50th percentile	0.14	6.02	11	87	10	64	1.6	77	48	39	19	24	5
1989 weekly 75th percentile	0.22	6.20	14	96	11	80	2.2	81	50	44	20	40	19
1989 weekly maximum	0.93	6.52	26	183	21	102	9.4	129	81	54	30	192	102
n for weekly statistics[c]	52	52	50	40	39	40	40	40	40	40	40	52	52

[a] Measured or estimated values.

[b] 2/1/89 through 1/31/90.

[c] Missing values for period 11/89 through 1/31/90.

Table 5-11. Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Linn Run, Pennsylvania (unless specified, units are $\mu eq/L$)

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} ($\mu g/L$)	Al_{im}[a] ($\mu g/L$)
Overall minimum	< 0.01	4.69	–21	165	6	17	0.5	103	37	12	4	7	0
Overall maximum	8.62	6.73	85	272	55	66	7.7	248	152	68	32	654	805
1989 weekly minimum[b]	< 0.01	4.84	–21	190	7	19	0.6	121	48	15	8	10	0
1989 weekly 25th percentile	0.11	5.37	0	207	15	25	1.5	160	58	20	10	22	28
1989 weekly 50th percentile	0.17	5.97	11	218	19	30	1.9	175	61	25	11	40	63
1989 weekly 75th percentile	0.40	6.24	30	233	26	33	2.7	196	67	33	12	147	163
1989 weekly maximum	1.16	6.70	85	272	55	61	5.2	248	76	59	19	564	805
n for weekly statistics[c]	49	52	52	40	39	40	40	40	40	38	40	52	52

[a] Measured or estimated values.
[b] 2/1/89 through 1/31/90.
[c] Missing values for period 11/89 through 1/90.

Table 5–12. Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Roberts Run, Pennsylvania (unless specified, units are μeq/L)

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} (μg/L)	Al_{im}[a] (μg/L)
Overall minimum	< 0.01	4.59	–52	135	0	16	0.8	69	58	8	10	23	8
Overall maximum	2.81	6.51	57	310	16	50	7.4	161	110	34	29	420	301
1989 weekly minimum[b]	0.03	4.66	–30	135	1	15	1.1	72	61	10	10	26	7
1989 weekly 25th percentile	0.08	5.07	–11	170	4	22	1.8	92	68	17	15	54	54
1989 weekly 50th percentile	0.14	5.33	–2	178	6	25	2.6	99	75	19	17	93	98
1989 weekly 75th percentile	0.31	5.70	3	190	9	36	3.4	105	79	22	18	123	145
1989 weekly maximum	1.34	6.40	46	208	14	50	5.5	125	87	28	28	420	225
n for weekly statistics[c]	50	52	52	40	38	40	40	40	40	40	40	52	52

[a] Measured or estimated values.

[b] 2/1/89 through 1/31/90.

[c] Missing values for period 11/89 through 1/31/90.

Table 5-13. Overall Maximum and Minimum, and 1989 Weekly Maximum, Minimum, and Quartiles of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Stone Run, Pennsylvania (unless specified, units are μeq/L)

	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} (μg/L)	Al_{im}[a] (μg/L)
Overall minimum	< 0.01	4.53	–41	55	0	11	0.6	74	47	9	7	12	0
Overall maximum	3.39	6.26	26	243	21	74	7.2	137	155	47	29	720	496
1989 weekly minimum[b]	0.01	4.78	–26	131	0	19	0.6	77	53	12	8	12	0
1989 weekly 25th percentile	0.09	5.08	–8	162	1	25	1.1	92	62	18	11	39	33
1989 weekly 50th percentile	0.13	5.31	–5	184	2	28	2.1	96	64	21	12	104	136
1989 weekly 75th percentile	0.25	5.77	7	199	3	32	2.6	103	67	23	14	212	270
1989 weekly maximum	0.97	6.09	22	225	7	49	5.0	117	77	26	29	424	463
n for weekly statistics[c]	41	50	50	41	41	41	41	41	41	41	52	52	50

[a] Measured or estimated values.
[b] 2/1/89 through 1/31/90.
[c] Missing values for period 11/89 through 1/90.

Table 5-14. Median Values of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Streamflows ≤ 20th Percentile during the ERP[a]

Stream	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} (μg/L)	Al_{im}[b] (μg/L)
Bald Mountain Brook	0.01	6.59	65	103	30	9	3.2	111	50	54	9	125	43
Buck Creek	0.01	6.20	42	140	26	11	4.6	131	43	52	10	254	47
Fly Pond Outlet	0.01	7.22	290	109	32	28	3.0	284	90	102	14	99	21
Seventh Lake Inlet	0.02	6.19	46	132	24	11	6.2	138	49	42	9	284	59
Biscuit Brook	0.07	6.31	33	134	26	20	1.4	135	51	18	5	23	3
Black Brook	0.02	6.82	147	140	37	17	1.1	266	59	12	5	12	13
E. Branch Neversink	0.04	4.91	-9	115	14	14	2.4	62	45	16	6	157	58
High Falls Brook	0.07	6.87	147	135	26	17	1.8	246	52	16	6	15	0
Baldwin Creek	0.05	6.44	47	198	15	45	2.3	179	85	22	18	20	11
Benner Run	0.06	6.21	27	64	9	91	2.2	84	46	48	22	25	0
Linn Run	0.06	6.40	47	217	21	30	2.5	211	64	25	11	22	0
Roberts Run	0.05	6.05	15	148	6	34	2.7	114	75	24	19	41	20
Stone Run	0.02	6.02	12	132	3	25	1.3	94	54	24	13	28	10

[a] Units = μeq/L unless otherwise specified.
[b] Measured or estimated values.

Table 5-15. **Median Values of Discharge, pH, ANC, Major Ions, DOC, Al_{td}, and Al_{im} for Streamflows ≥ 95th Percentile during the ERP**[a]

Stream	Q (m^3/s)	pH	ANC	SO_4^{2-}	NO_3^-	Cl^-	DOC (mg/L)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_{td} ($\mu g/L$)	Al_{im}[b] ($\mu g/L$)
Bald Mountain Brook	0.44	4.77	-10	118	69	9	4.6	93	27	21	12	586	331
Buck Creek	0.70	4.57	-22	126	70	10	7.5	111	29	22	13	778	375
Fly Pond Outlet	0.12	6.19	46	125	56	29	6.0	173	43	49	14	367	21
Seventh Lake Inlet	1.79	4.78	-4	132	66	11	7.2	135	37	22	12	589	225
Biscuit Brook	1.90	5.38	8	115	62	15	3.6	132	48	13	8	149	70
Black Brook	0.66	6.10	50	122	50	17	3.7	181	40	10	11	115	34
E. Branch Neversink	10.53	4.50	-25	107	48	15	5.2	57	40	10	11	420	347
High Falls Brook	1.25	6.04	34	116	38	17	4.1	164	39	12	9	119	21
Baldwin Creek	0.42	5.89	8	208	17	32	2.4	160	83	19	21	52	19
Benner Run	0.85	5.23	-3	121	7	40	3.0	75	50	28	18	97	68
Linn Run	1.15	5.12	-4	210	19	23	2.4	133	53	17	11	409	387
Roberts Run	0.99	4.71	-25	189	6	22	2.9	84	67	16	17	172	196
Stone Run	0.97	4.80	-16	209	2	26	2.8	94	64	18	14	328	426

[a] Units $\mu eq/L$ unless otherwise specified.
[b] Measured or estimated values.

Table 5-16. **Number of Episodes for Which Ion Changes Contributed to ANC Depressions and Mean Rank of Ion Change Contributions (1 = most important) to ANC Depressions**

Region/Stream	No. Episodes[a]	No. Episodes Ion Changes Contributed to ANC Depressions						Mean Rank of Importance[b] of Ion Changes to ANC Depressions					
		SO_4^{2-}	NO_3^-	Cl^-	A^-	ΣC_B	Al	SO_4^{2-}	NO_3^-	Cl^-	A^-	ΣC_B	Al[c]
Adirondacks													
Bald Mountain Brook	14	10	5	9	12	14	0	2.6	2.4	3.9	2.2	1.4	–
Buck Creek	18	10	15	12	17	17	1	3.1	2.4	4.3	1.9	1.8	3.0
Fly Pond Outlet	21	18	11	8	14	21	4	2.3	2.8	3.6	2.8	1.0	4.0
Seventh Lake Inlet	18	9	13	8	16	17	0	2.3	2.3	3.9	1.8	2.0	–
Catskills													
Biscuit Brook	23	1	20	5	21	18	0	3.0	1.5	3.4	2.3	1.7	–
Black Brook	11	4	9	4	9	11	0	3.2	2.2	3.5	2.6	1.1	–
East Br. Neversink River	20	7	20	9	19	15	0	3.4	2.2	3.4	1.9	1.8	–
High Falls Brook	25	5	13	7	22	23	2	2.0	1.9	3.4	2.4	1.2	3.5
Pennsylvania													
Baldwin Creek	13	8	7	6	5	7	3	1.1	2.4	3.0	2.6	1.3	2.3
Benner Run	21	19	4	3	13	10	2	1.1	3.0	2.0	2.3	1.9	3.0
Linn Run	25	15	12	7	17	24	1	2.3	3.2	3.0	2.8	1.1	2.0
Roberts Run	24	10	10	7	20	21	3	2.1	2.8	3.1	2.2	1.1	3.0
Stone Run	23	20	11	11	19	11	2	1.5	3.3	3.4	2.6	1.5	3.5

[a] With enough ion measurements to perform analysis.

[b] Mean rank for episodes in which ion changes made contributions to ANC depressions.

[c] – = no episodes measured in which Al ion changes contributed to ANC depressions.

Table 5-17. Rank (1 = most important) of Ion Changes Contributing to ANC Depressions During Episodes with Lowest Minimum ANC Values in Adirondack Streams

Stream	Start Date[a]	Hydrologic Stimulus[b]	ANC Minimum (μeq/L)	Rank of Ion Changes Contributing to Episodic ANC Depressions			
				1	2	3	4[c]
Bald Mountain Brook	3/12/90	Snowmelt	-21	ΣC_B	NO_3^-	A^-	—
	3/27/89	Snowmelt	-20	ΣC_B	A^-	NO3$^-$	Cl^-
	5/16/90	Rain	-13	ΣC_B	A^-	—	—
	9/20/89	Rain	-13	ΣC_B	SO_4^{2-}	A^-	—
	11/16/89	Rain	-6	ΣC_B	A^-	Cl^-	—
Buck Creek	11/16/89	Rain	-30	A^-	NO_3^-	ΣC_B	Cl^-
	3/12/90	Snowmelt	-29	NO_3^-	ΣC_B	A^-	—
	4/1/90	Snowmelt	-28	ΣC_B	A^-	NO_3^-	Cl^-
	5/16/90	Rain	-26	A^-	ΣC_B	NO_3^-	—
	4/3/89	Snowmelt	-25	ΣC_B	A^-	Al	Cl^-
Fly Pond Outlet	3/27/89	Snowmelt	17	ΣC_B	NO_3^-	A^-	—
	3/12/90	Snowmelt	19	ΣC_B	A^-	NO_3^-	—
	4/10/90	Snowmelt	25	ΣC_B	A^-	SO_4^{2-}	—
	4/4/89	Snowmelt	31	ΣC_B	SO_4^{2-}	NO_3^-/A^-	
	4/3/90	Snowmelt	39	ΣC_B	SO_4^{2-}	NO_3^-/A^-	
Seventh Lake Inlet	3/12/90	Snowmelt	-20	ΣC_B	NO_3^-	A^-	—
	3/27/89	Snowmelt	-18	ΣC_B	A^-	NO_3^-	—
	11/16/89	Rain	-9	A^-	NO_3^-	ΣC_B	—
	5/16/90	Rain	-9	A^-	ΣC_B	NO_3^-	—
	5/6/89	Rain	-8	A^-	ΣC_B	NO_3^-	Cl^-

[a] Episodes with incomplete ion chemistry not included in analysis.

[b] Snowmelt includes rain-on-snow events.

[c] — = no ion change that contributed to ANC depression.

Table 5-18. Rank (1 = most important) of Ion Changes Contributing to ANC Depressions During Episodes with Lowest Minimum ANC Values in Catskill Streams

Stream	Start Date[a]	Hydrologic Stimulus[b]	ANC Minimum (μeq/L)	Rank of Ion Changes Contributing to Episodic ANC Depressions			
				1	2	3	4[c]
Biscuit Brook	4/10/90	Rain	-6	NO_3^-	ΣC_B	A^-	—
	5/5/89	Rain	-2	ΣC_B	NO_3^-	A^-	—
	1/25/90	Snowmelt	-2	NO_3^-	A^-	ΣC_B	—
	9/19/89	Rain	-2	A^-	NO_3^-	ΣC_B	—
	3/12/90	Rain	-2	NO_3^-	A^-	—	—
Black Brook	10/17/89	Rain	17	ΣC_B	NO_3^-	A^-	—
	5/5/89	Rain	18	ΣC_B	NO_3^-	A^-	—
	4/10/90	Rain	25	ΣC_B	NO_3^-	A^-	—
	9/18/89	Rain	36	ΣC_B	A^-	NO_3^-	—
	11/16/89	Rain	36	ΣC_B	NO_3^-	A^-	—
East Branch Neversink River	10/18/89	Rain	-45	A^-	ΣC_B	NO_3^-	—
	9/19/89	Rain	-39	A^-	ΣC_B	SO_4^{2-}	NO_3^-
	4/10/90	Rain	-37	NO_3^-	ΣC_B	A^-	—
	1/25/90	Snowmelt	-34	NO_3^-	A^-	ΣC_B	—
	10/31/89	Rain	-32	A^-	ΣC_B	NO_3^-	SO_4^{2-}
High Falls Brook	5/5/89	Rain	12	ΣC_B	NO_3^-	A^-	—
	10/19/89	Rain	21	ΣC_B	NO_3^-	A^-	—
	1/25/90	Snowmelt	25	NO_3^-	ΣC_B	A^-	—
	2/22/90	Rain	27	ΣC_B	NO_3^-	A^-	—
	4/10/90	Rain	28	ΣC_B	NO_3^-	A^-	—

[a] Episodes with incomplete ion chemistry not included in analysis.

[b] Snowmelt includes rain-on-snow events.

[c] — = no ion change that contributed to ANC depression.

Table 5-19. Rank (1 = most important) of Ion Changes Contributing to ANC Depressions During Episodes with Lowest Minimum ANC Values in Pennsylvania Streams

Stream	Start Date[a]	Hydrologic Stimulus	ANC Minimum (μeq/L)	Rank of Ion Changes Contributing to Episodic ANC Depressions			
				1	2	3	4[b]
Baldwin Creek	3/30/89	Rain	-1	ΣC_B	Cl^-	—	—
	5/6/89	Rain	4	ΣC_B	NO_3^-	Cl^-	—
	6/20/89	Rain	4	A^-	NO_3^-	Cl^-	—
	3/24/89	Rain	5	SO_4^{2-}	Al	Cl^-	—
	2/15/89	Rain	6	ΣC_B	SO_4^{2-}	—	—
Benner Run	11/16/89	Rain	-15	SO_4^{2-}	A^-	—	—
	5/14/89	Rain	-10	SO_4^{2-}	A^-	—	—
	5/9/89	Rain	-9	SO_4^{2-}	ΣC_B	A^-	—
	2/2/90	Rain	-6	ΣC_B	SO_4^{2-}	—	—
	2/15/90	Rain	-5	SO_4^{2-}	A^-	ΣC_B	—
Linn Run	3/4/89	Rain	-17	ΣC_B	NO_3^-	SO_4^{2-}	A^-
	4/17/89	Rain	-15	ΣC_B	—	—	—
	11/16/89	Rain	-13	ΣC_B	NO_3^-	A^-	Cl^-
	2/14/89	Rain	-11	ΣC_B	SO_4^{2-}	NO_3^-	—
	4/1/90	Rain	-10	SO_4^{2-}	ΣC_B	A^-	NO_3^-
Roberts Run	6/20/89	Rain	-52	ΣC_B	A^-	—	—
	6/3/89	Rain	-45	ΣC_B	SO_4^{2-}	A^-	Cl^-
	6/25/89	Rain	-39	ΣC_B	A^-	NO_3^-	—
	2/2/90	Rain	-33	ΣC_B	A^-	Al	—
	3/29/89	Rain	-28	ΣC_B	A^-	—	—
Stone Run	6/3/89	Rain	-41	SO_4^{2-}	ΣC_B	A^-	—
	1/16/90	Rain	-38	SO_4^{2-}	ΣC_B	A^-	—
	2/2/90	Rain	-33	A^-	SO_4^{2-}	—	—
	2/15/90	Rain	-31	SO_4^{2-}	ΣC_B	NO_3^-	—
	4/10/90	Rain	-25	ΣC_B	SO_4^{2-}	—	—

[a] Episodes with incomplete ion chemistry not included in analysis.

[b] — = no ion change that contributed to ANC depression.

SECTION 6
EFFECTS ON FISH

In Section 6, we describe results from studies of the effects of stream chemistry and episodic acidification on fish. Section 6.1 presents results from *in situ* bioassays, which measure direct toxic effects on individual fish. Section 6.2 discusses fish movements in response to stream chemistry, based on radiotelemetry tracking of individual fish locations and fish traps that monitored upstream and downstream fish movements. Section 6.3 analyzes results from surveys of fish community composition and brook trout abundance in relation to stream chemistry. Summary conclusions regarding the effects of episodic acidification on fish populations in ERP streams are presented in Section 7.

6.1 DIRECT TOXICITY

In situ bioassays were conducted each fall and spring (fall 1988, spring 1989, fall 1989, spring 1990) during periods when major events and episodic acidification were expected to occur. Tables 6-1[1] through 6-6 summarize fish mortality and chemical conditions during each experiment. Figures 6-1[1] through 6-3 illustrate cumulative changes in fish mortality and changes in stream chemistry through time during three example bioassay periods. As discussed in Section 4.4.1, analyses of bioassay results focus on the cumulative percent mortality at the end of 20 days.

In situ bioassays measure the toxic effects of stream chemistry during the bioassay period. They also serve as indicators of the relative toxicity of ERP study streams. As expected, median fish mortality was significantly ($p < 0.05$) lower in reference streams (Fly Pond Outlet, Black Brook, High Falls Brook, Benner Run, and Baldwin Creek) than in nonreference streams (Table 6-7; Figure 6-4). Mortality after 20 days never exceeded 20% in reference streams, but ranged between 0 and 100% in nonreference streams. In general, higher levels of mortality occurred in streams with more severe chemical characteristics, as described in Section 5.2.1. For example, maximum levels of brook trout mortality measured during ERP bioassays were > 80% in Buck Creek, East Branch Neversink River, Stone Run, and Linn Run; between 40% and 50% in Bald Mountain Brook and Roberts Run; and 20% to 30% in Seventh Lake Inlet and Biscuit Brook (Tables 6-1 to 6-3). In most streams, bioassay periods did not coincide with the most severe

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[1] Since this section contains so many tables and figures, we have placed them all at the end of the section. Figures appear first, beginning on page 200, then tables, beginning on page 261.

chemical conditions (lowest pH, highest Al_{im}; see Figures 5-1 to 5-13); thus, the maximum mortality levels recorded are a conservative estimate of maximum stream toxicity. In every stream, low levels of mortality (≤ 10%) occurred during at least some bioassays, indicating that chemical conditions were not toxic throughout the year.

We analyzed the bioassay results to determine the specific chemical conditions associated with high levels of fish mortality. Three issues were addressed: (1) the association between fish mortality and a simple classification of stream chemistry based on ANC, (2) the chemical variables most closely correlated with levels of fish mortality, and (3) the influence of exposure magnitude and duration on fish mortality.

Bioassay periods were classified according to ANC as nonacidic (ANC always > 0 μeq/L), chronically acidic (ANC always ≤ 0 μeq/L), and acidic episode (initial ANC > 0 μeq/L with at least two consecutive values < 0 μeq/L during the 20-day period). Fish exposed to acidic episodes experienced significantly ($p < 0.10$) higher mortality than did fish in nonacidic bioassays; mortality levels were similar (not significantly different) in bioassays with acidic episodes versus those in the chronically acidic class (Table 6-8; Figure 6-5). Results were consistent across all fish species, and for common pool fish as well as common pool and resident fish combined.

What chemical variables appear most important in controlling the level of fish mortality? We examined three: pH, Al_{im}, and various forms of the acidic stress index (ASI), an integrated index that combines pH, Al_{im}, and Ca. The ASI was developed by J. Baker et al. (1990a) from laboratory bioassay data; it is equivalent to the expected fish mortality (percent) caused by exposure to constant levels of a given pH, Al_{im}, and Ca combination in a controlled laboratory environment (see Section 2.4.2). Three different forms of the ASI were evaluated:

1. ASI_t, based on a laboratory bioassay with brook trout swim-up fry.
2. ASI_s, based on a laboratory bioassay with rainbow trout swim-up fry.
3. $ASI_{t\text{-}ad}$, based on a laboratory bioassay with adult brook trout.

Equations for calculating these indices are presented in Table 6-9. Equation forms and coefficients were estimated using regression analysis by J. Baker et al. (1990a). Observe that $ASI_{t\text{-}ad}$ is calculated from Al_{im} alone; neither pH nor Ca were statistically significant ($p \leq 0.05$).

Simple summary statistics were calculated for each chemical variable for each bioassay period: time-weighted median values for pH, Al_{im}, and each ASI; minimum pH; and maximum values for

Al_{im} and each ASI. Both median Al_{im} and $\log_{10}$[median Al_{im}] were considered. In addition, separate analyses were conducted for the observed percent mortality and an adjusted mortality, corrected for background mortality using Abbott's formula (Ashton, 1972; Hewlett and Plackett, 1979):

$$Q = (Q' - C)/(1 - C) \qquad (6\text{-}1)$$

where Q = the adjusted percent fish mortality (i.e., the percentage of fish expected to die during the bioassay if no other sources of mortality were operating besides the acidification-related chemical stress).

Q′ = the observed percent mortality.

C = the "control" mortality in the absence of toxicant stress.

Because the ERP bioassays included no true control, C was defined as the minimum observed mortality in a given bioassay set (i.e., bioassays initiated at approximately the same time, with the same species and fish source, and in a given region).

The association between fish mortality and each chemical variable was evaluated using bivariate plots (e.g., Figures 6-6 to 6-14) and regression analysis (ordinary least squares regression and maximum likelihood logistic regression). All plots indicated a relatively high level of scatter. However, overall, median Al_{im} (untransformed) was the best predictor of fish mortality. The logistic model of fish mortality as a function of median Al_{im} had the highest regression coefficient (r^2) for brook trout and blacknose dace and second highest r^2 for sculpin (Table 6-10). For sculpin, $ASI_{t\text{-}ad}$, calculated from Al_{im} (see Table 6-9), provided a slightly better fit ($r^2 = 0.63$) than median Al_{im} ($r^2 = 0.61$). Adjustments for background mortality resulted in only minor model improvement (see Table 6-10). Based on these results, subsequent analyses focused on more complex expressions of fish exposure to Al_{im} and used only observed (unadjusted) fish mortality.

Previous studies, reviewed in Section 2.4.2, suggest that both exposure magnitude (concentration) and duration (days of exposure) are important characteristics that influence the severity of effects of episodes on fish. Higher median concentrations of Al_{im} were associated with higher fish mortality in ERP bioassays, as demonstrated by the plots and regression analyses just discussed (Figures 6-6, 6-11, and 6-13; Table 6-10). In addition, fish exposed for longer periods of time to a given Al_{im} concentration generally had higher mortality rates (Figures 6-15 and 6-16). However, any given bioassay can be characterized by a continuum of concentration-duration combinations, as illustrated in Figures 6-17 to 6-22, and it is difficult to distinguish what specific concentration or duration results in increased fish mortality. Furthermore, patterns of chemical conditions during bioassays with high mortality were highly variable (Figure 6-23).

We examined five alternative expressions of aluminum exposure:

1. Time-weighted median Al_{im} concentration.
2. Maximum Al_{im} concentration.
3. The total duration of time (days) during the bioassay when Al_{im} concentrations exceeded three different threshold concentrations: 100, 200, and 300 μg/L (TDUR100, TDUR200, TDUR300).
4. The maximum sustained period of time when Al_{im} levels exceeded the three threshold concentrations (> 100, 200, and 300 μg/L) (MDUR100, MDUR200, MDUR300).
5. An integrated function of concentration and duration (INT), essentially the area or integral under the curves in Figure 6-23 above each threshold Al_{im} concentration (100, 200, and 300 μg/L). Because of the wide range of values for this integrated concentration-duration function, values were $\log_{10}$ transformed (LINT100, LINT200, LINT300). Analyses for blacknose dace also considered the entire area under the curve (Al_{im} > 0 μg/L, LINT0).

All calculations of exposure were based on linear interpolations between measured or estimated Al_{im} levels in water chemistry samples, as described in Section 4.4.1.

Multivariate logistic regression analyses were used to identify which of these expressions of chemical exposure were important predictors of fish mortality. Median and minimum pH and median Ca and DOC were included as additional independent variables. Laboratory bioassays have shown that high levels of Ca and DOC can reduce the toxicity of Al_{im} (Brown, 1983; Peterson et al., 1989). The toxic effects of low pH may contribute to fish mortality; also Al_{im} toxicity varies with pH (Fivelstad and Leivestad, 1984; Clark and LaZerte, 1985; Sadler and Lynam, 1987). Comparisons among alternative models were based on the deviance statistic for logistic regression [–2(log likelihood function); Agresti, 1990], the variance of the residuals (predicted minus observed mortality), a logistic-regression analog for r^2 (Agresti, 1990) equivalent to the proportion of the variation in mortality explained by the model, and results from stepwise regression analyses (SAS Institute, 1989). Analyses were conducted for common pool brook trout bioassays (all three regions combined), blacknose dace (Adirondacks only), and sculpin (slimy and mottled sculpin combined in both Catskill and Pennsylvania streams). Region was included as an independent variable for brook trout and sculpin analyses, to determine whether mortality-chemistry relationships varied among the ERP regions. Sculpin analyses included a species variable to distinguish between slimy and mottled sculpin.

For brook trout, stepwise regression selected large numbers of variables (> 10) as statistically significant ($p < 0.05$) predictors of mortality. However, models with more than 3–5 variables were highly unstable, that is, different sets of predictor variables yielded models with very similar statistics (deviance, variance of residuals, and r^2). The best 1-variable model predicted brook trout mortality as a function of median Al_{im}, with a model r^2 value of 0.59 (Table 6-11; Figure 6-24). The best 3-variable model predicted mortality as a function of median Al_{im}, minimum pH, and median Ca, with $r^2 = 0.72$ (Table 6-12). The best 5-variable model predicted mortality as a function of median Al_{im}, minimum pH, median Ca, median DOC, and a Catskill regional variable (indicating lower mortality in Catskill bioassays than in Adirondack or Pennsylvania bioassays at a given combination of Al_{im}, pH, Ca, and DOC levels), with $r^2 = 0.79$ (Table 6-13). As an alternative to logistic regression, we also conducted a stepwise, weighted ordinary least squares regression, using the logit transformation of percent mortality and weighted by the inverse of the variance of the logit-transformed mortality (McCullagh and Nelder, 1989). A 3-variable model was selected, predicting mortality as a function of median Al_{im}, minimum pH, and median Ca, with parameter estimates similar to those in the 3-variable logistic regression model (Table 6-14).

Observe that none of the Al_{im} duration variables (TDUR and MDUR) or integrated concentration-duration variables (LINT) were selected as significant predictors of brook trout mortality except in higher order models (> 5 predictor variables). Also, as expected, Al_{im} is positively associated with brook trout mortality (higher mortality at higher Al_{im}) and Ca is negatively associated (lower mortality with higher Ca). However, somewhat unexpectedly, pH is positively associated with mortality (higher mortality with higher pH, for given levels of Al_{im} and Ca), suggesting that the primary influence of pH on brook trout is as a modifier of Al_{im} toxicity, rather than a direct contributor to toxic effects (at least within the range of conditions that occurred within ERP bioassays).

For blacknose dace, stepwise logistic regression selected only a single-variable model, predicting percent mortality as a function of the integrated function of Al concentration and duration for Al_{im} concentrations > 200 μg/L ($r^2 = 0.97$; Table 6-15; Figure 6-25). No other variables were significant at $p < 0.05$ after LINT200. Based on the criterion of minimum deviance, the LINT200 variable provided a distinctly better model fit than any other single-variable model or any multiple-variable model relying solely on simple summary statistics such as median or minimum/maximum inorganic Al or pH.

For sculpin, stepwise regression selected a 4-variable model predicting sculpin mortality as a function of median Al_{im}, a regional variable (distinguishing between Catskill and Pennsylvania bioassays), a species variable (distinguishing between slimy and mottled sculpin), and an Al_{im} duration variable, TDUR300, the total duration of time with Al_{im} > 300 μg/L. However, the model improvement gained by adding variables 3 and 4 (species and TDUR300) was relatively small; model r^2 values are 0.80, 0.81, and 0.83 for the best 2-, 3-, and 4-variable models, respectively. Thus, as for brook trout, variables that explicitly account for exposure duration (TDUR, MDUR, and LINT) were relatively poor predictors of sculpin mortality in ERP bioassays. Median Al_{im} was the single best predictor (r^2 = 0.61), although mortality levels were substantially higher in Pennsylvania bioassays than in Catskill bioassays at a given median Al_{im} concentration (Figures 6-26 and 6-27). Table 6-16 provides parameter estimates and model statistics for the 2-variable model, predicting sculpin mortality as a function of median Al_{im} and region.

Simonin et al. (1993) conducted similar multivariate regression analyses using ERP *in situ* bioassay data for the Adirondacks, although with some differences in specific predictor variables considered. Brook trout mortality was best correlated with a 2-variable model that included DOC and a concentration-duration variable for Al_{im} (median Al_{im} during the episode times the duration of the episode). The best overall model for blacknose dace included only one variable, median Al_{im}. They also suggested that the time to initiation of an episode was important. Bioassay fish that had been in streams 15–24 days before the occurrence of an episode survived better than fish exposed to an episode soon after the start of a bioassay. Longer times prior to episodic acidification may allow fish to recover from handling stress and acclimate to stream chemistry.

What chemical variables and exposure characteristics are most important in controlling the effects of episodes on fish mortality? The ERP database is unique—fish bioassays were conducted in a relatively large number of streams (n = 13) during multiple seasons in combination with intensive chemical monitoring. However, despite the quality of the database, our ability to address this question is still limited. Episode chemistry is highly variable and difficult to characterize. Furthermore, many of the key features (pH, Al, episode magnitude, and duration) are highly correlated in the field, making it difficult to distinguish effects of individual factors. Controlled experiments are needed to better delineate the relative importance of episode magnitude, duration, total exposure (concentration times dose), timing of exposure, and each chemical variable and their interactive effects. However, analysis of the ERP database has demonstrated the following:

- Chemical conditions toxic to fish occurred at some time during the study in all ERP streams except the five reference streams (Fly Pond Outlet, Black Brook, High Falls Brook, Benner Run, and Baldwin Creek). Maximum observed mortality rates were generally highest in those streams with the most severe chemical conditions: > 80% in Buck Creek, East Branch Neversink River, Stone Run, and Linn Run; between 40% and 50% in Bald Mountain Brook and Roberts Run; and 20% to 30% in Seventh Lake Inlet and Biscuit Brook (Tables 6-1 to 6-3).

- All streams also had some bioassays with low mortality (< 10%), suggesting that toxic conditions do not occur throughout the year.

- Episodic acidification can be toxic to fish. Mortality rates were significantly higher during bioassays with acidic episodes than in bioassays with ANC > 0, but similar (not significantly different) in chronically acidic bioassays (ANC ≤ 0 throughout the bioassay) and bioassays with acidic episodes (Figure 6-5).

- Inorganic Al was the most important chemical variable for predicting fish mortality. Ca, pH, and DOC were also important predictors of brook trout mortality (Tables 6-13 and 6-14).

- Fish exposed for longer periods to high Al_{im} had higher mortality rates (Figures 6-15 and 6-16). However, somewhat surprisingly, a simple summary statistic, time-weighted median Al_{im}, usually provided as good or better predictions of fish mortality than did more complex expressions of chemical exposure incorporating peak levels as well as duration. For brook trout and sculpin, median Al_{im} was the best single-variable predictor of mortality (Tables 6-11 and 6-16).

- Mortality of blacknose dace was predicted best by an integrated function of duration and Al_{im} concentrations > 200 μg/L. High mortality (≥ 50%) is predicted to occur at LINT > about 2.0 (Figure 6-25), equivalent to an Al_{im} concentration of 300 μg/L for one day or 250 μg/L for two days.

- Based on their toxic responses to Al_{im}, the relative sensitivity of the fish species tested in ERP bioassays, from most to least sensitive, is blacknose dace > brook trout ≥ mottled and slimy sculpins. Median Al_{im} levels predicted to cause 50% mortality in *in situ* bioassays are about 120 μg/L for blacknose dace, 200 μg/L for brook trout, 200 μg/L for sculpin in Pennsylvania streams, and 300 μg/L for sculpin in Catskill streams.

- For both brook trout and sculpin, relationships between mortality and stream chemistry were significantly different among ERP regions. (Blacknose dace bioassays were conducted in only one region, the Adirondacks.) Reasons for inter-regional differences are not known, but could include differences in the sensitivity of fish strains, the acclimation of native fish to low ionic strength and acidic conditions, stream chemistry not accounted for in our analyses, or experimental protocols.

6.2 FISH MOVEMENT

Chemical conditions within low-order, softwater stream systems, such as the ERP study sites, can be quite variable spatially. ANC and pH levels often increase gradually as waters flow down a drainage system (e.g., Driscoll et al., 1987b; Kaufmann et al., 1988). Even within a given stream reach, groundwater inflows and tributaries may provide microhabitats with chemistry distinctly different, often more alkaline, than the main stream. If fish move into such areas during episodes, the chemistry measured at the ERP continuous monitoring site may be a poor index of the chemical conditions to which free-ranging fish are actually exposed.

The locations of individual brook trout were tracked using radiotelemetry (Section 4.4.2.1) to determine whether fish respond to episodic acidification by moving downstream or into more alkaline microhabitats. In selected streams in the Adirondacks, fish traps were also used to monitor up- and downstream fish movements in relation to stream chemistry (Section 4.4.2.2). This section summarizes results from these studies as analyzed by and presented in Gagen (1991) for Pennsylvania [also, Carline et al. (1992) and DeWalle et al. (1991)], by Murdoch et al. (1991) for the Catskills, and by D. Bath [Adirondack Lake Survey Corporation (ALSC), Ray Brook, New York, 1992, pers. comm.] for the Adirondacks [also Kretser et al. (1991)]. The objective was to evaluate how fish behavior influenced the effects of episodic acidification on fish populations in the ERP study streams.

A net downstream movement of radio-tagged brook trout occurred in all streams and study periods that experienced stressful chemical conditions (Table 6-17), but little to no net downstream movement occurred in streams with relatively high pH (> 5.1–5.2) and low Al_{im} (< 150–160 μg/L) throughout the study period (Table 6-18). Downstream fish movement either was associated with chronically acidic conditions at the start of the experiment (pH < 5.2 and/or Al_{im} > 150–200 μg/L) or coincided with the occurrence of one or more major episodes (Al_{im} > 160 μg/L for 1.5 or more days; see Table 6-17). Minor episodes (such as in Stone Run, fall 1989, with a maximum Al_{im} of 156 μg/L) caused no discernible net downstream movement (Table 6-18).

Telemetry studies were generally conducted concurrently with one or more *in situ* bioassays (see Section 6.1). All study periods in which bioassays indicated high levels of brook trout mortality (≥ 50%) had significant net downstream movement of radio-tagged brook trout (Buck Creek, spring 1990; East Branch Neversink, spring 1989; Linn Run, spring 1989; and Stone Run, spring 1990; Table 6-17). However, net downstream movement also occurred when bioassays indicated nontoxic conditions (3–10% mortality; Bald Mountain Brook and Buck Creek, fall 1989; Linn Run 1988; Table 6-17). Thus, brook trout appear to exhibit behavioral responses even when exposed to sublethal pH and Al levels. Study periods with no net downstream movement also had relatively low mortality rates as indicated by bioassays (0–23%; Table 6-18).

Results from the fish traps in Bald Mountain Brook and Fly Pond Outlet (Adirondacks) were not as clear, however. No brook trout were caught in the traps at pH ≤ 5.0, moving up- or downstream (Tables 6-19 and 6-20). Furthermore, the largest monthly downstream movement of trout was recorded in May 1989 in Fly Pond Outlet at pH > 6.0, presumably as a result of the brook trout stocking that occurred in April 1989 as part of the fish transplant experiments (see Table 4-17). Fifty percent of the trout caught in the trap in May had been transplanted into Fly Pond Outlet in April. At pH > 5.0, brook trout were caught moving both up- and downstream, although more than twice as many fish moved downstream as upstream. Likewise, most (95%) blacknose dace caught in the traps were moving downstream (Table 6-19). The largest monthly downstream movement of dace occurred in Bald Mountain Brook in May 1989, following stocking of dace in April and coincident with an early May episode that lasted 15 days.

Gagen (1991) conducted a detailed analysis of individual fish responses and chemical exposures during radiotelemetry studies in Linn Run (spring 1989) and Stone Run (spring 1990), Pennsylvania. Both study periods had significant net downstream fish movement (Figures 6-28 and 6-29) and high levels of fish mortality in bioassays (91–93%); also, one-third of the radio-tagged fish in each stream were recovered dead during the study period. In contrast, no radio-tagged fish were recovered dead in other radiotelemetry studies in Pennsylvania and mortality rates in coincident bioassays were relatively low (0–23%).

In Linn Run, spring 1989, total dissolved aluminum (Al_{td}) levels at the start of the study were relatively low (Al_{td} < 100 μg/L) but major episodes, with Al_{td} ≥ 350 μg/L at the continuous monitoring station (CMS), occurred on days 3–5, 12–15, 18–20, 22–24, and 26–29 (Figure 6-28). By day 4, one day after the onset of the first episode, radio-tagged fish occurred in locations with Al_{td} levels 100–200 μg/L less than at the CMS, although most fish remained within 200 m of the CMS and were still exposed to relatively high Al levels (Al_{td} > 200 μg/L; Figures 6-30 and 6-31). Two fish were recovered dead on day 6. By day 11, before the second major episode, 3 of 12 radio-tagged trout had moved 500–700 m downstream into an area where ANC was higher relative to the mainstream. During the episode on day 12, three fish appeared in areas with relatively low Al_{td} (≤ 100 μg/L), whereas the remaining fish were exposed to Al_{td} > 300 μg/L (Figure 6-31).

One of the fish that avoided exposure to high Al had moved into an alkaline microhabitat within 200 m of the continuous monitoring site; another had moved almost 1,600 m downstream. Two fish were recovered dead on day 12 and another on day 15, for a total of 5 dead fish out of the 15 released. In general, fish recovered dead were those exposed to high Al_{td} levels during episodes (Figure 6-32); fish that survived avoided exposure to peak Al levels (e.g., Figure 6-33).

No major episodes occurred during the spring 1990 telemetry study in Stone Run, but Al levels remained relatively high throughout most of the study period (Al_{td} 100–300 μg/L, Figure 6-29; median Al_{im} 218 μg/L, Table 6-17). Fish were released at sites with ANC and Al_{td} levels similar to those at the CMS (Al_{td} about 150 μg/L). Two days after the release, many of the fish had moved to areas with slightly lower Al_{td} (60–100 μg/L), at sites near the CMS (< 50 m downstream), to almost 400 m downstream (Figure 6-34). Stream chemistry remained relatively stable through day 8. By this time, 9 of 10 fish had moved 400 m or more downstream and 5 of these fish were in areas with Al_{td} < 50 μg/L. Three of the 10 fish released were recovered dead during the study period: 2 on day 10 and 1 on day 16.

Murdoch et al. (1991) analyzed results from the spring 1989 telemetry study in the East Branch of the Neversink River and High Falls Brook in the Catskills. Significant net downstream movement occurred in East Branch Neversink, associated with chronically low pH (< 5.0) and elevated Al levels (Al_{td} 250–300 μg/L, Al_{im} 157–284 μg/L), while brook trout in well-buffered High Falls Brook (pH > 6.0, Al_{td} < 100 μg/L) exhibited a small net upstream movement (Figure 6-35). Water samples collected at fish locations in High Falls Brook indicated relatively uniform chemical quality, similar to that at the CMS. No significant springs or tributaries enter High Falls Brook between the confluence of the stream with the West Branch of the Neversink and the waterfall 1 km above the CMS. The study area within the East Branch of the Neversink River, on the other hand, contains several springs and tributaries with higher pH and ANC than the main channel (Figure 6-36). Radio-tagged fish were released near the confluence of one such spring (pH 6.2) and two fish remained at that junction throughout the study, in a pool with relatively high pH. Likewise, in the fall 1989 telemetry study (also in the East Branch of the Neversink), several radio-tagged fish moved into tributaries with higher pH than the main channel (Murdoch et al., 1991).

In the Adirondacks, significant net downstream movement (> 100 m) occurred in Buck Creek in fall 1989 and spring 1990 associated with low pH (median values 5.2 and 4.8) and elevated Al_{im} levels (median values 187 and 308 μg/L; Table 6-17). Fish began moving downstream within three days of the start of the study in fall 1989; by day 16, all but two brook trout had migrated downstream into Seventh Lake (pH > 6.0; D. Bath, ALSC, pers. comm.). The two fish that remained in Buck Creek appeared at the mouth of a small tributary. When pH levels in Buck Creek increased to > 5.0, several of the trout that had migrated to Seventh Lake moved back into the lower reaches of the creek, but remained downstream of the CMS. In spring 1990, four of six radio-tagged trout moved downstream into Seventh Lake by day 6. The remaining fish migrated into a small tributary with pH 6.2 and Al_{td} < 200 μg/L, where they remained throughout the study period.

Therefore, in each region and study, some radio-tagged fish were able to avoid exposure to the high Al and low pH measured at the CMS by moving downstream or into more alkaline micro-habitats. Aluminum levels measured at these fish locations were often substantially less than those measured at the CMS (by 100–200 μg Al_{td}/L or more). However, other fish, and in most cases the majority of radio-tagged fish, were exposed to relatively high, potentially lethal Al levels.

Two factors may limit the degree to which fish can avoid exposure to adverse chemical conditions: (1) the availability of suitable microhabitats and other "refuge areas" with higher pH and lower Al levels and (2) the ability of fish to detect and actively avoid stressful chemical conditions. The availability of suitable refuge areas is highly variable among and within stream systems, because of variations in soil and bedrock chemistry and hydrologic flowpaths (DeWalle et al., 1991). Many small headwater streams have little or no groundwater input, and as a result, few if any alkaline microhabitats. Other systems, such as the East Branch of the Neversink River, tend to be more spatially variable (see Figure 6-36). The occurrence of numerous groundwater seeps and more alkaline tributaries may be responsible, at least in part, for the maintenance of a residual trout population in the East Branch of the Neversink despite low pH and high Al levels in the stream during much of the year (see Section 6.3).

Fish movements into areas of higher pH and lower Al may result from either active or passive fish behavior. Fish may be able to detect stressful chemical conditions and actively seek out suitable refuge areas. As an alternative, fish stressed by exposure to low pH/high Al may move randomly, but then remain in areas of higher pH/lower Al that they happen upon—a passive avoidance behavior. Likewise, fish that are physiologically stressed may be less able to maintain their position in the stream and more susceptible to being carried downstream by the current, a passive behavior that would result in net downstream movement.

The ERP data are not sufficient to distinguish between active and passive fish behavior. However, Gagen (1991) hypothesized that the fish movements downstream and into alkaline microhabitats were largely passive rather than active, directed avoidance behavior. He cites two observations in support of this hypothesis. Radio-tagged fish in Linn Run and Stone Run did not take full advantage of the available microhabitats to avoid exposures to toxic chemical conditions. Also, net downstream movements resulted primarily from reduced upstream movement rather than increased downstream movement, relative to fish in reference streams. Individual fish in reference streams also moved substantial distances downstream, but these downstream movements were offset by other individuals moving upstream, with little to no change in median fish location. If fish behavioral responses are largely passive, rather than active, a lower percentage of fish would be expected to successfully locate refuge areas and avoid exposure to episodic acidification.

We should be aware that the ERP telemetry studies involved relatively large fish (170–220 mm in length; see Tables 4-15 to 4-17). Smaller fish, young-of-the-year, and especially swim-up fry are probably less mobile and may be less able to avoid adverse chemical conditions.

Behavioral avoidance may both mitigate and accentuate the effects of episodic acidification on fish populations in streams. If fish move into refuge areas during episodes and then return, fish behavioral responses would be expected to reduce the overall effect on the fish population. However, if fish move out of the stream system during episodes but do not return, or return in smaller numbers, and if fish move in response to sublethal pH/Al levels, as suggested by the bioassay-telemetry comparisons, then the population-level effects of episodic acidification would be greater than effects predicted based on mortality tests alone. Downstream fish migration may be an important mechanism of fish population loss, especially if upstream migrations are inhibited by steep gradients, waterfalls, or temporary log and debris dams.

6.3 EFFECTS ON FISH POPULATIONS

The number of fish in a stream reach at any given time reflects the dynamic balance between fish recruitment (reproduction and immigration) and fish loss (mortality and emigration). Episodic acidification can increase fish mortality and emigration, as demonstrated in Sections 6.1 and 6.2, and may also decrease fish reproduction (J. Baker et al., 1990). To what degree, therefore, does episodic acidification result in long-term declines in fish population density and biomass in streams?

All ERP study streams except the East Branch of the Neversink River had chemical conditions during low flow considered suitable for fish survival and reproduction. The median pH measured during low flow (20th percentile low flow; see Section 5.2) was 4.9 in the East Branch of the Neversink, but ranged from 6.0 to 7.2 in the other 12 ERP streams (Table 5-14). Median Al_{im} concentrations during low flow were < 60 μg/L in all streams (Table 5-14). Thus, if stream assessments were based solely on chemical measurements during low flow, we would predict that all but one of the study sites should support a diverse and healthy fish community.

However, most streams had substantially lower pH and higher Al_{im} during periods of increased discharge (Figures 5-15 and 5-16). For example, median pH values associated with the 95th percentile high flow were 4.5–4.8 in Buck Creek, Bald Mountain Brook, Seventh Lake Inlet, East Branch of the Neversink, Roberts Run, and Stone Run (Table 5-15). Median Al_{im} levels during high flow were > 300 μg/L in Buck Creek, Bald Mountain Brook, East Branch of the Neversink, Linn Run, and Stone Run. We would expect these streams to support fewer fish and fewer fish species compared to ERP streams that maintain relatively high pH and low Al_{im} during events. For example, Fly Pond Outlet, Biscuit Brook, Black Brook, High Falls Brook, Benner Run, and Baldwin Creek all had high flow median Al_{im} < 100 μg/L.

In Section 5.2.1, ERP study streams were ranked according to the overall severity of stream chemistry during the study period, from most to least severe, as follows:

1. The East Branch of the Neversink River was chronically acidic (median ANC ≤ 0) and had the most severe chemical conditions (lowest pH, highest Al_{im} for the longest duration).

2. Stone Run and Roberts Run were also chronically acidic, but pH and Al_{im} levels were not as extreme as in the East Branch of the Neversink.

3. Buck Creek and Linn Run were not chronically acidic but had severe acidic episodes, with low pH and high Al_{im} for long durations.

4. Bald Mountain Brook and Seventh Lake Inlet had episodes of moderate severity.

5. Biscuit Brook and Benner Run experienced acidic episodes but they were of short duration, and as a result, would be expected to have only minor effects on fish populations.

6. Fly Pond Outlet, Black Brook, High Falls Brook, and Baldwin Creek were classified as nonacidic (with ANC always > 0, except for one brief excursion below 0 in Baldwin Creek) and had relatively high pH and low Al_{im} throughout the study period.

We can compare fish community composition and brook trout abundance in each stream to these qualitative rankings, as well as to summary statistics of stream chemistry during high flow, to evaluate the effects of episodic acidification on fish populations.

Ten fish species were caught in ERP streams (Table 6-21). Species were classified as *acid-sensitive*, *intermediately sensitive*, or *acid-tolerant*, based on data on the effects of low pH and high Al on fish summarized by Baker and Christensen (1991). Acid-sensitive fish species (blacknose dace, slimy sculpin, or mottled sculpin) were caught in six streams: Buck Creek, Black Brook, High Falls Brook, Biscuit Brook, Benner Run, and Baldwin Creek. With the exception of Buck Creek, these streams all maintain relatively high pH (median pH > 5.2) and low Al_{im} ($\leq$ 70 μg/L) during high flow (Table 5-15) and were ranked as 5 or 6 in terms of the severity of stream chemistry. Dace caught in Buck Creek occurred only in the lower section of the stream immediately above Seventh Lake.[2] In contrast, the East Branch of the Neversink River, Stone Run, and Linn Run, three streams with severe chemical conditions during high flow (median Al_{im} > 300 μg/L; rankings 1, 2, and 3, respectively), had only a single, acid-tolerant species, brook trout. Roberts Run (ranking 2) also had only brook trout, except for a single brown trout specimen caught during the study. All other streams had two or more fish species. These results support the hypothesis that chemical conditions during high flow can eliminate acid-sensitive fish populations and alter fish community composition.

Brook trout occurred in all 13 ERP streams. However, brook trout density and biomass were lower in streams with lower pH and higher Al_{im} levels during high flow (Figures 6-37 to 6-40). Rank correlation analyses (Steel and Torrie, 1980) indicate a significant association ($p < 0.05$) between brook trout abundance and both median weekly and high flow chemistry values for both pH and Al_{im} (Table 6-22). Rank correlations with median weekly pH provided the highest correlation coefficients ($r = 0.85$ for brook trout density and 0.89 for biomass), but in general, no single variable stands out distinctly and consistently as the best predictor of brook trout density or biomass. Correlations between weekly and high flow chemistry (see Figures 5-15 and 5-16) and between pH and Al_{im} make it difficult to distinguish the relative importance of these chemical features based on observational data alone.

[2]The study reach in Buck Creek was only 100 m above Seventh Lake, a circumneutral lake with a diverse fish community (see Section 3.1.1). It is likely that many of the acid-sensitive and intermediately sensitive fish caught in Buck Creek were temporary migrants from Seventh Lake. The study reach in Seventh Lake Inlet was 700 m upstream of the lake.

Brook trout density and biomass were also significantly ($p < 0.001$) correlated with the qualitative rankings of stream chemical severity (rank correlation coefficients, $r = 0.83$ for brook trout density and 0.92 for biomass; Figure 6-41). Statistical comparisons between ranks were not possible because of the small number of streams per rank. Thus, streams were grouped as nonacidic (ranking 6; $n = 4$), episodically acidic (rankings 3–5; $n = 6$), and chronically acidic (rankings 1–2; $n = 3$). Analysis of variance and the Tukey-Kramer multiple comparison test (Miller, 1986) provided the same results. Both brook trout density and biomass were significantly ($p < 0.05$) higher in nonacidic streams than in streams that had acidic episodes or were chronically acidic. However, brook trout density and biomass were not significantly different in streams with episodic acidification compared to chronically acidic streams. Average levels of brook trout density (fish/0.1 ha) in the three groups were 215 for nonacidic streams, 82 in streams with acidic episodes, and 46 in chronically acidic streams. Likewise, average values for brook trout biomass (g/0.1 ha) were 2355 in nonacidic streams, 1256 in streams with acidic episodes, and 704 in chronically acidic streams.

No regional differences were evident in the relationships between brook trout abundance and stream chemistry (see Figures 6-37 to 6-41), although several site-specific variations deserve notice:

- Linn Run stands out as a distinct outlier in plots of brook trout abundance as a function of stream pH (median weekly and high flow pH; Figures 6-37 and 6-38). Brook trout density and biomass in Linn Run (4 fish/0.1 ha and 253 g/0.1 ha) are lower than expected given the measured median weekly pH of 5.97 and median high flow pH of 5.12. As discussed in Section 5, Linn Run has the flashiest response to storm events (Figure 5-11), experiences the greatest increase in Al_{im} during episodes, and tends to mobilize higher levels of Al_{im} at a given ANC and pH than do other ERP streams (Figure 5-22). Al_{im} concentrations > 200 μg/L commonly occur in Linn Run at pH levels ≤ 5.4, but only at pH ≤ 5.2 in Stone Run, Bald Mountain Brook, Buck Creek, and Seventh Lake Inlet, and at pH < 5.0 in Roberts Run and East Branch of the Neversink River. [No Al_{im} values > 200 μg/L were recorded for the remaining six ERP streams.] These differences in the pH-Al relationship probably account for the occurrence of Linn Run as an outlier in trout abundance-stream pH relationships. We believe that low levels of brook trout density and biomass in Linn Run result primarily from the very high concentrations of Al_{im} that occur in the stream during storm events (maximum value, 805 μg/L; Table 5-11).

- Bald Mountain Brook is an outlier on plots of brook trout abundance as a function of both high flow Al_{im} and high flow pH (Figures 6-38 and 6-40), although median weekly Al_{im} and pH levels provide reasonable predictions of trout density and biomass in the stream. Trout density and biomass in Bald Mountain Brook (159 fish/0.1 ha and 1609 g/0.1 ha) are higher than expected given median high flow values of pH 4.77 and Al_{im} 331 μg/L. Reasons for the relatively high fish abundance are uncertain, although two factors may play some role. Visual comparisons of Figures 5-1 to 5-13 suggest that chemical conditions in Bald Mountain Brook recover (i.e., return to near baseflow levels of pH and Al_{im}) more rapidly following events than in other ERP streams, such as Buck Creek, Seventh Lake Inlet, and Roberts Run. Thus, fish in Bald Mountain Brook may be exposed to adverse chemical conditions for relatively short periods of time. In addition, immediately below the ERP study site, Bald Mountain Brook merges with Fly Pond Outlet, a stream with circumneutral pH and high trout density (292 fish/0.1 ha). Fish may migrate from Fly Pond Outlet to Bald Mountain Brook, particularly during low flow periods. The potential importance of spatial variability within the drainage system is discussed further later in this section.

- Brook trout density and biomass were distinctly higher in Black Brook (309 fish/0.1 ha, 3469 g/0.01 ha) and Fly Pond Outlet (292 fish/0.01 ha, 2364 g/0.01 ha) than in other streams, such as Baldwin Creek (133 fish/0.1 ha, 1759 g/0.01 ha) and High Falls Brook (127 fish/0.01 ha, 1827 g/0.1 ha), with similar chemistry (i.e., relatively high pH and low Al_{im} even during events). Such differences may reflect the dominant influence of other habitat features on trout productivity in streams with suitable acid-base chemistry. For example, Fly Pond Outlet and Black Brook had the highest Ca levels (median weekly concentrations of 235 and 258 μeq/L, respectively) among ERP streams (compared to 66–209 μeq/L in other ERP streams; see Tables 5-1 to 5-13).

The above analyses are based on average values for trout density and biomass in each stream, calculated from fish surveys conducted in fall 1988, spring 1989, fall 1989, and spring 1990. Fish abundance varied among sampling dates (Table 6-23), although in general, the pattern of inter-stream differences in trout density and biomass were relatively consistent over time (Figures 6-42 to 6-44).

Brook trout were transplanted into ERP study reaches to establish consistent, initial levels of fish biomass in all streams, by region (see Section 4.4.4). These transplants had short-term effects (over several months) on brook trout density or biomass in some streams, but no discernible long-term effects (Figures 6-42 to 6-44). Over time, brook trout populations returned to levels observed before the transplants and were generally consistent with density and biomass levels expected given the chemical conditions in the streams.

Transplant experiments were also conducted with forage fish: blacknose dace in the Adirondacks and slimy or mottled sculpin in Catskill and Pennsylvania streams. Few to none of these fish were recovered in subsequent surveys in streams with median pH < 5.2 and $Al_{im} > 100\text{-}150$ μg/L during high flow (Buck Creek, Bald Mountain Brook, Seventh Lake Inlet, East Branch of the Neversink River, Linn Run, Stone Run, and Roberts Run), whereas larger numbers of stocked fish were caught in Fly Pond Outlet, Biscuit Brook, Baldwin Creek, and Benner Run. Sculpin are difficult to capture with electrofishing; thus, population abundance and stocking recovery rates could not be quantified. Average recovery rates for blacknose dace (percent of stocked fish caught in the next survey) were 32% in Fly Pond Outlet, 7% in Bald Mountain Brook, 2% in

Seventh Lake Inlet, and 0 in Buck Creek (see Figure 6-45). Large numbers of blacknose dace remained only in Fly Pond Outlet (median high flow pH 6.2, Al_{im} 20 μg/L). Chemical conditions in Bald Mountain Brook, Seventh Lake Inlet, and Buck Creek resulted in high and rapid rates of dace loss, through fish mortality and/or emigration. Of the dace stocked into Bald Mountain Brook, 25–35% were captured in downstream fish traps (Section 6.2). These results support the conclusion that low pH and elevated Al_{im} during high flow can eliminate acid-sensitive fish populations.

Many investigators have concluded that fish early life stages and reproduction are critical periods for fish populations in acidified lakes and streams (J. Baker et al., 1990a). Detailed studies of effects on reproduction were not conducted as part of the ERP. However, the occurrence of young-of-the-year fish in field surveys is indicative of reproductive success (during the period of study). No young-of-the-year brook trout were caught in any survey in Buck Creek, Seventh Lake Inlet, East Branch of the Neversink River, or Linn Run—all streams with low pH and/or high Al_{im} during high flow. Small numbers of young-of-the-year trout were caught in fall 1989 in Bald Mountain Brook, but none in fall 1988 or spring 1989, 1990, and 1991. Young-of-the-year trout were abundant in Fly Pond Outlet, Black Brook, High Falls Brook, Biscuit Brook, Benner Run, and Baldwin Run. Numbers of young-of-the-year caught in Stone Run and Roberts Run varied among sampling years (Figure 6-46). Gagen (1991) concluded that year-to-year variations in reproductive success in Stone Run and Roberts Run resulted from annual variations in precipitation and associated variations in episode severity during spring, when brook trout fry emerge from the gravel. A strong year class occurred in 1988, coincident with below normal precipitation during winter and spring 1988, whereas higher than normal precipitation in winter/spring 1989 resulted in more severe episodes, decreased reproductive success, and a small year class.

Associations between stream chemistry and the occurrence of young-of-the-year fish, as well as fish community composition, were confirmed in longitudinal profiles of fish distribution and stream chemistry in Catskill and Pennsylvania ERP streams (Figures 6-47 to 6-53).[3] Young-of-the-year trout and acid-sensitive fish species were caught only in stream sections and tributaries with pH > 5.5-6.0 at the time of the survey. For example, the East Branch of the Neversink River supports a sparse population of brook trout but no young-of-the-year trout or sculpin. Deer Shanty Brook (pH 4.9), a tributary to the East Branch of the Neversink River, has an unnamed tributary with a

[3]Adirondack ERP streams were relatively short, most with lakes or barriers to fish movement not very far upstream or downstream from the ERP study reach (see Section 3.1.1). For this reason, we have not presented longitudinal profiles for Adirondack streams.

high pH (6.3) that supports a moderate population of adult and juvenile brook trout as well as slimy sculpin (Figure 6-47). This isolated population of sculpin is of particular interest because the nearest known source of sculpin is Flat Brook, a tributary to the East Branch of the Neversink nearly 3 km downstream from the gauging station (Murdoch et al., 1991). Gagen (1991) conducted a detailed study of several tributaries to Linn Run. Grove Run, E-Run, and Cabin Run had total dissolved Al_{td} concentrations < 20 μg/L and pH > 6.2 during a 4-day episode in April 1987, whereas Al_{td} levels peaked at 425 and 525 μg/L at two sites in Linn Run (Figure 6-48). All three tributaries support sculpin populations and had reasonable numbers of young-of-the-year brook trout.

The occurrence of tributaries or microhabitats with suitable acid-base chemistry may mitigate, to some degree, the effects of episodic acidification on fish populations. Fish from such areas may immigrate into and recolonize the mainstream during low flow. Telemetry studies confirmed that some fish are able to avoid exposure to adverse chemical conditions by moving into alkaline refuge areas (Section 6.2). However, streams with low pH and high Al_{im} during episodes consistently supported fewer fish and fewer fish species than did nonacidic streams (Figures 6-37 to 6-41; Table 6-21). In addition, there is no evident association between fish population status and the degree of spatial variability in stream chemistry within the drainage system. For example, despite the occurrence of tributary streams with high pH, Linn Run still supports very few brook trout. Therefore, we conclude that recolonization from alkaline tributaries or microhabitats can maintain low densities of fish in streams that experience toxic episodes, but is not sufficient to sustain fish densities and biomass at levels expected in the absence of adverse acid-base chemistry.

Sculpin are absent from streams that support low numbers of brook trout (Table 6-21). Yet, ERP *in situ* bioassays indicate that sculpin are as tolerant, or more so, of low pH and high Al_{im} than brook trout (Section 6.1). Gagen (1991) proposed that differences in the population-level effects of episodic acidification on sculpin and brook trout result from differences in fish mobility. Phinney (1975) observed that brook trout can rapidly move more than 1 km to recolonize stream sections. Brown and Downhower (1982) reported that summer movements of mottled sculpin were generally < 10 m. Thus, sculpin would be expected to recolonize stream reaches at a much slower rate than brook trout and, as a result, the effects of toxic episodes on sculpin populations would be more severe and long lasting. Sculpin populations are acid sensitive (see Table 6-21; Baker and Christensen, 1991), even though individual sculpin were relatively acid tolerant in the *in situ* bioassays.

The ERP results demonstrate that streams with suitable conditions during low flow, but adverse chemical conditions during high flow, support fewer fish species and substantially lower brook trout numbers and biomass than do nonacidic streams. Streams that experienced acidic episodes had significantly lower numbers and biomass of brook trout than nonacidic streams; differences between chronically and episodically acidic streams were not statistically significant. In general, reduced trout abundance occurred in ERP streams with median high flow pH < 5.0 and Al_{im} > 100-200 μg/L. Acid-sensitive fish species were absent from streams with median high flow pH < 5.2 and Al_{im} > 100 μg/L.

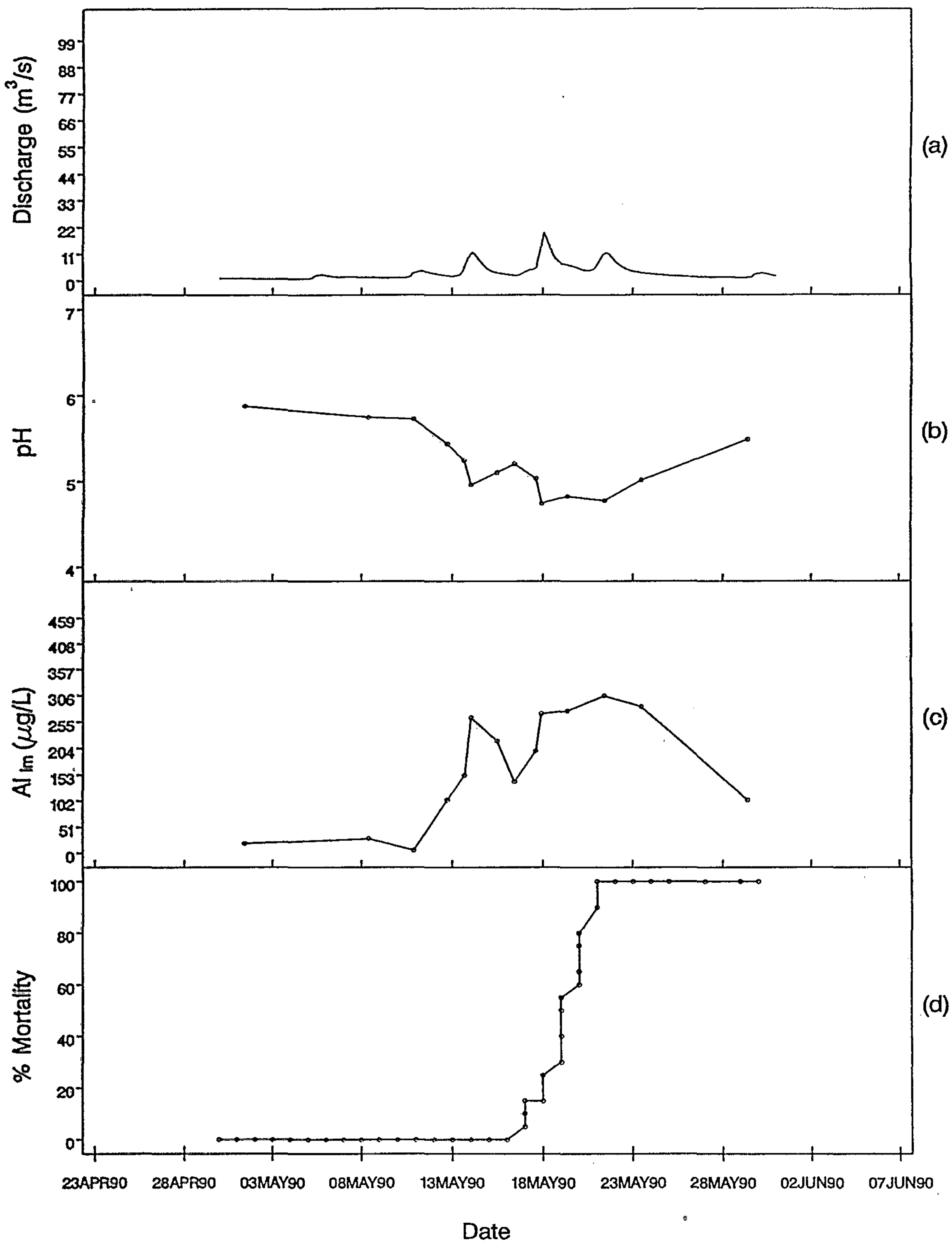


Figure 6-1. *In situ* bioassay in Bald Mountain Brook, Adirondacks, in spring 1990: (a) discharge, (b) pH, (c) Al_{im}, and (d) cumulative percent mortality of blacknose dace over time.

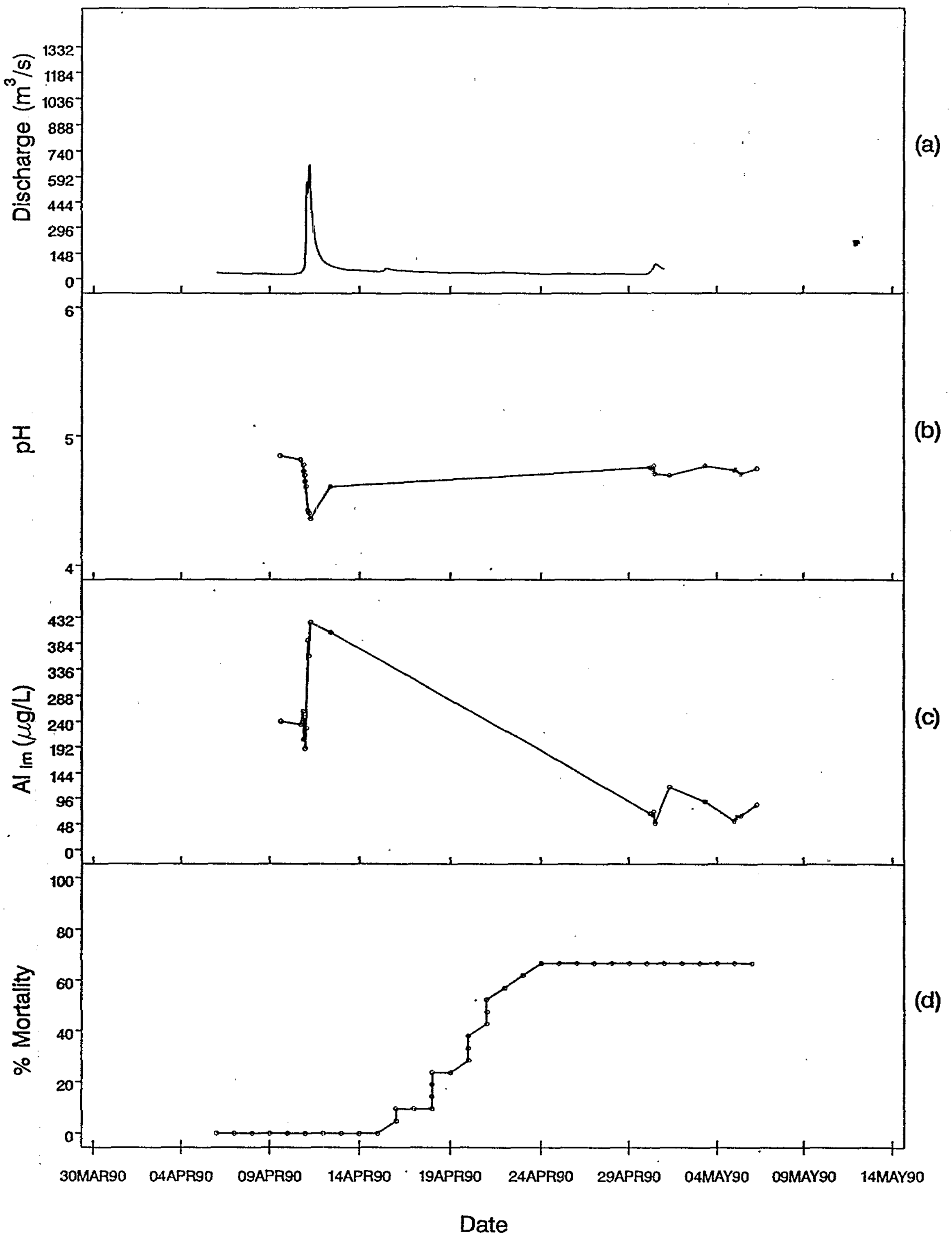


Figure 6-2. ***In situ*** **bioassay in East Branch of the Neversink River, Catskills, in spring 1990: (a) discharge, (b) pH, (c) Al_{im}, and (d) cumulative percent mortality of brook trout over time.**

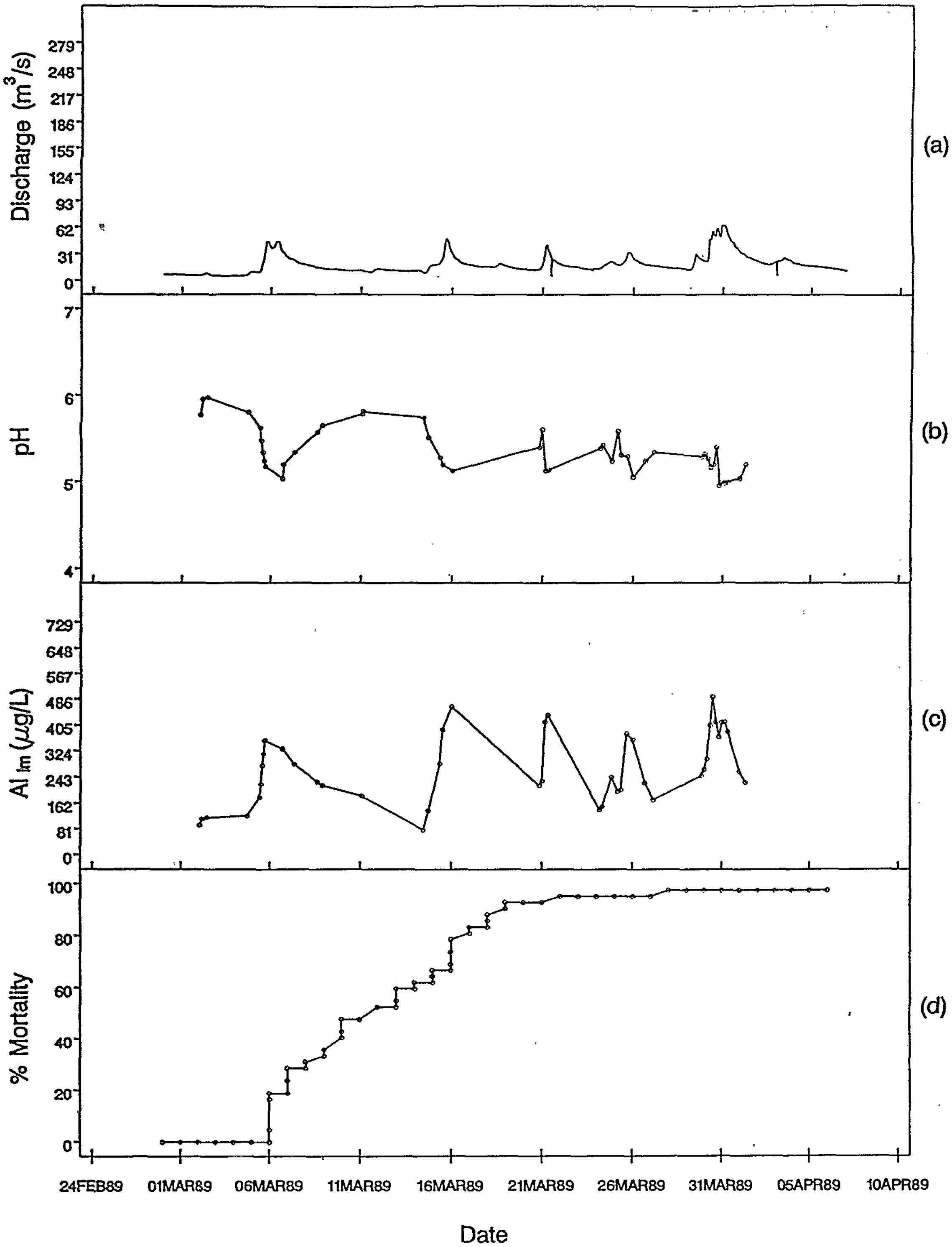


Figure 6-3. ***In situ*** **bioassay in Linn Run, Pennsylvania, in spring 1989: (a) discharge, (b) pH, (c) Al_{im}, and (d) cumulative percent mortality of brook trout over time.**

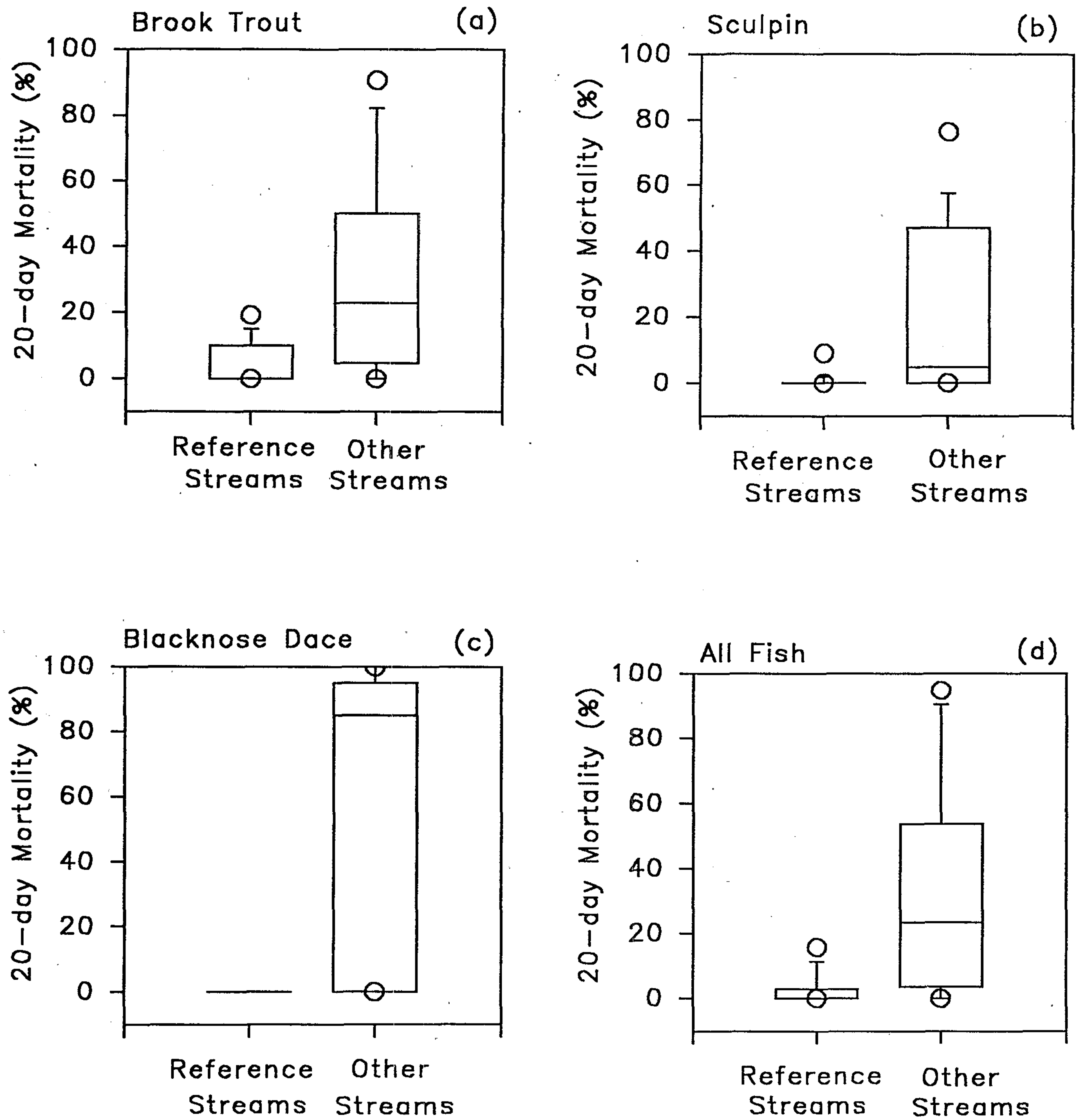


Figure 6-4. **Box plots of percent mortality after 20 days in *in situ* bioassays in reference and nonreference streams. Line in box indicates median % mortality; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.**

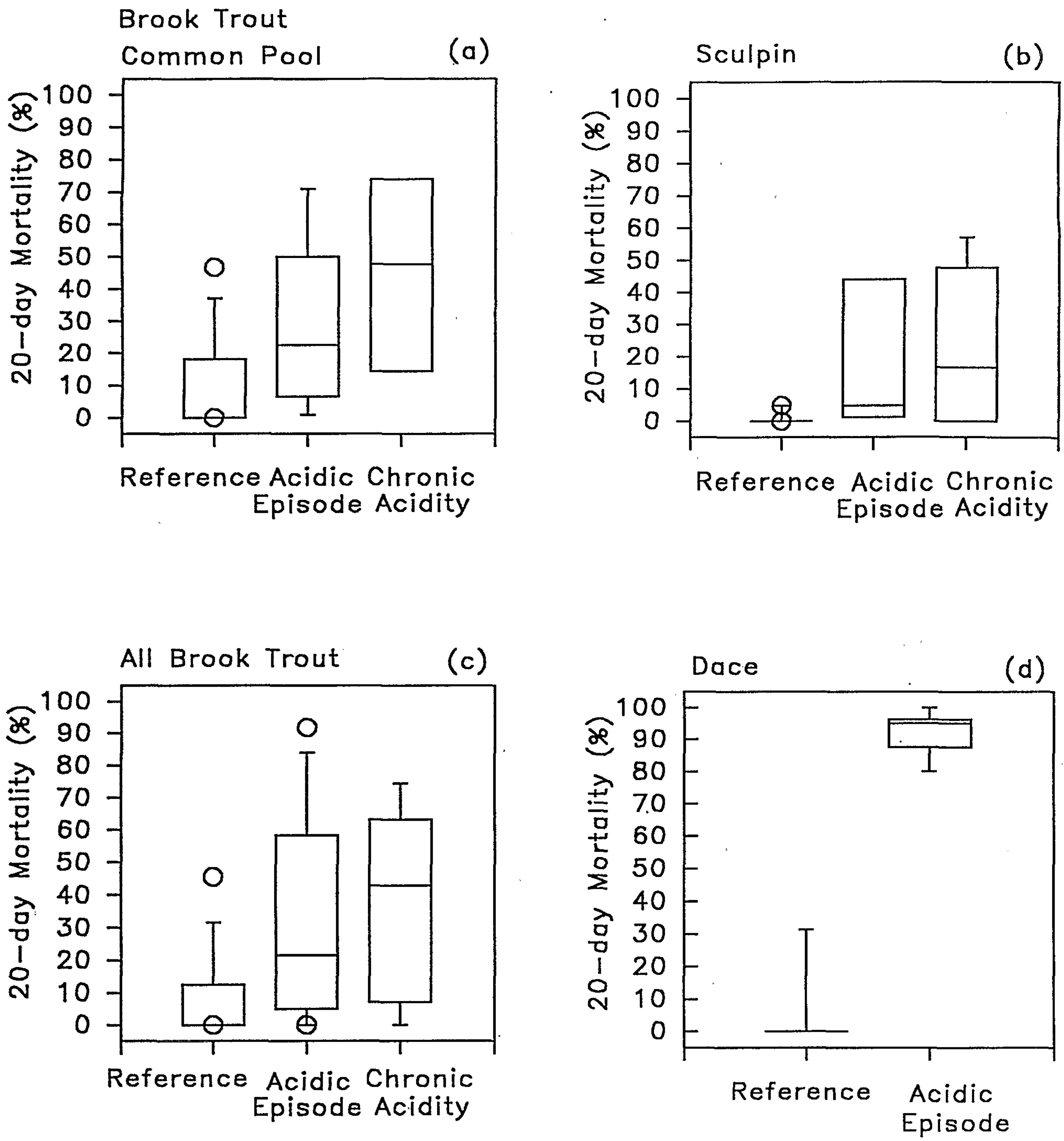
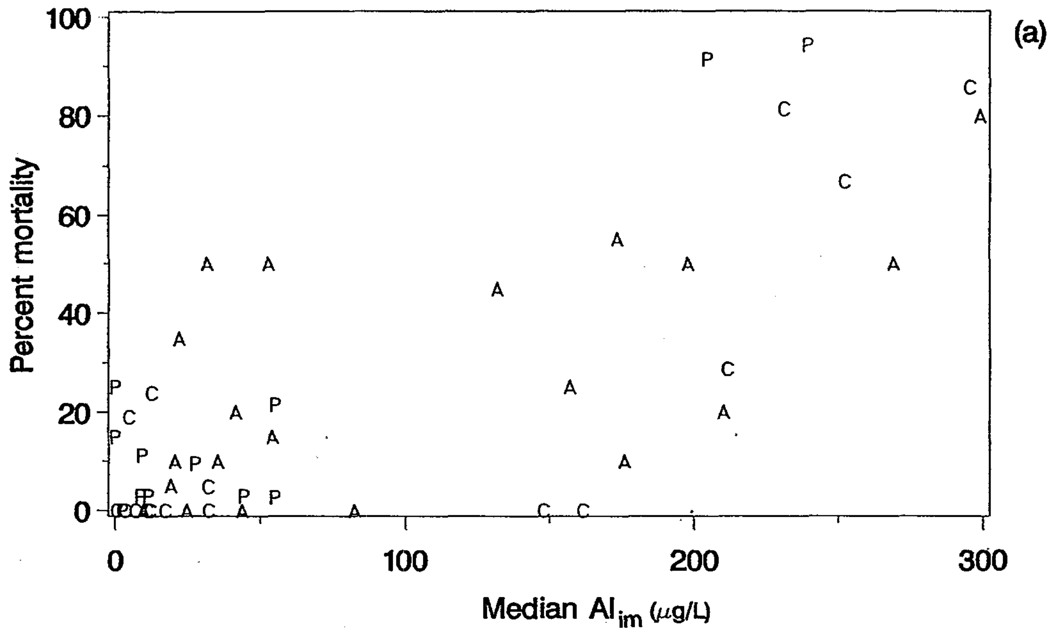


Figure 6-5. **Box plots of percent mortality after 20 days in *in situ* bioassays classified according to ANC: reference (nonacidic with ANC always > 0); chronic acidity (ANC always ≤ 0); and acidic episode (initial ANC > 0 with at least two consecutive values ≤ 0 during 20-day period). Line in box indicates median % mortality; upper and lower borders of box show 25th and 75th quartiles; whiskers indicate 10th and 90th percentiles; circles represent observations beyond 10th and 90th percentiles.**



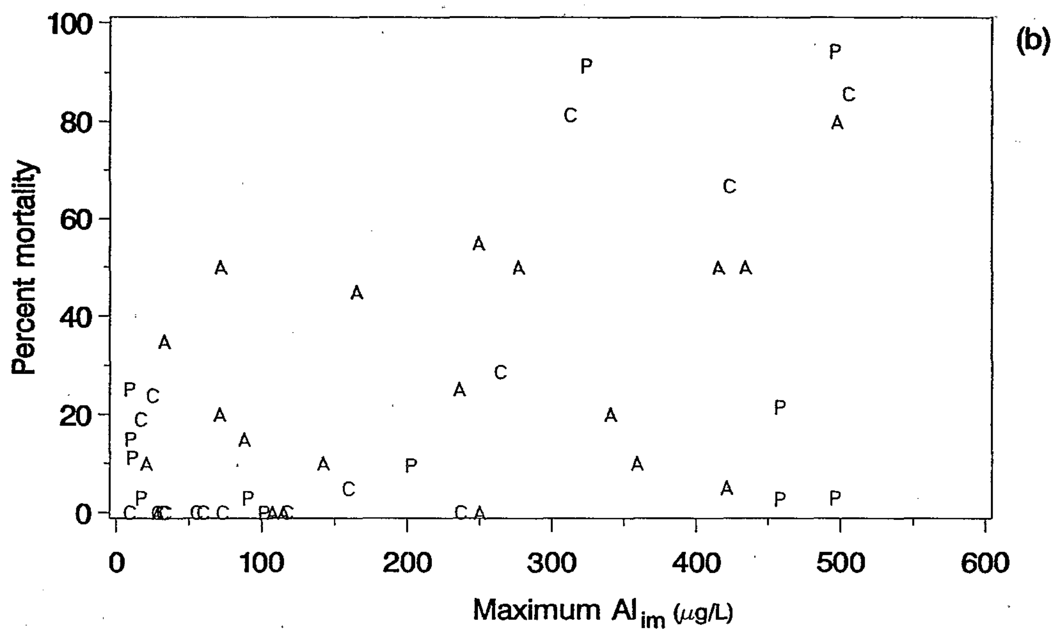


Figure 6-6. **Bivariate plot of percent survival of brook trout (common pool fish only) after 20 days in *in situ* bioassays as a function of (a) time-weighted median Al_{im} (µg/L) and (b) maximum measured or estimated Al_{im} (µg/L) during the 20-day period. Bioassays conducted in Adirondack streams denoted by A, Catskills by C, and Pennsylvania by P.**

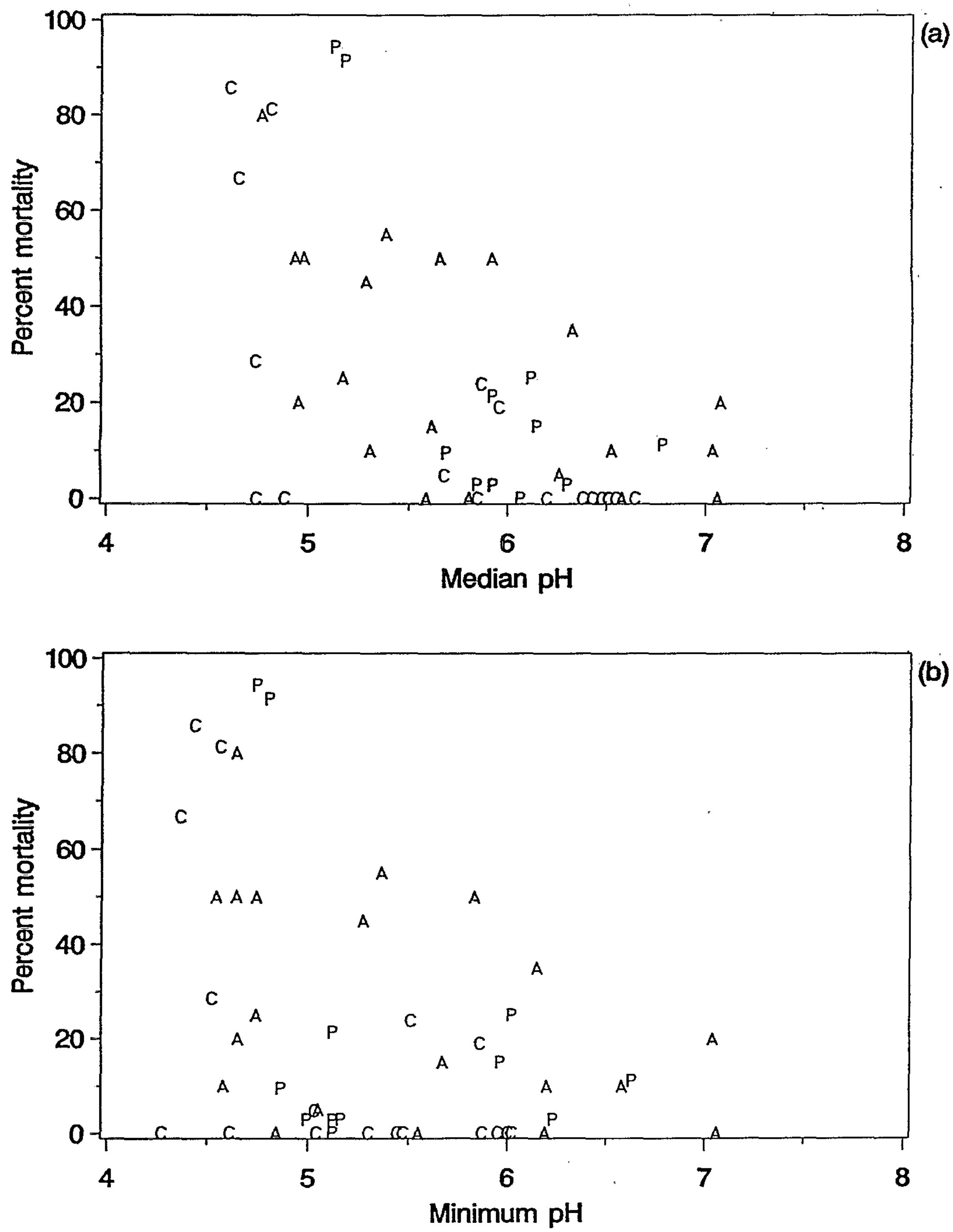


Figure 6-7. **Bivariate plot of percent survival of brook trout (common pool fish only) after 20 days in *in situ* bioassays as a function of (a) time-weighted median pH and (b) minimum measured pH during the 20-day period. Bioassays conducted in Adirondack streams denoted by A, Catskills by C, and Pennsylvania by P.**

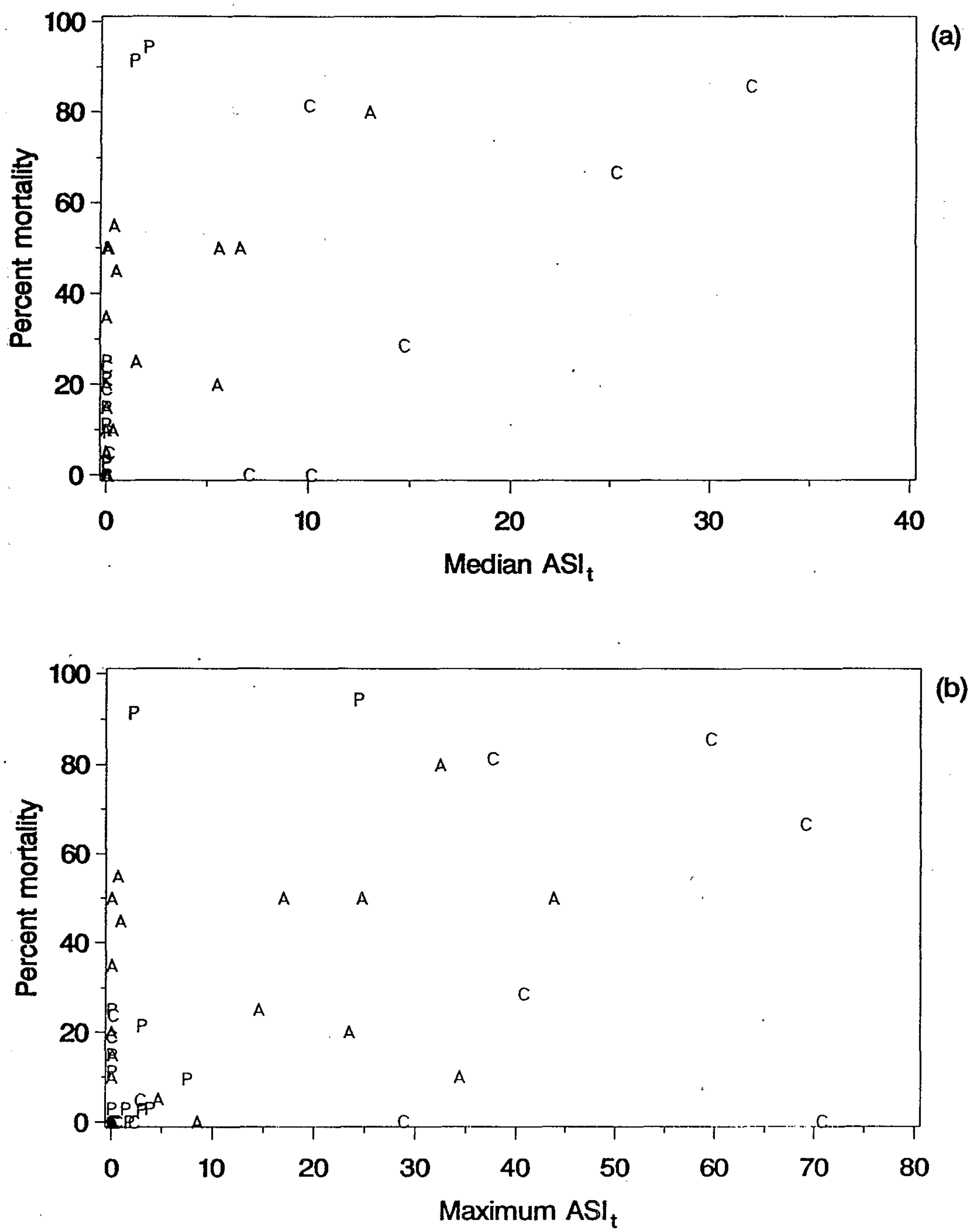


Figure 6-8. Bivariate plot of percent survival of brook trout (common pool fish only) after 20 days in *in situ* bioassays as a function of (a) time-weighted median acidic stress index based on brook trout fry (ASI_t, see Table 6-9) and (b) maximum ASI_t during the 20-day period. Bioassays conducted in Adirondack streams denoted by A, Catskills by C, and Pennsylvania by P.

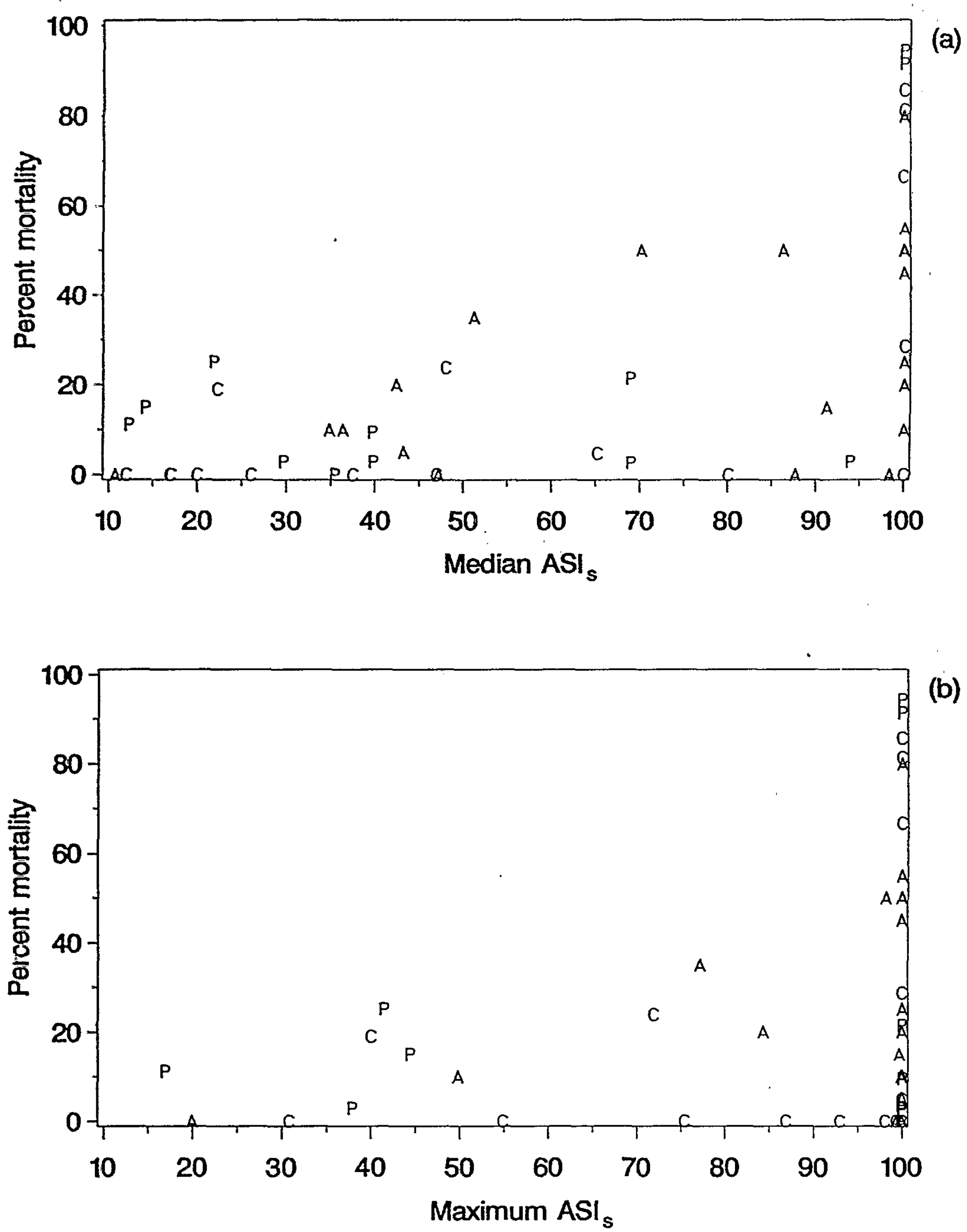


Figure 6-9. **Bivariate plot of percent survival of brook trout (common pool fish only) after 20 days in *in situ* bioassays as a function of (a) time-weighted median acidic stress index based on rainbow trout fry (ASI_s, see Table 6-9) and (b) maximum ASI_s during the 20-day period. Bioassays conducted in Adirondack streams denoted by A, Catskills by C, and Pennsylvania by P.**

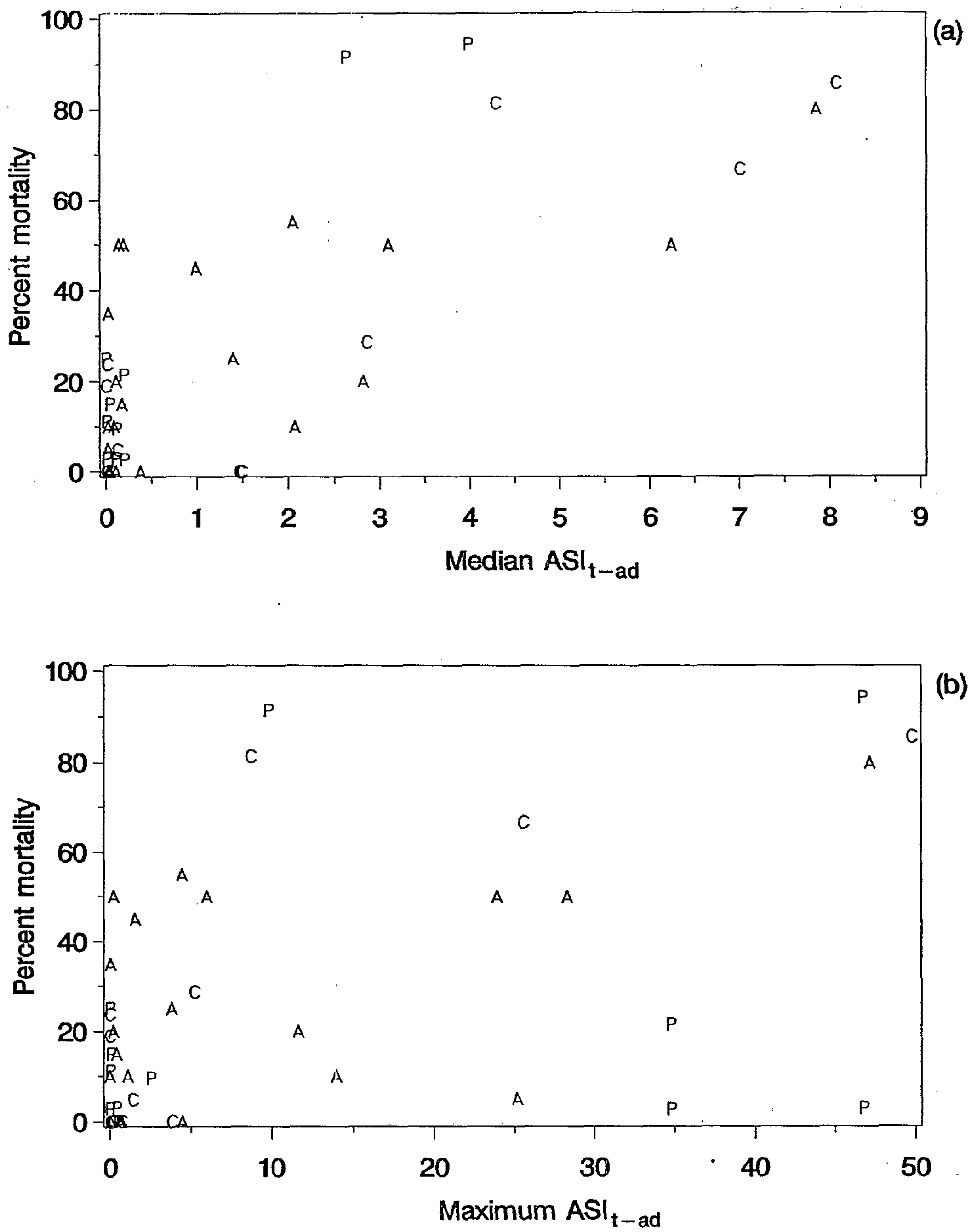


Figure 6-10. Bivariate plot of percent survival of brook trout (common pool fish only) after 20 days in *in situ* bioassays as a function of (a) time-weighted median acidic stress index based on brook trout adults ($ASI_{t\text{-}ad}$, see Table 6-9) and (b) maximum $ASI_{t\text{-}ad}$ during the 20-day period. Bioassays conducted in Adirondack streams denoted by A, Catskills by C, and Pennsylvania by P.

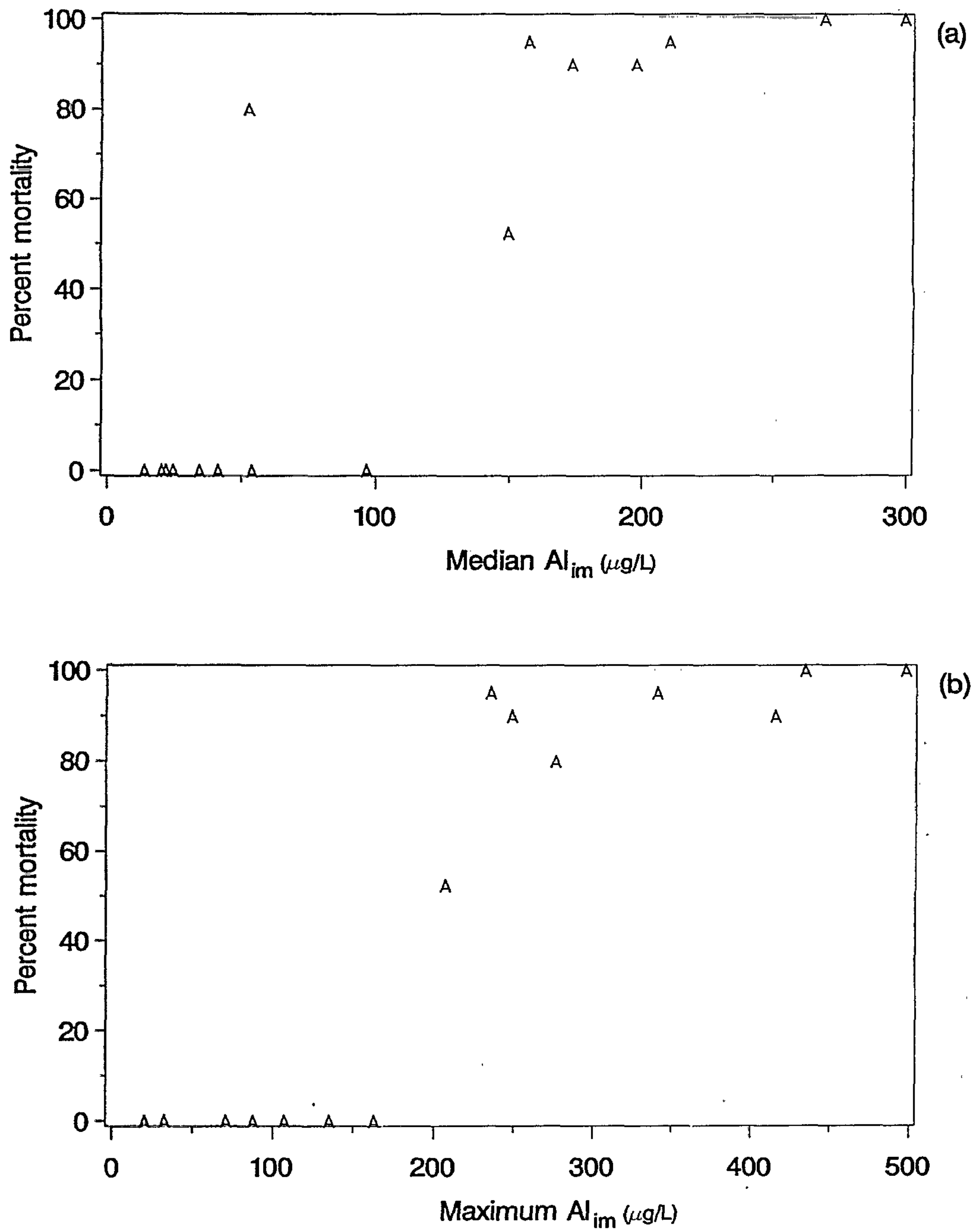


Figure 6-11. Bivariate plot of percent survival of blacknose dace after 20 days in *in situ* bioassays as a function of (a) time-weighted median Al_{im} (μg/L) and (b) maximum measured or estimated Al_{im} (μg/L) during the 20-day period. Bioassays conducted in Adirondack streams denoted by A.

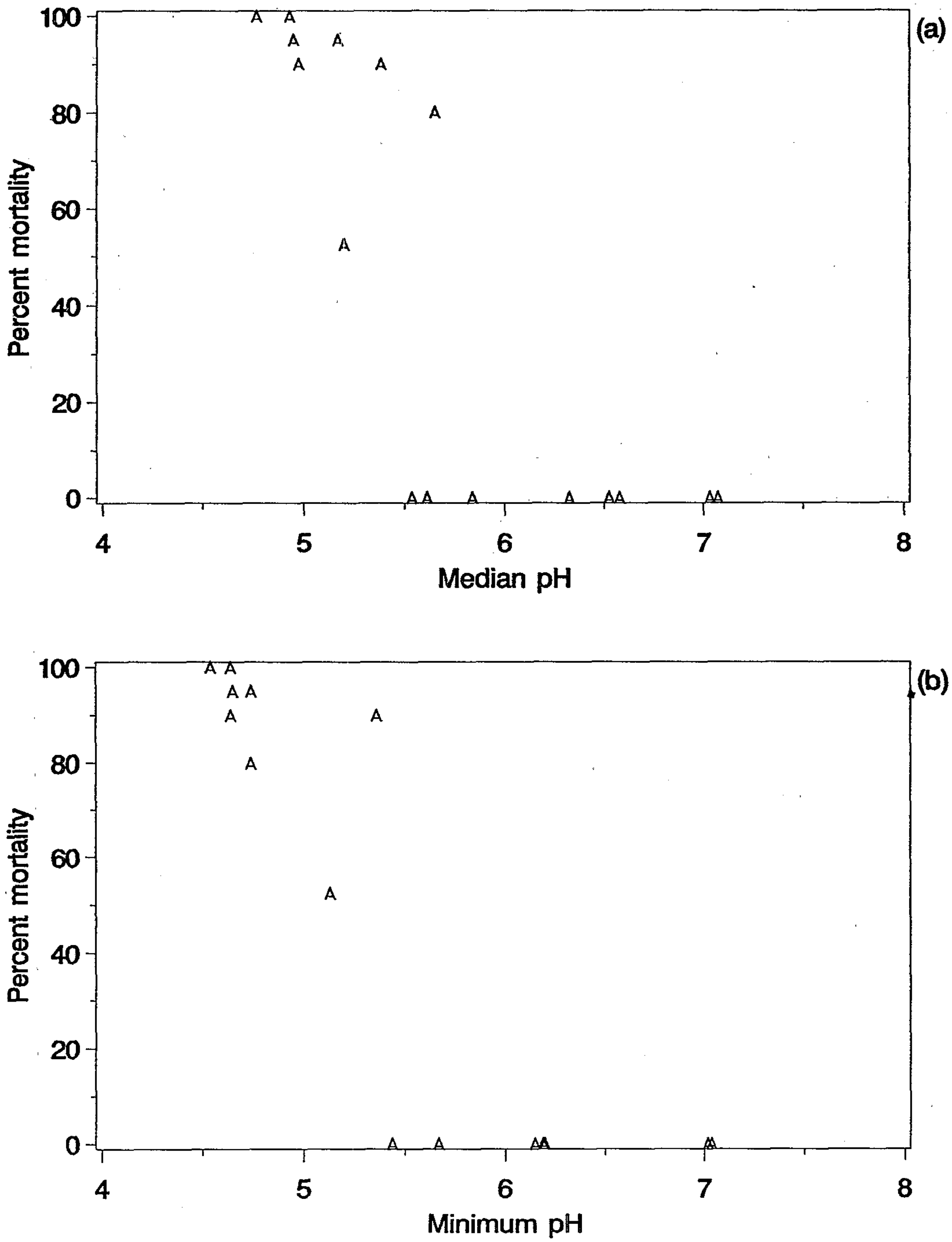


Figure 6-12. Bivariate plot of percent survival of blacknose dace after 20 days in *in situ* bioassays as a function of (a) time-weighted median pH and (b) minimum measured pH during the 20-day period. Bioassays conducted in Adirondack streams denoted by A.

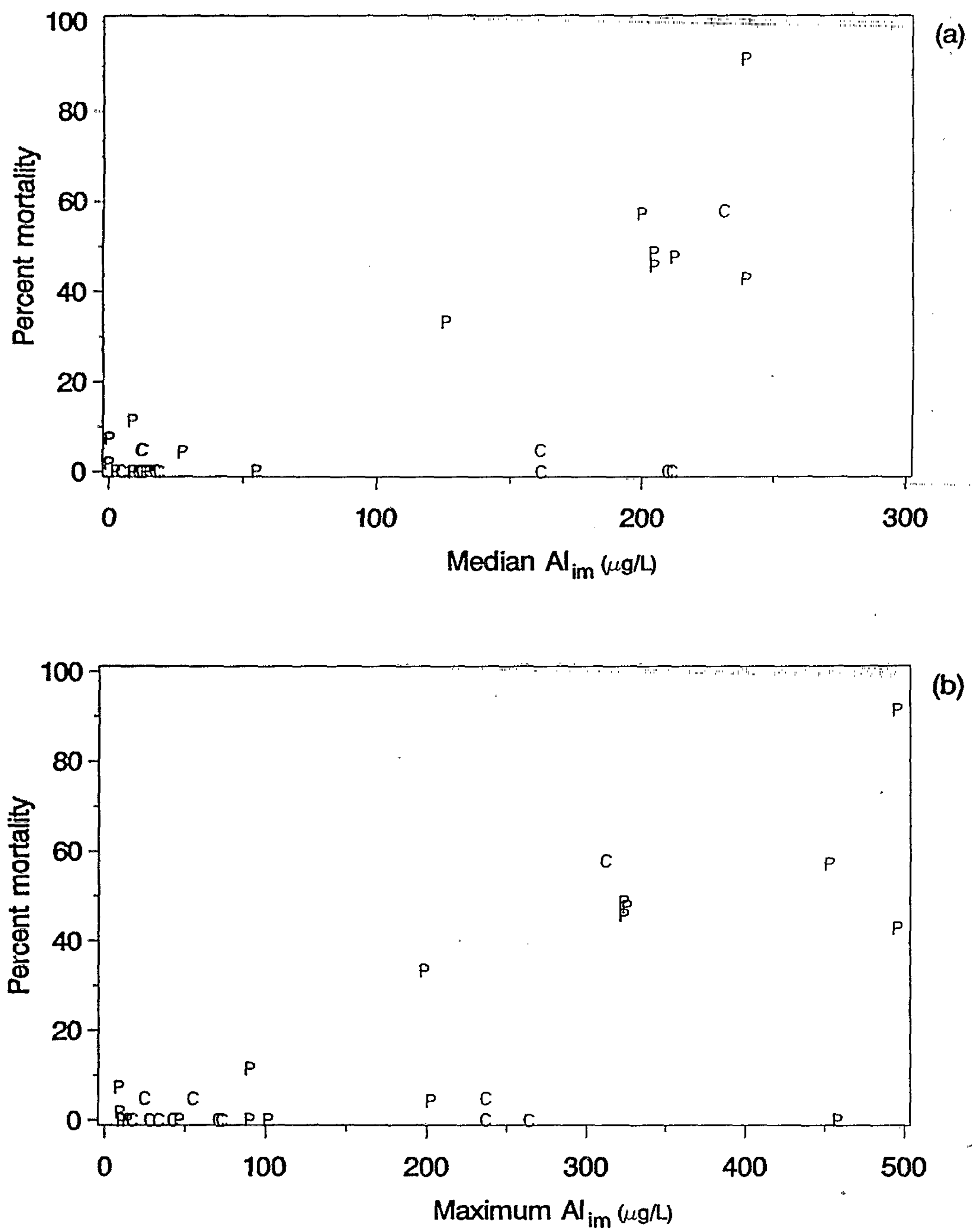


Figure 6-13. **Bivariate plot of percent survival of slimy and mottled sculpin after 20 days in *in situ* bioassays as a function of (a) time-weighted median Al_{im} (μg/L) and (b) maximum measured or estimated Al_{im} (μg/L) during the 20-day period. Bioassays conducted in Catskill streams denoted by C and Pennsylvania by P.**

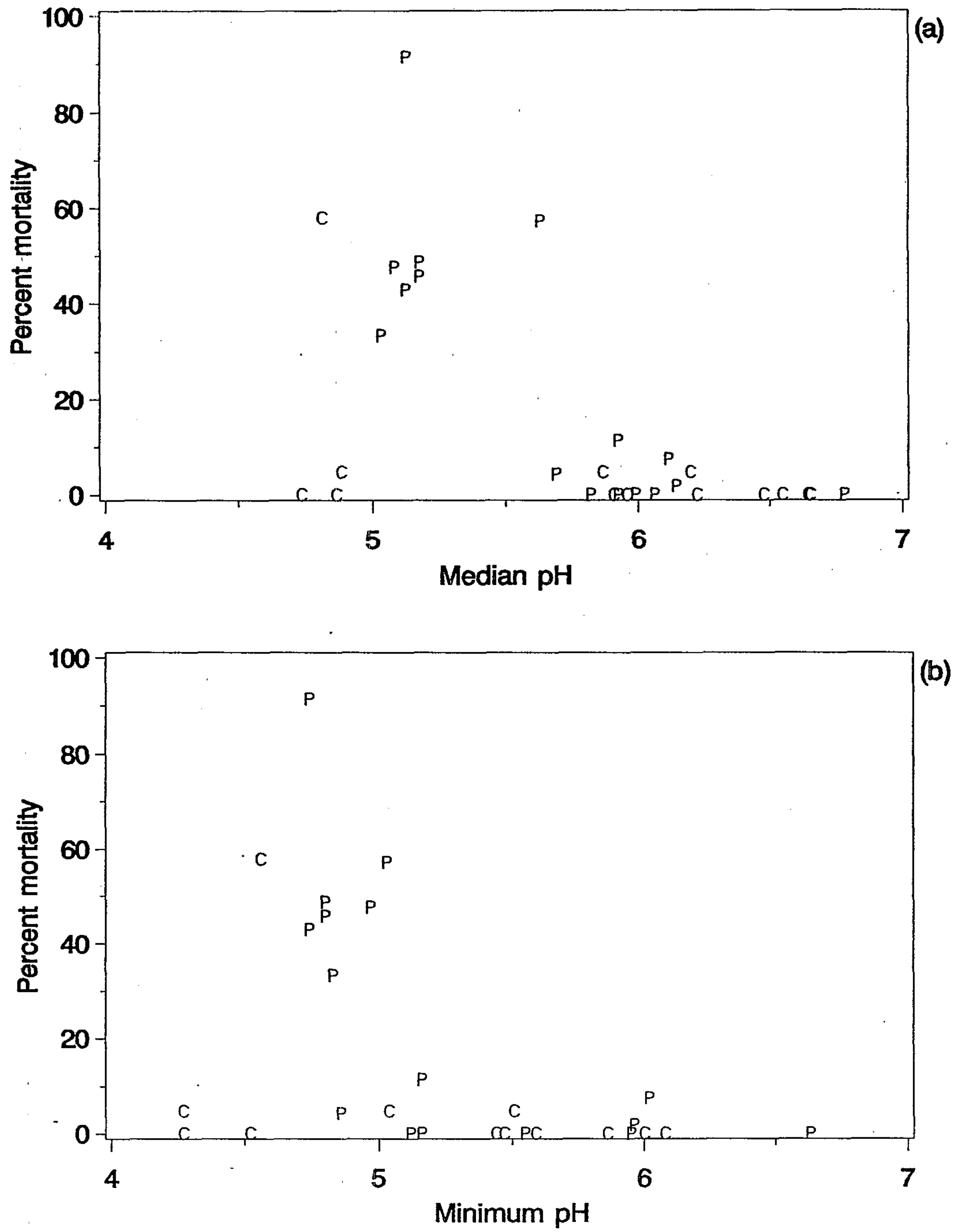


Figure 6-14. **Bivariate plot of percent survival of slimy and mottled sculpin after 20 days in *in situ* bioassays as a function of (a) time-weighted median pH and (b) minimum measured pH during the 20-day period. Bioassays conducted in Catskill streams denoted by C and Pennsylvania by P.**

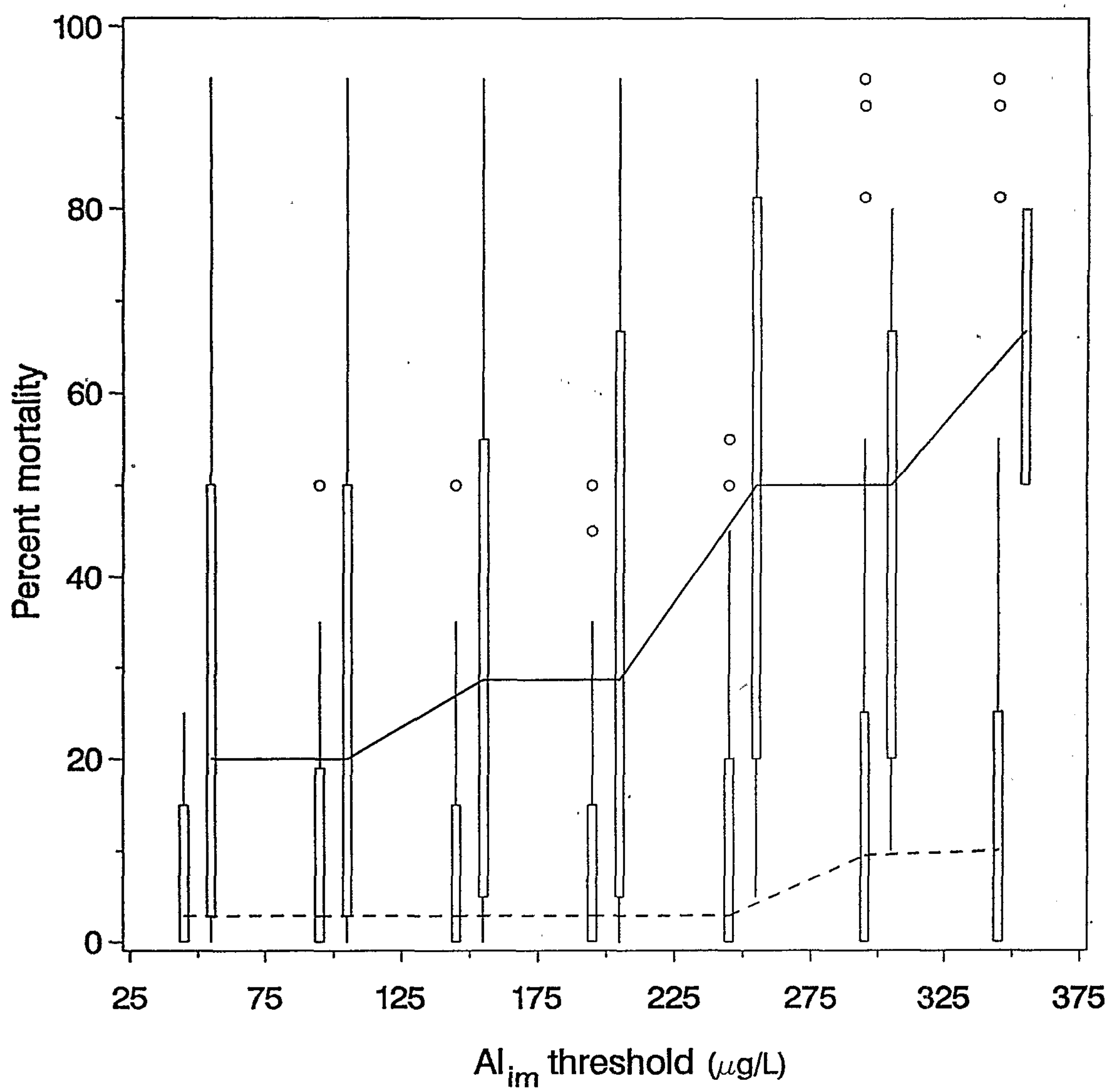


Figure 6-15. **Boxplots of 20-day percent mortality of brook trout in *in situ* bioassays with Al_{im} concentrations continuously above selected thresholds for periods less than or equal to one day (dashed line) or longer than one day (solid line). Boxes indicate 25th through 75 percentile distribution of observed percent mortality for that group of bioassays; vertical lines (whiskers) extend 1.5 times the interquartile range; and open circles are individual outlier data points; horizontal lines join median values for each group.**

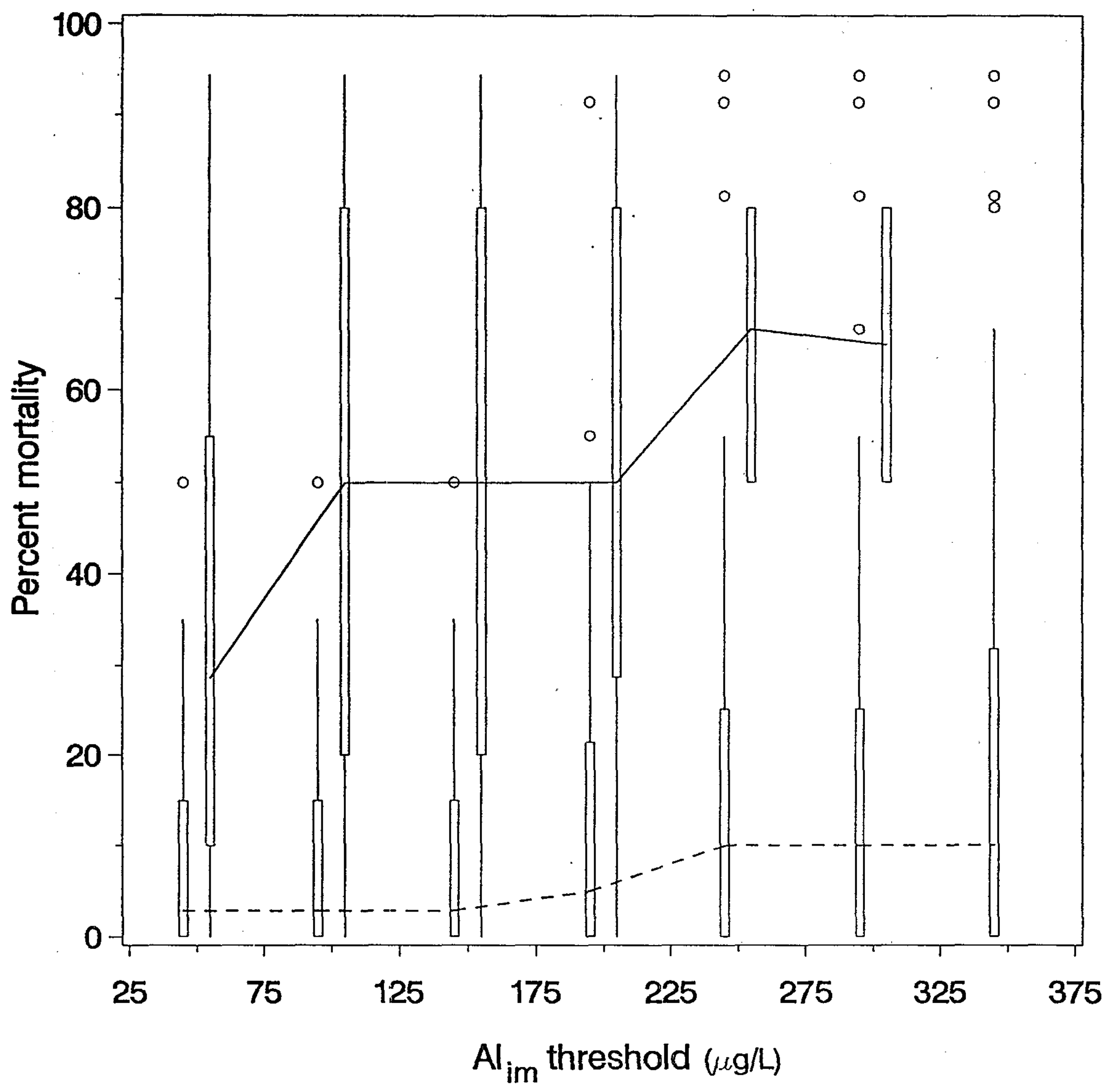


Figure 6-16. Boxplots of 20-day percent mortality of brook trout in *in situ* bioassays with Al_{im} concentrations continuously above selected thresholds for periods less than or equal to 8 days (dashed line) or longer than 8 days (solid line). Boxes indicate 25th through 75 percentile distribution of observed percent mortality for that group of bioassays; vertical lines (whiskers) extend 1.5 times the interquartile range; and open circles are individual outlier data points; horizontal lines join median values for each group.

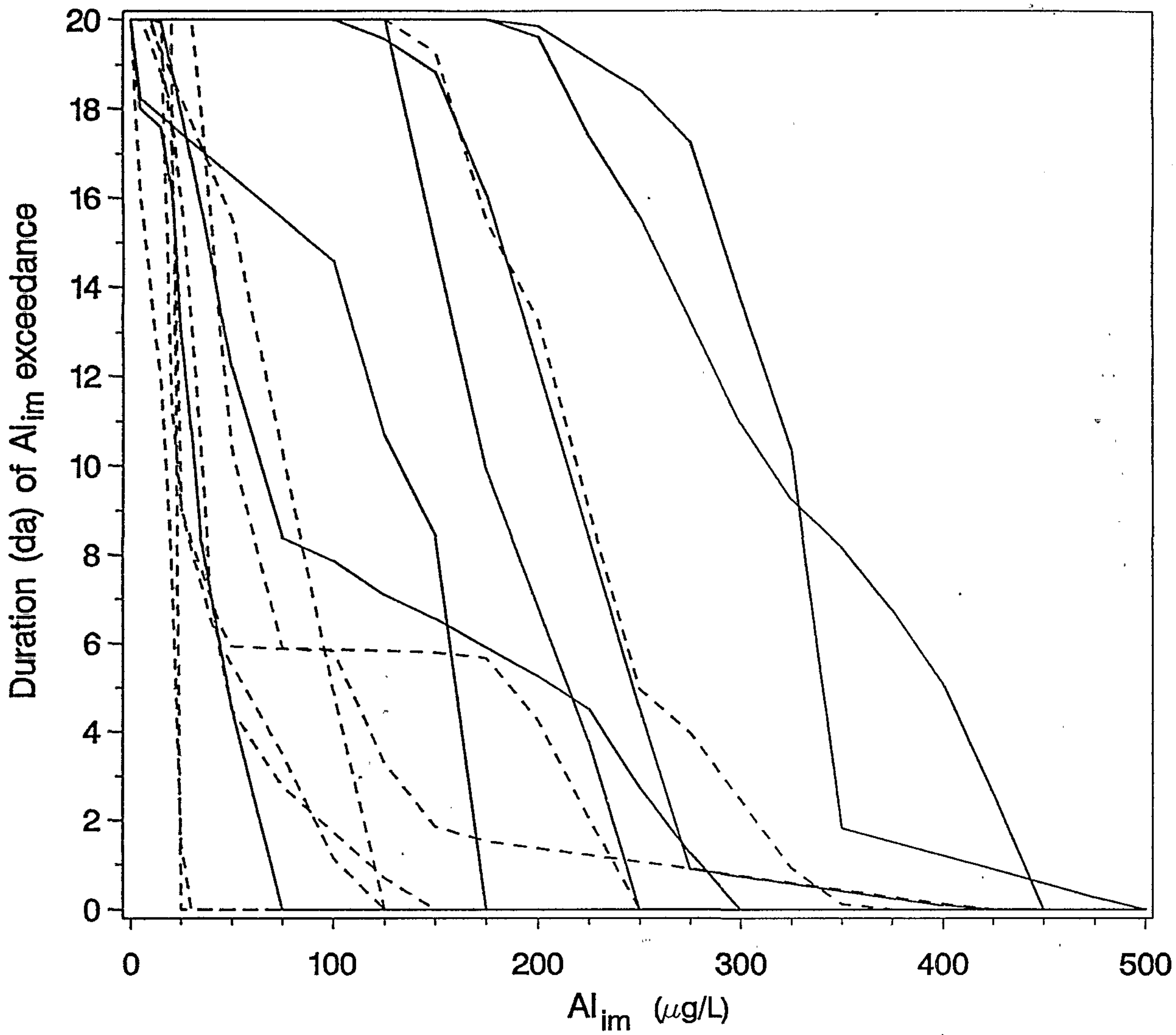


Figure 6-17. Concentration duration curves (total period of time, days, with Al_{im} levels above each threshold concentration, μg/L) for brook trout *in situ* bioassays with low mortality (≤ 10%, dashed lines) and high mortality (> 40%, solid lines) in Adirondack streams.

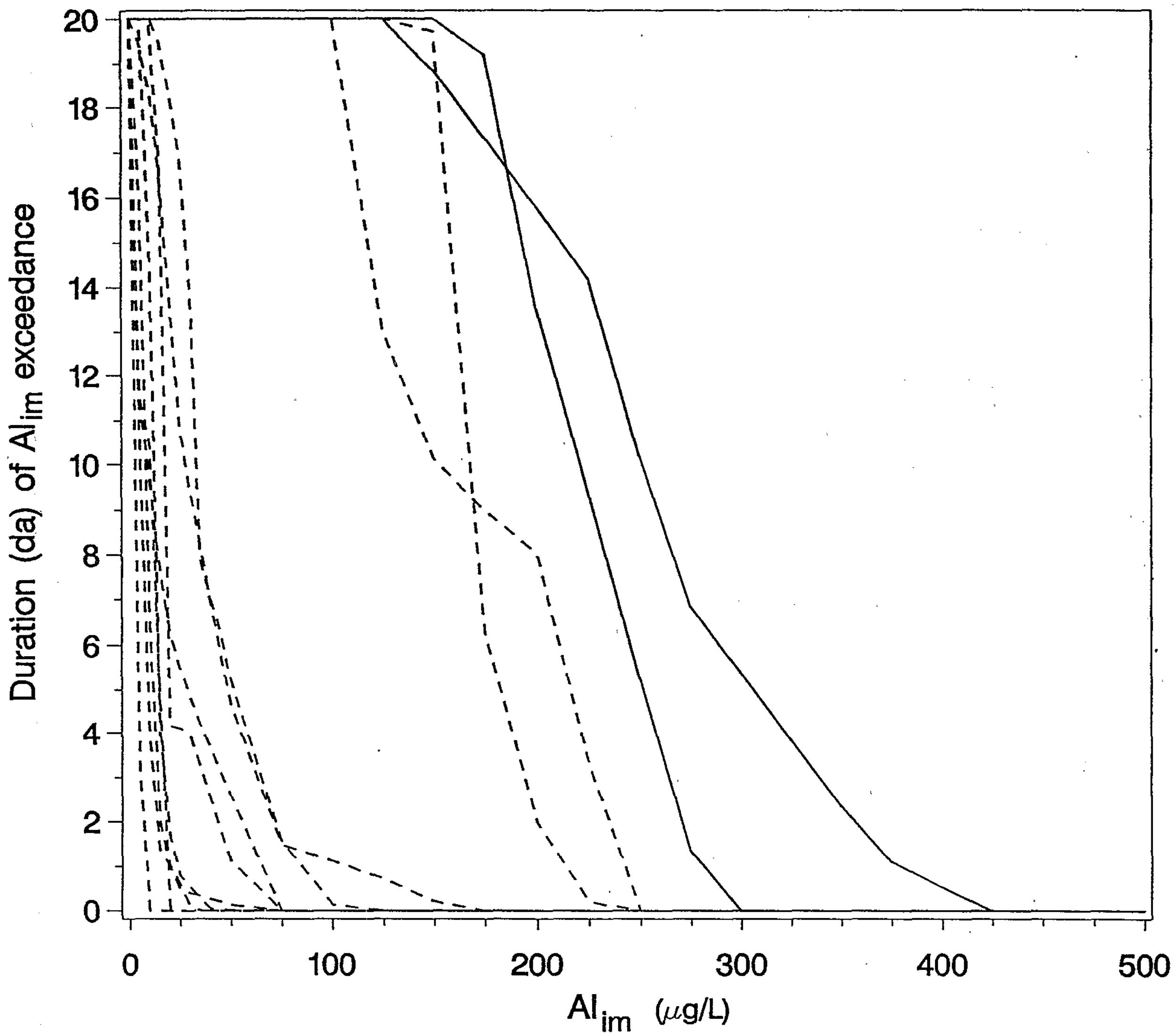


Figure 6-18. Concentration duration curves (total period of time, days, with Al_{im} levels above each threshold concentration, µg/L) for brook trout *in situ* bioassays with low mortality (≤ 10%, dashed lines) and high mortality (> 40%, solid lines) in Catskill streams.

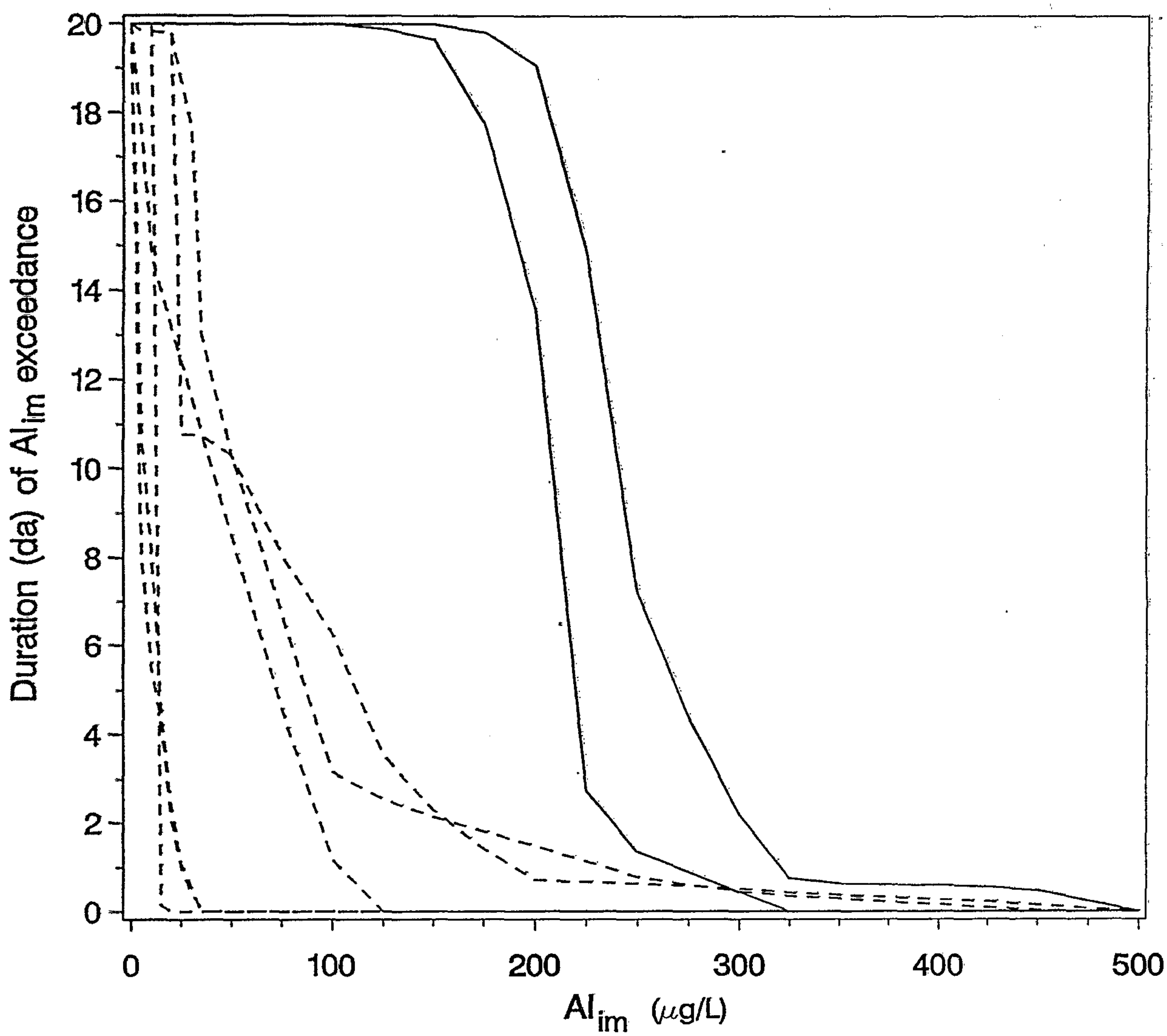


Figure 6-19. Concentration duration curves (total period of time, days, with Al_{im} levels above each threshold concentration, μg/L) for brook trout *in situ* bioassays with low mortality ($\leq$ 10%, dashed lines) and high mortality (> 40%, solid lines) in Pennsylvania streams.

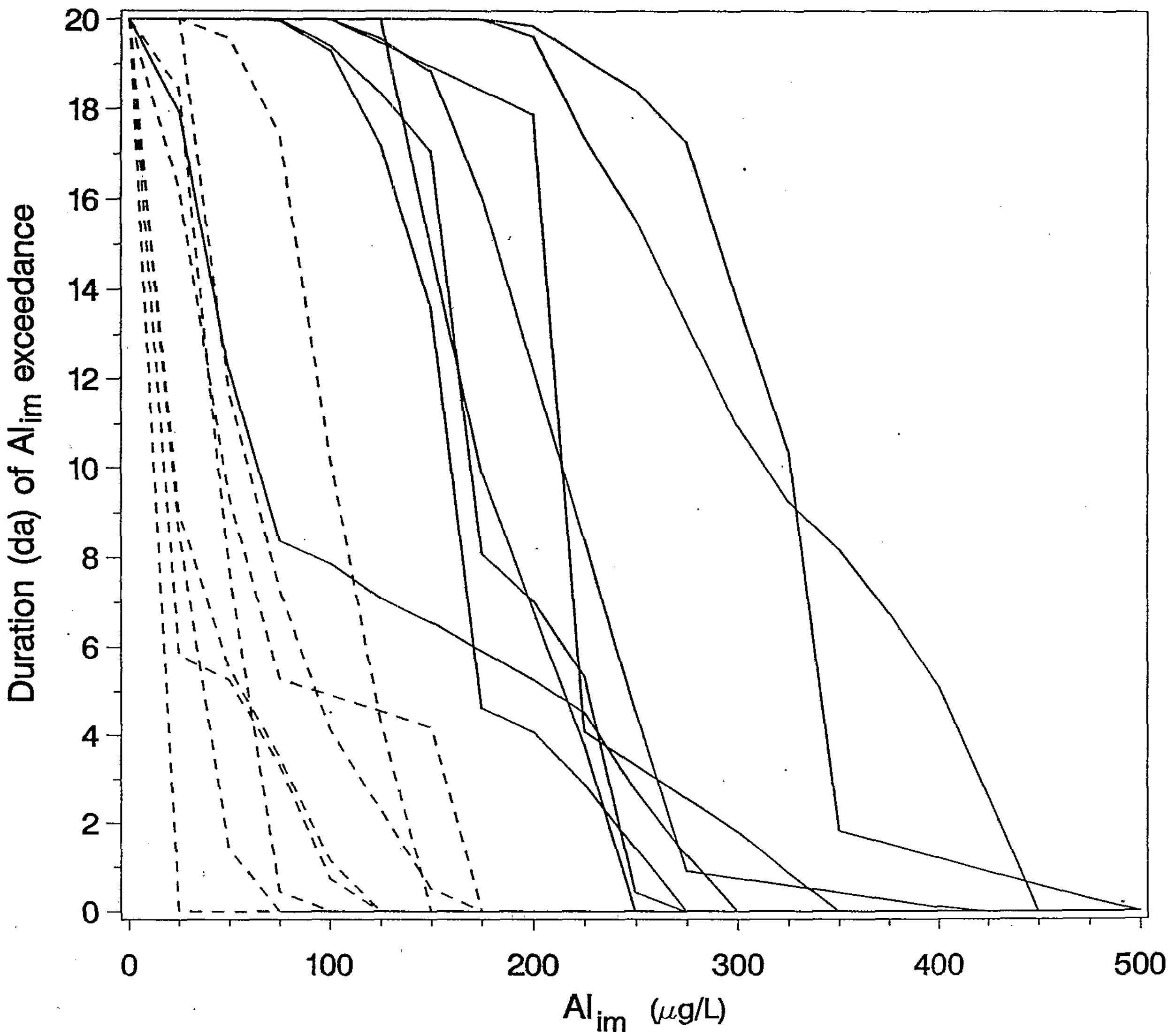


Figure 6-20. Concentration duration curves (total period of time, days, with Al_{im} levels above each threshold concentration, μg/L) for blacknose dace *in situ* bioassays with low mortality (≤ 10%, dashed lines) and high mortality (> 40%, solid lines) in Adirondack streams.

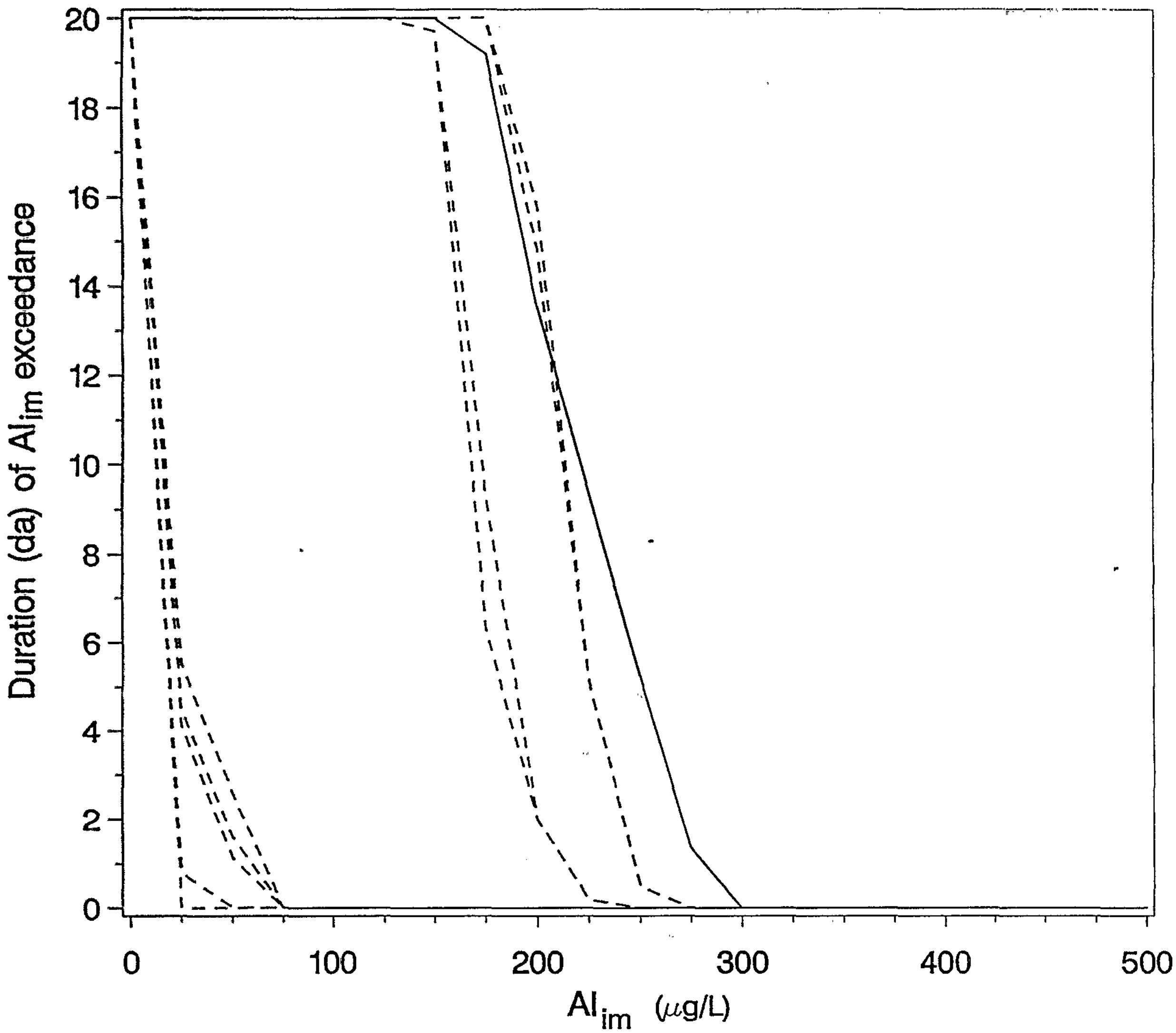


Figure 6-21. Concentration duration curves (total period of time, days, with Al_{im} levels above each threshold concentration, μg/L) for sculpin *in situ* bioassays with low mortality ($\leq$ 10%, dashed lines) and high mortality (> 40%, solid lines) in Catskill streams.

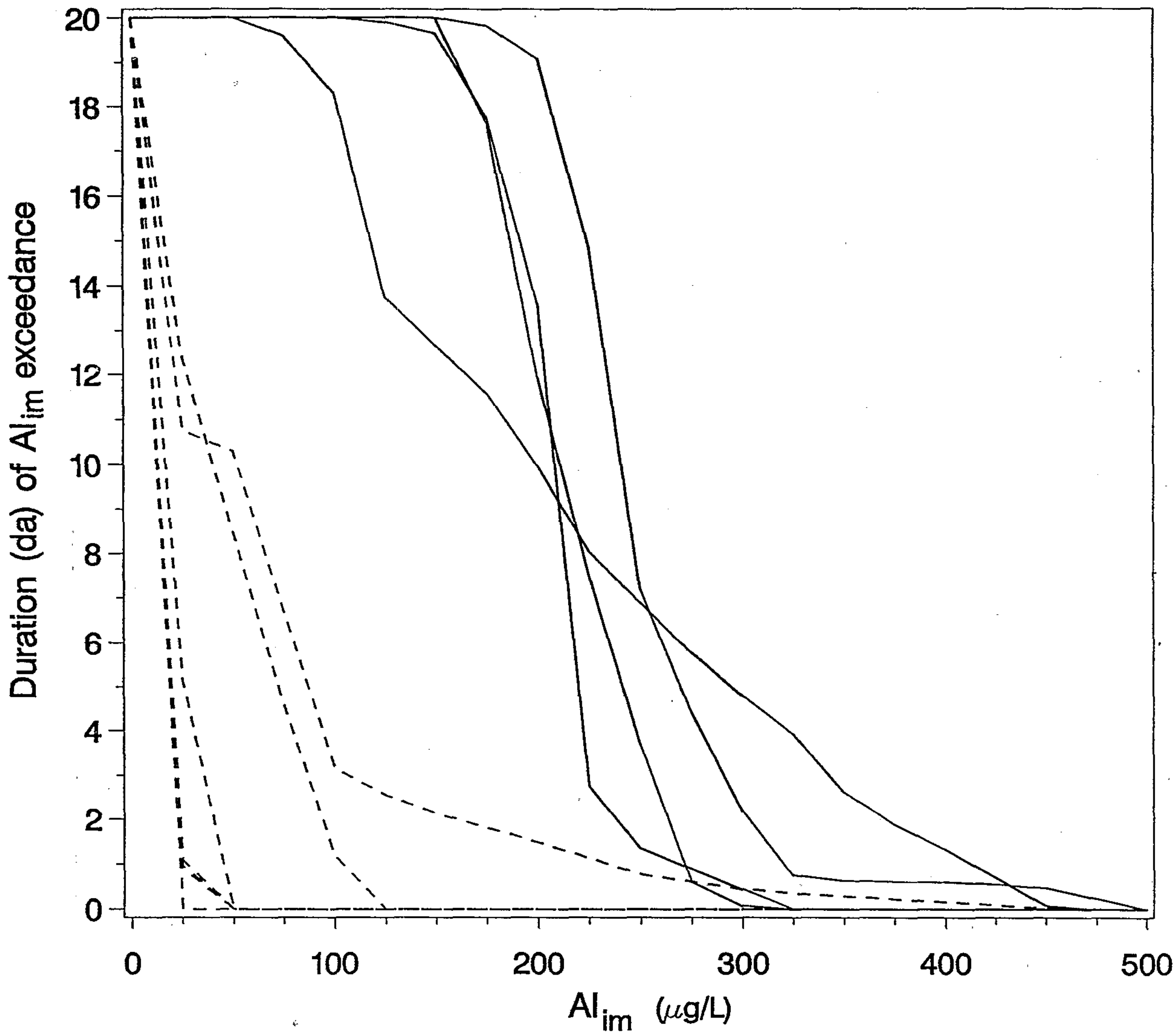


Figure 6-22. Concentration duration curves (total period of time, days, with Al_{im} levels above each threshold concentration, μg/L) for sculpin *in situ* bioassays with low mortality ($\leq$ 10%, dashed lines) and high mortality (> 40%, solid lines) in Pennsylvania streams.

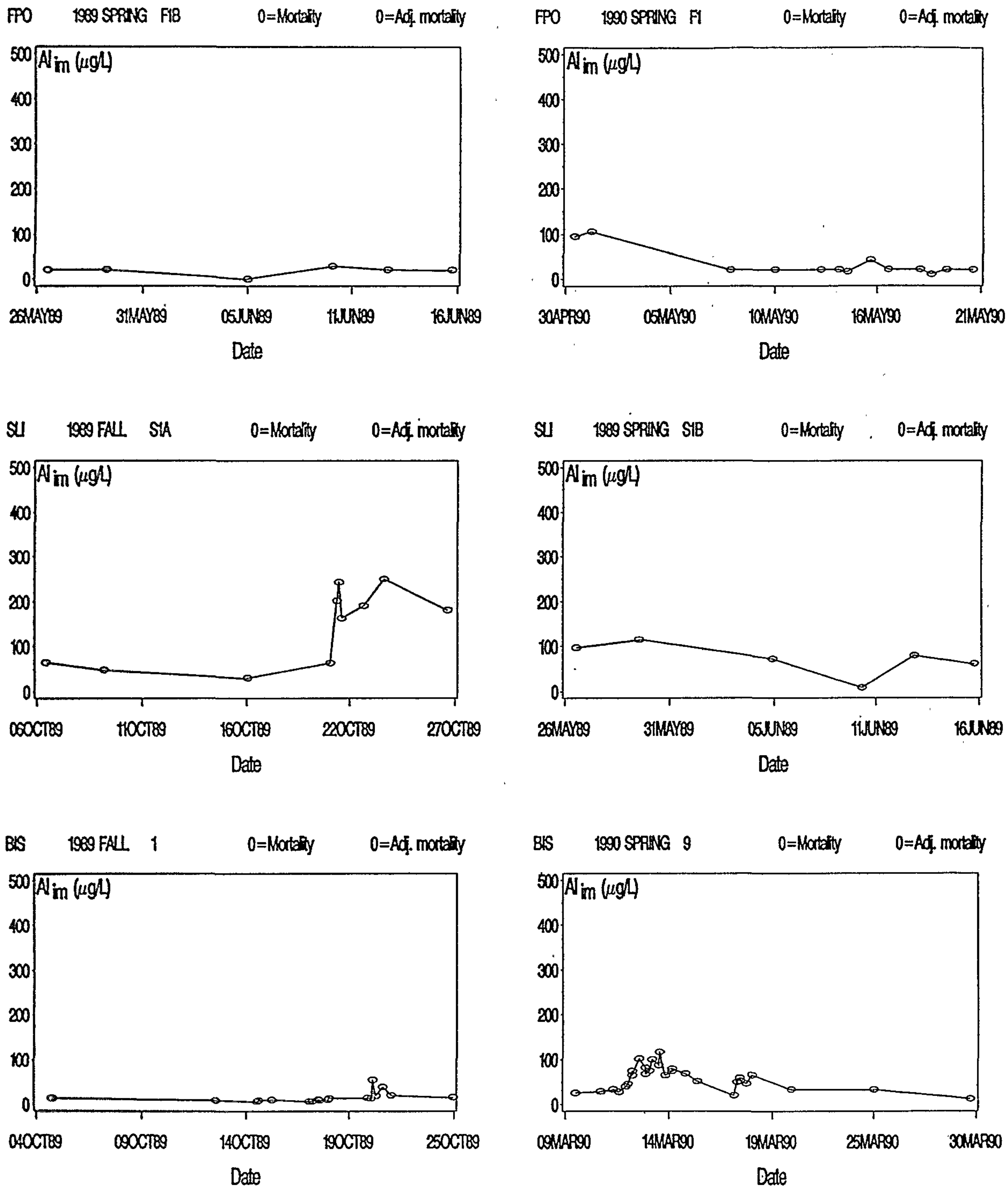


Figure 6-23. Inorganic Al concentrations (µg/L) during each common pool brook trout *in situ* bioassay. Open circles, connected by linear interpolation, indicate both measured and estimated Al_{im} values. Bioassays are ordered from low to high mortality (20-day percent mortality). Adjusted percent mortality (see text for explanation), stream, season, year, and bioassay code are also indicated (page 1 of 9).

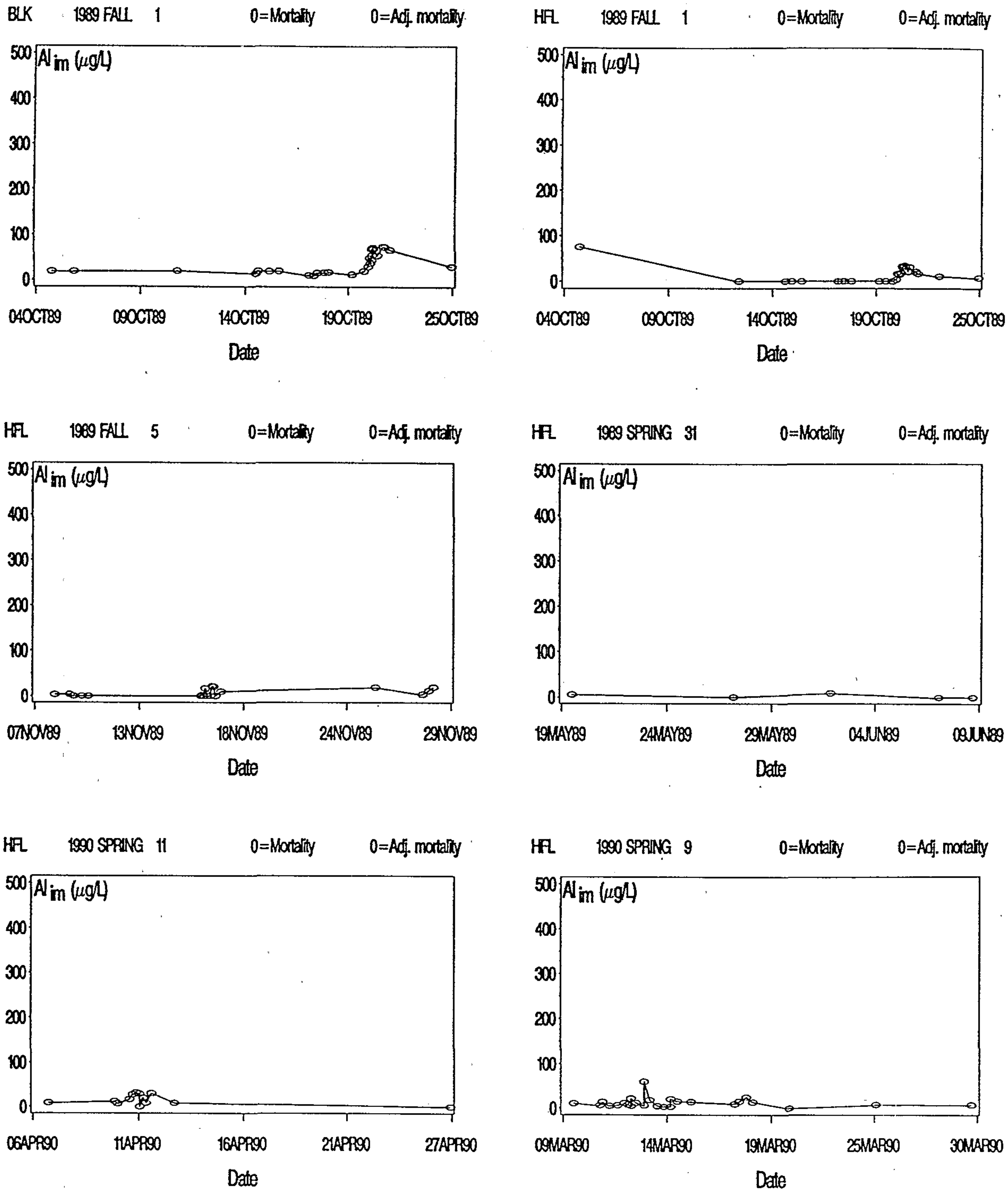


Figure 6-23. **Inorganic Al concentrations (µg/L) during each common pool brook trout *in situ* bioassay. Open circles, connected by linear interpolation, indicate both measured and estimated Al_{im} values. Bioassays are ordered from low to high mortality (20-day percent mortality). Adjusted percent mortality (see text for explanation), stream, season, year, and bioassay code are also indicated (page 2 of 9).**

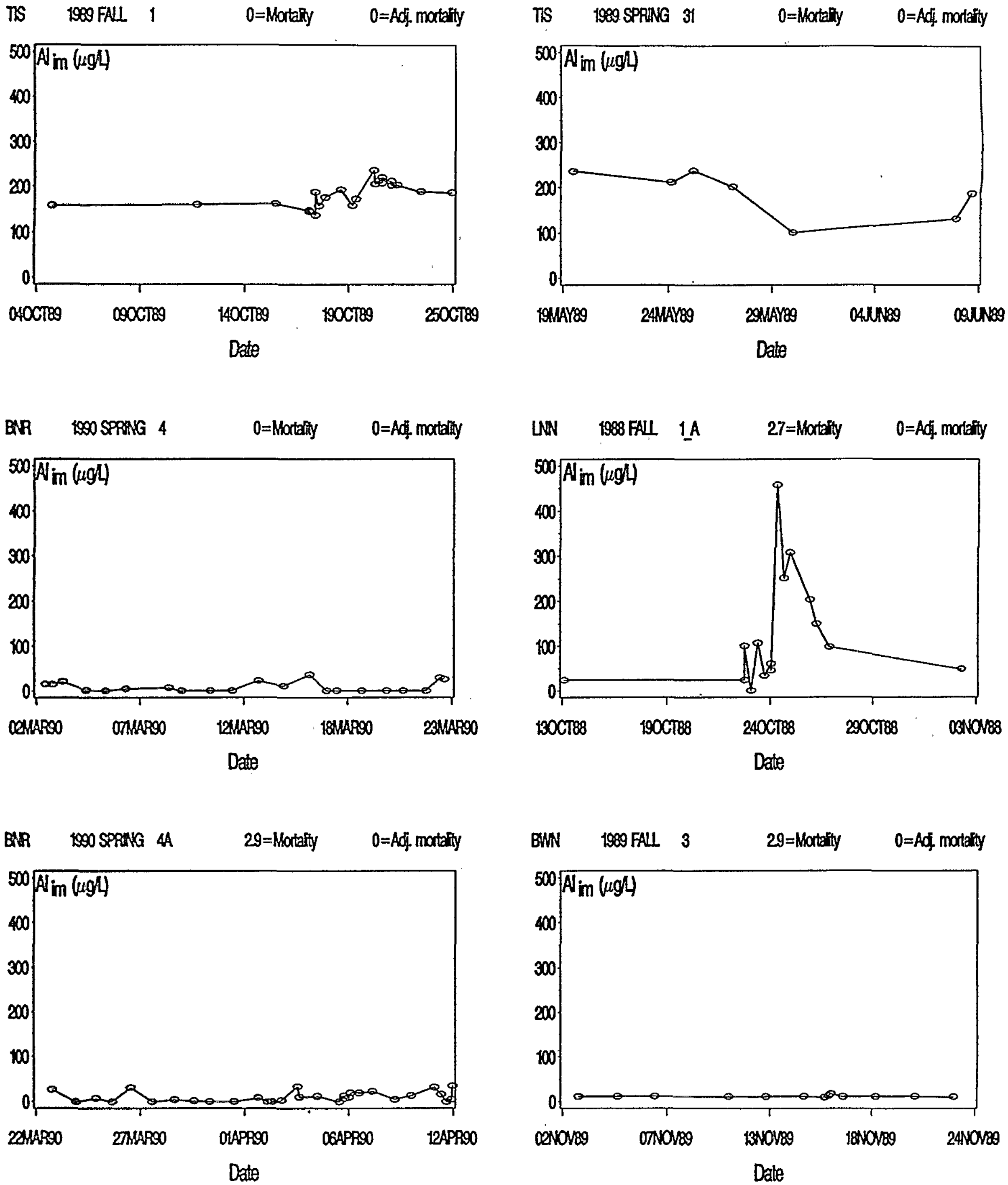


Figure 6-23. Inorganic Al concentrations (µg/L) during each common pool brook trout *in situ* bioassay. Open circles, connected by linear interpolation, indicate both measured and estimated Al_{im} values. Bioassays are ordered from low to high mortality (20-day percent mortality). Adjusted percent mortality (see text for explanation), stream, season, year, and bioassay code are also indicated (page 3 of 9).

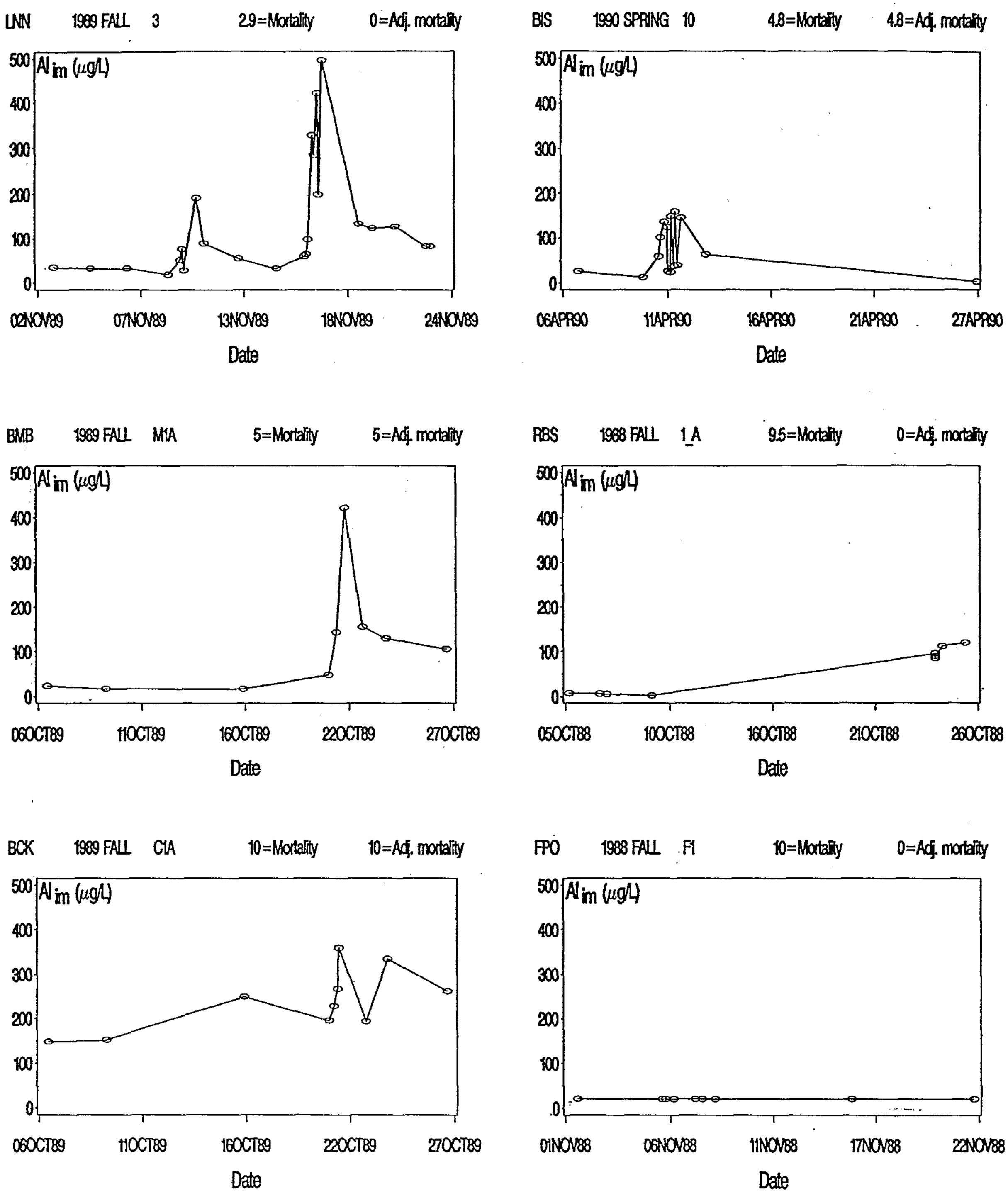


Figure 6-23. Inorganic Al concentrations (µg/L) during each common pool brook trout *in situ* bioassay. Open circles, connected by linear interpolation, indicate both measured and estimated Al_{im} values. Bioassays are ordered from low to high mortality (20-day percent mortality). Adjusted percent mortality (see text for explanation), stream, season, year, and bioassay code are also indicated (page 4 of 9).

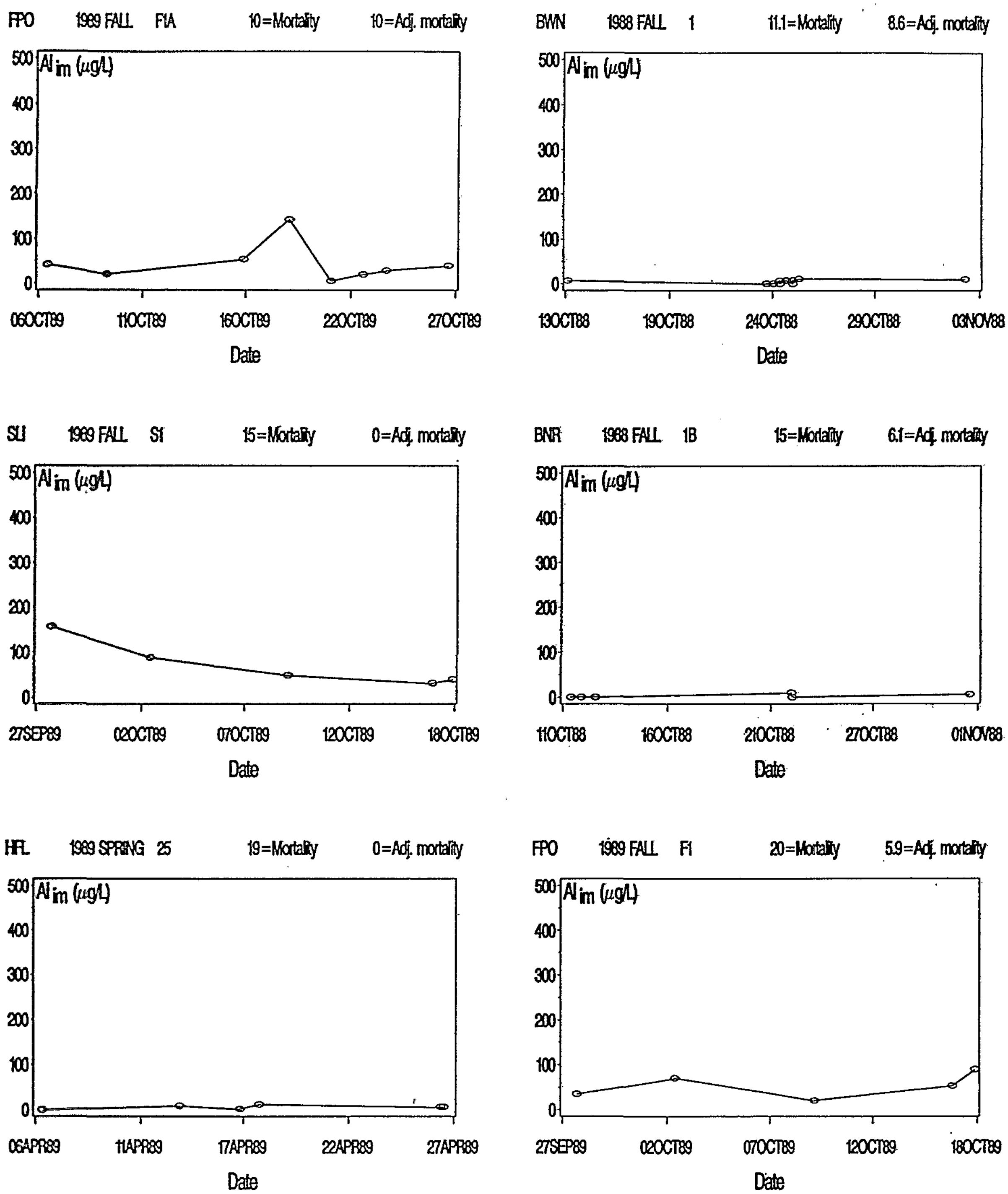


Figure 6-23. Inorganic Al concentrations (µg/L) during each common pool brook trout *in situ* bioassay. Open circles, connected by linear interpolation, indicate both measured and estimated Al_{im} values. Bioassays are ordered from low to high mortality (20-day percent mortality). Adjusted percent mortality (see text for explanation), stream, season, year, and bioassay code are also indicated (page 5 of 9).

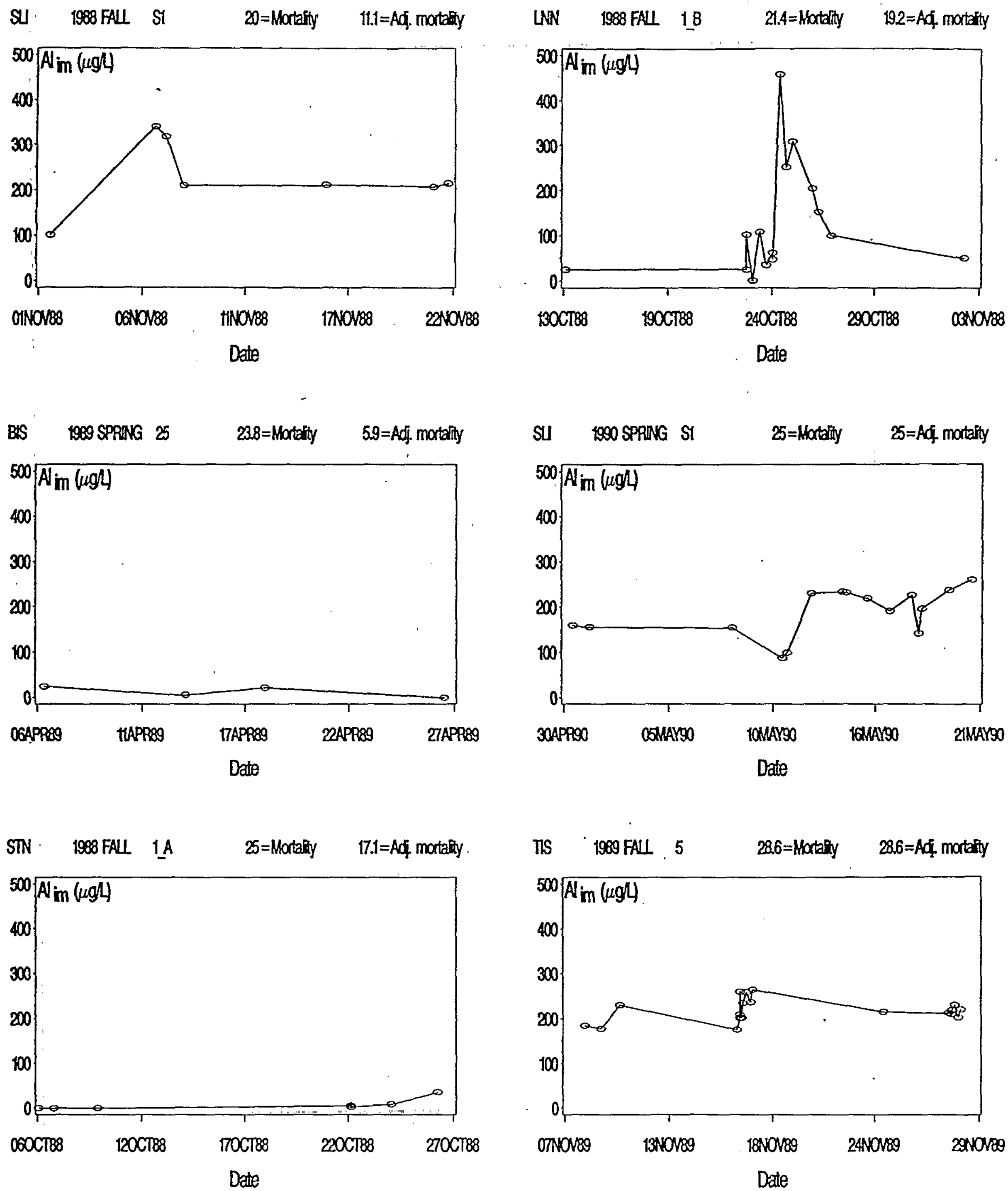


Figure 6-23. Inorganic Al concentrations (µg/L) during each common pool brook trout *in situ* bioassay. Open circles, connected by linear interpolation, indicate both measured and estimated Al_{im} values. Bioassays are ordered from low to high mortality (20-day percent mortality). Adjusted percent mortality (see text for explanation), stream, season, year, and bioassay code are also indicated (page 6 of 9).

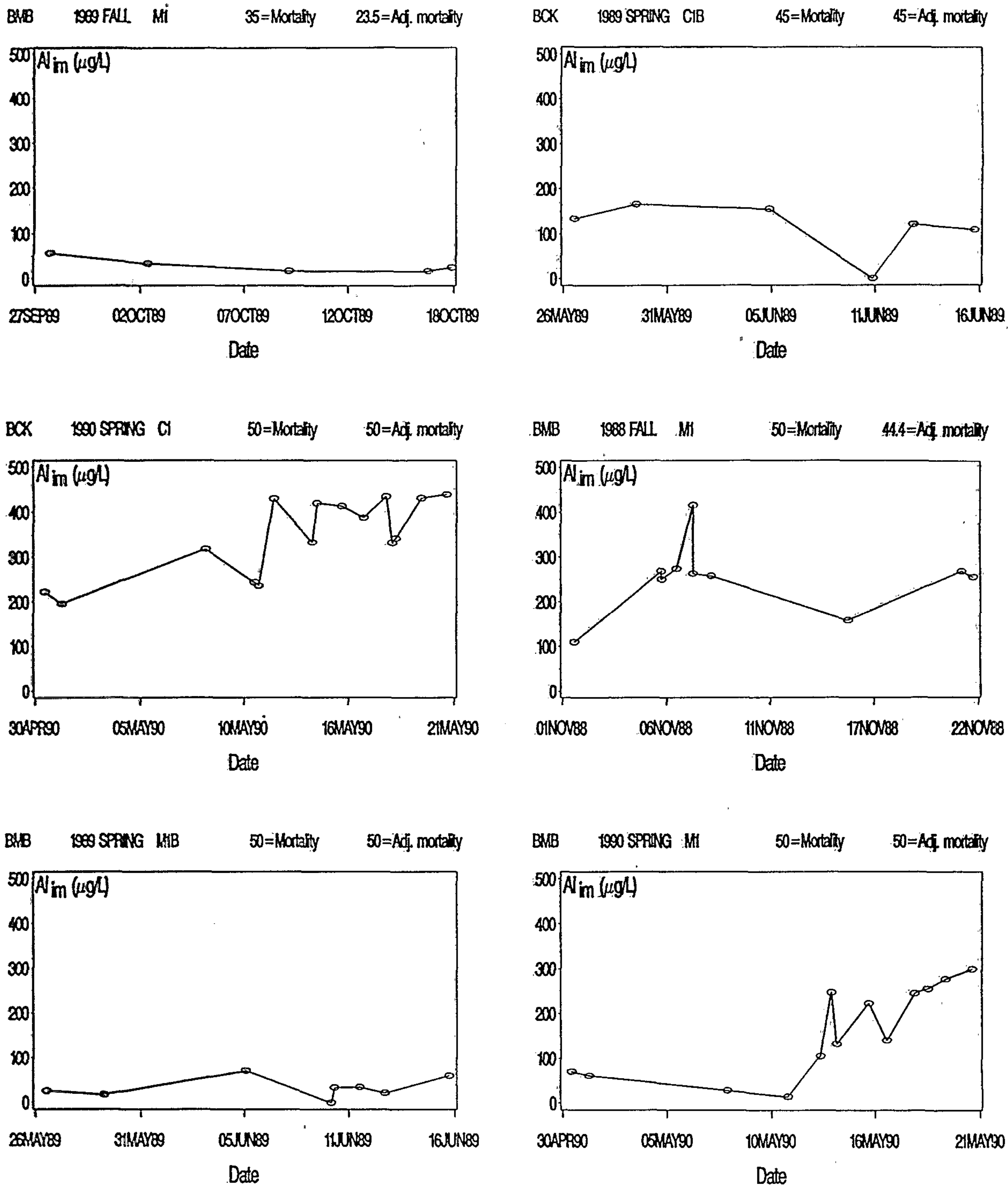


Figure 6-23. Inorganic Al concentrations (µg/L) during each common pool brook trout *in situ* bioassay. Open circles, connected by linear interpolation, indicate both measured and estimated Al_{im} values. Bioassays are ordered from low to high mortality (20-day percent mortality). Adjusted percent mortality (see text for explanation), stream, season, year, and bioassay code are also indicated (page 7 of 9).

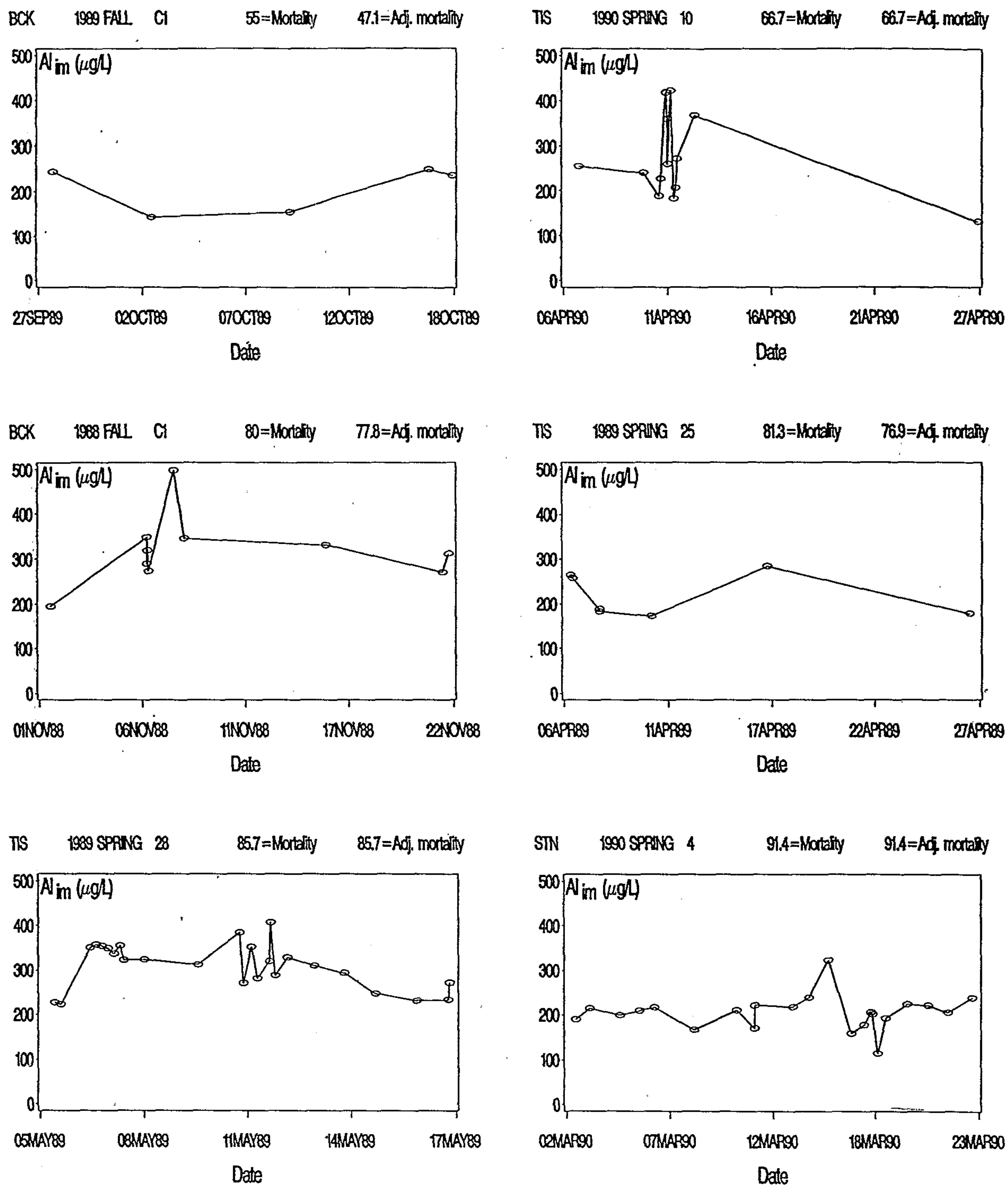


Figure 6-23. **Inorganic Al concentrations (µg/L) during each common pool brook trout *in situ* bioassay. Open circles, connected by linear interpolation, indicate both measured and estimated Al_{im} values. Bioassays are ordered from low to high mortality (20-day percent mortality). Adjusted percent mortality (see text for explanation), stream, season, year, and bioassay code are also indicated (page 8 of 9).**

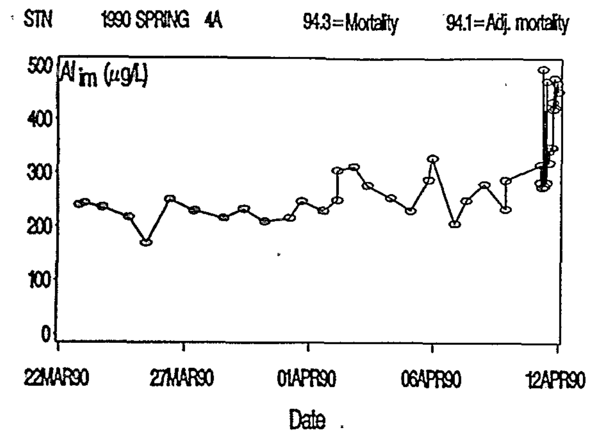


Figure 6-23. Inorganic Al concentrations (µg/L) during each common pool brook trout *in situ* bioassay. Open circles, connected by linear interpolation, indicate both measured and estimated Al_{im} values. Bioassays are ordered from low to high mortality (20-day percent mortality). Adjusted percent mortality (see text for explanation), stream, season, year, and bioassay code are also indicated (page 9 of 9).

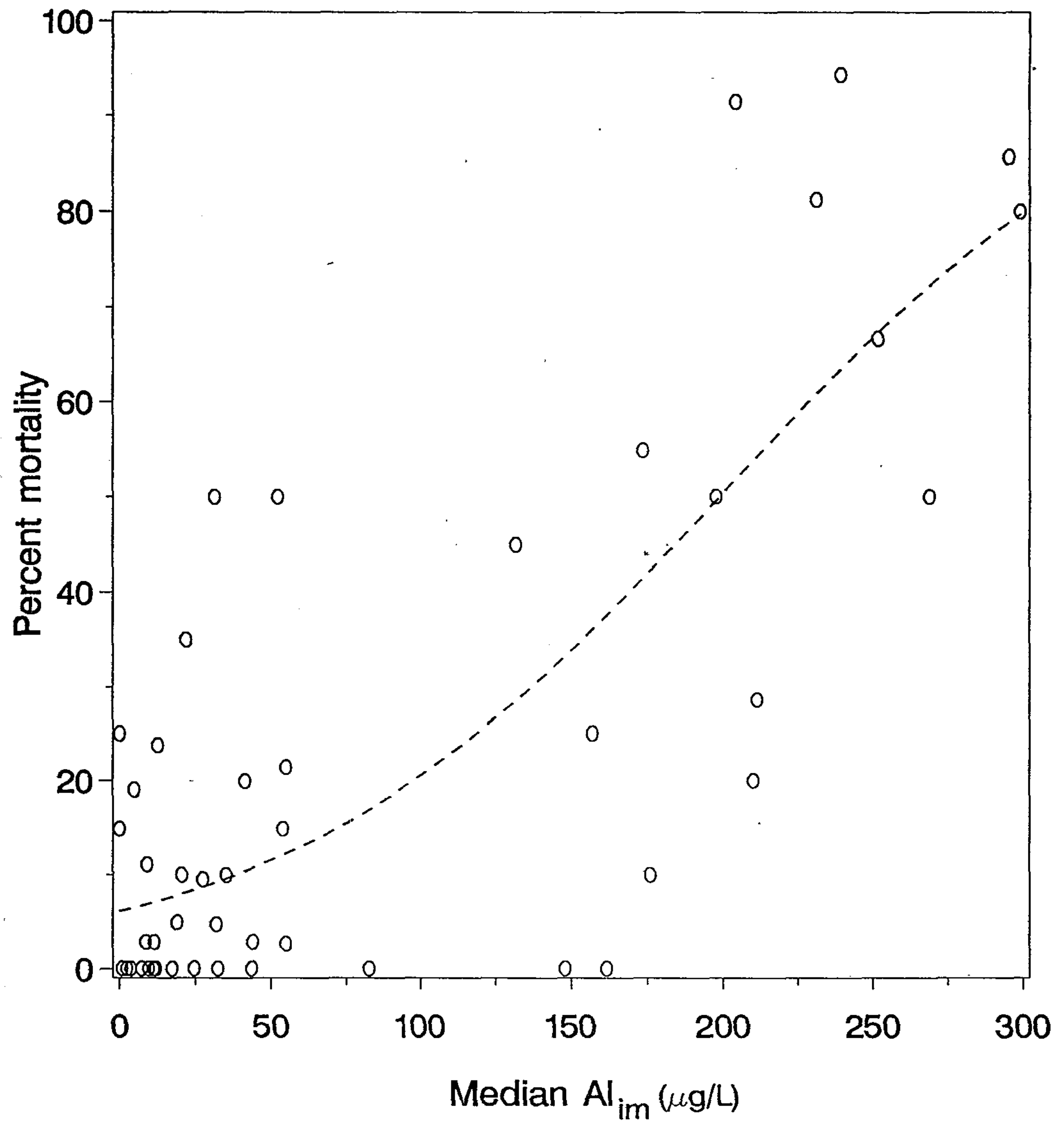


Figure 6-24. 20-day percent mortality of brook trout as a function of the time-weighted median Al_{im} concentration (μg/L): observed mortality (open circles) and predicted mortality (dashed line) based on best single-variable logistic model (see Table 6-11).

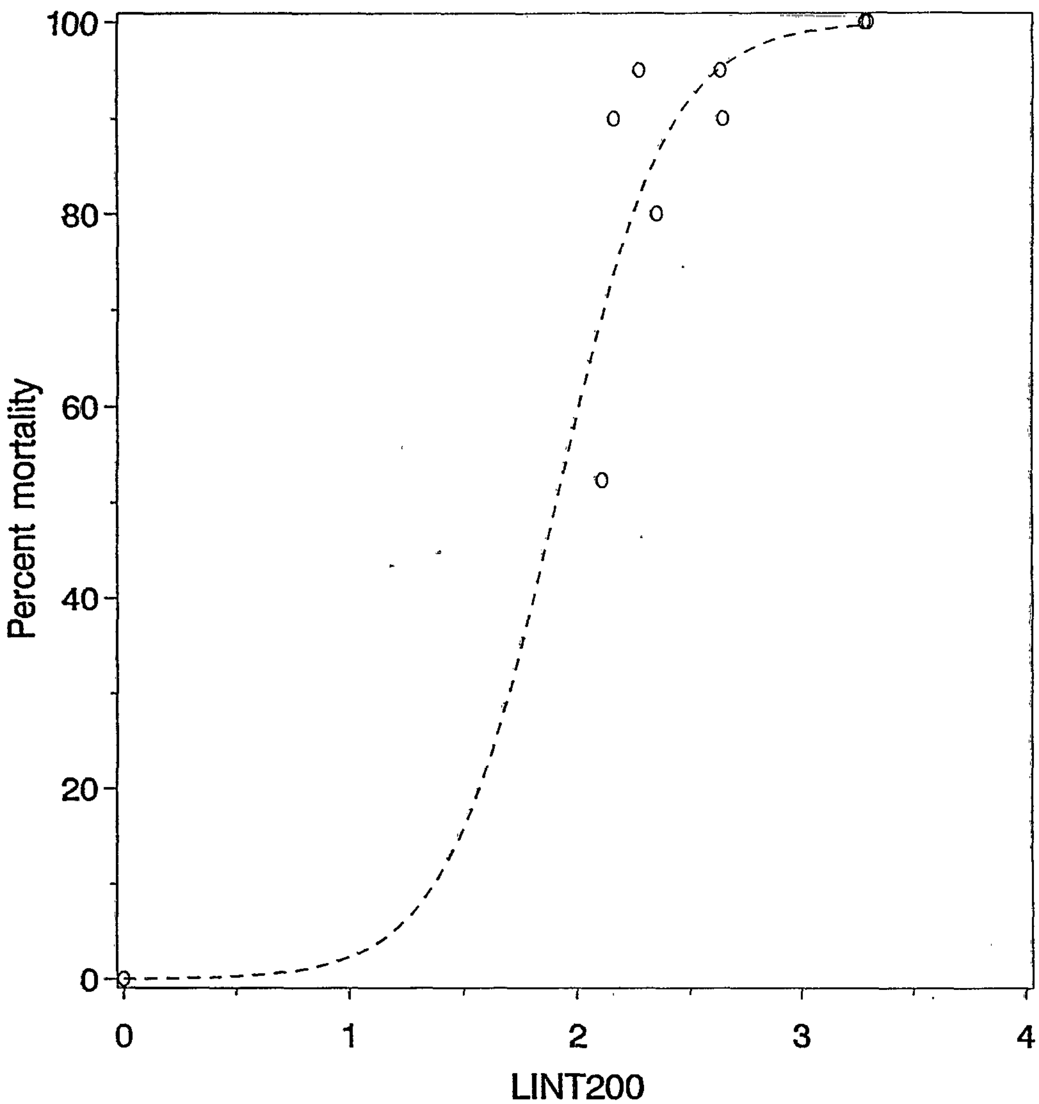


Figure 6-25. 20-day percent mortality of blacknose dace as a function of the log of the integral of concentration duration for Al_{im} > 200 μg/L: observed mortality (open circles) and predicted mortality (dashed line) based on best overall logistic model (see Table 6-15). Eight of 16 bioassays had observed mortality = 0.

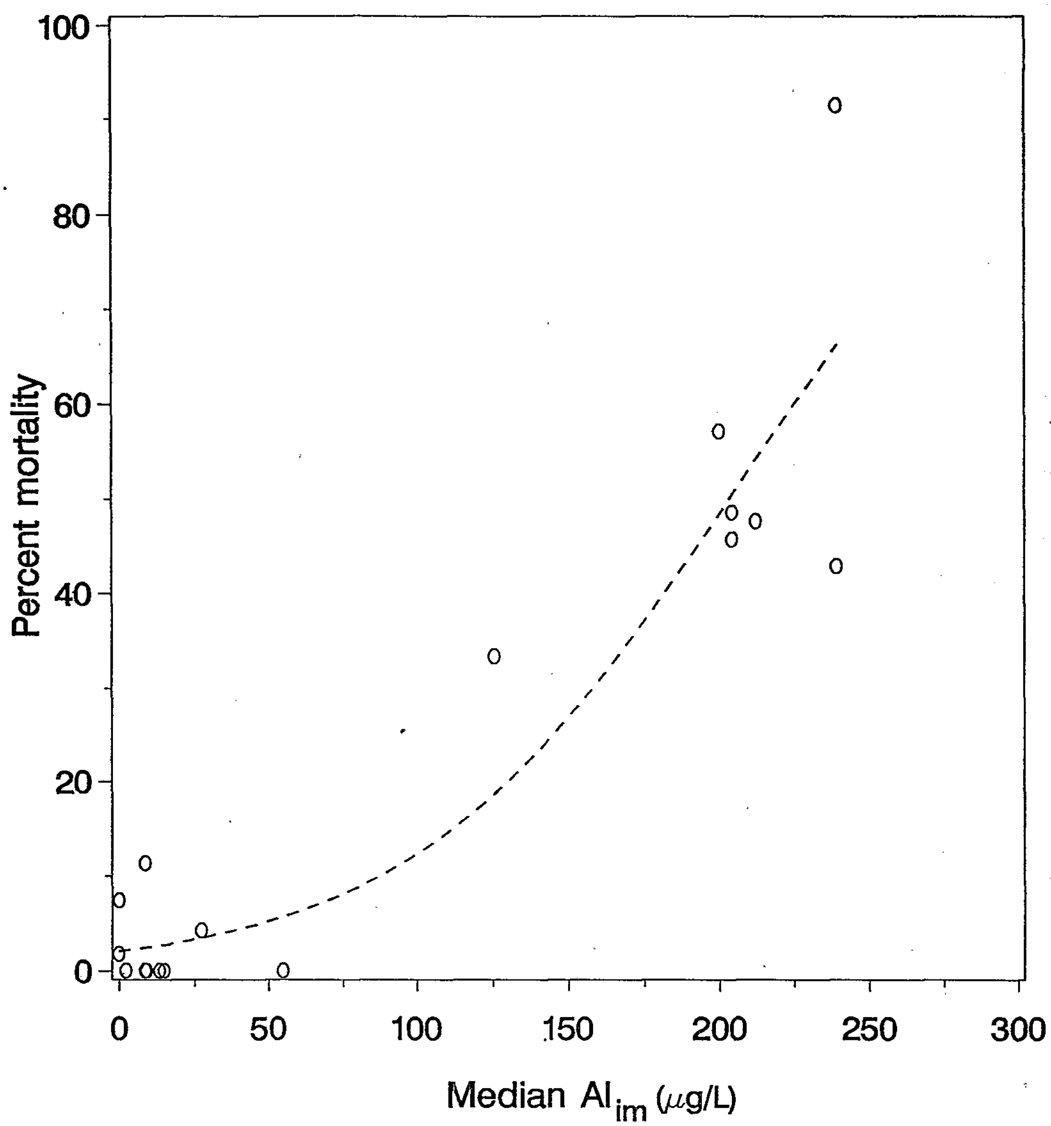


Figure 6-26. 20-day percent mortality of sculpin (mottled and slimy) in Pennsylvania streams as a function of the time-weighted median Al_{im} concentration (µg/L): observed mortality (open circles) and predicted mortality (dashed line) (see Table 6-16).

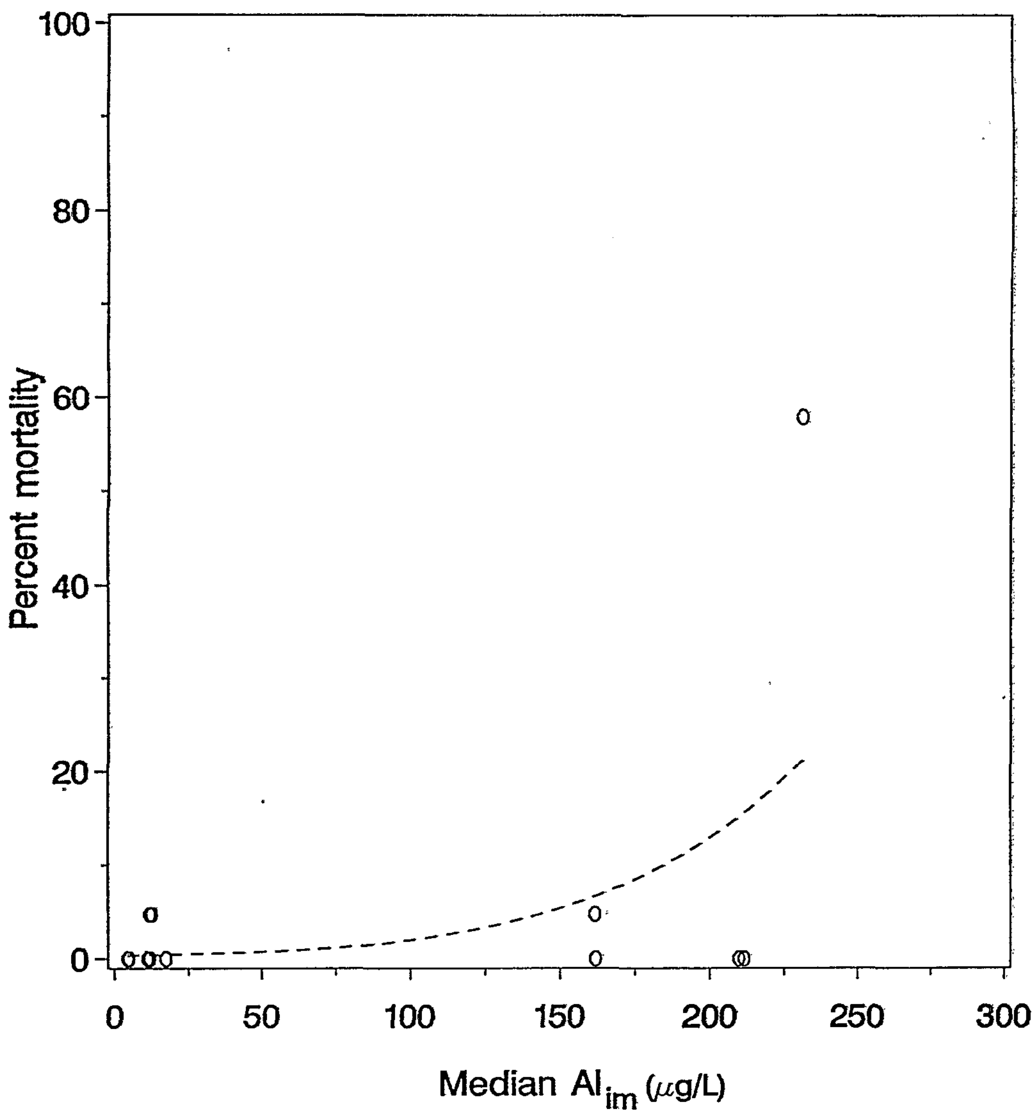


Figure 6-27. 20-day percent mortality of sculpin (slimy) in Catskill streams as a function of the time-weighted median Al_{im} concentration (μg/L): observed mortality (open circles) and predicted mortality (dashed line) (see Table 6-16).

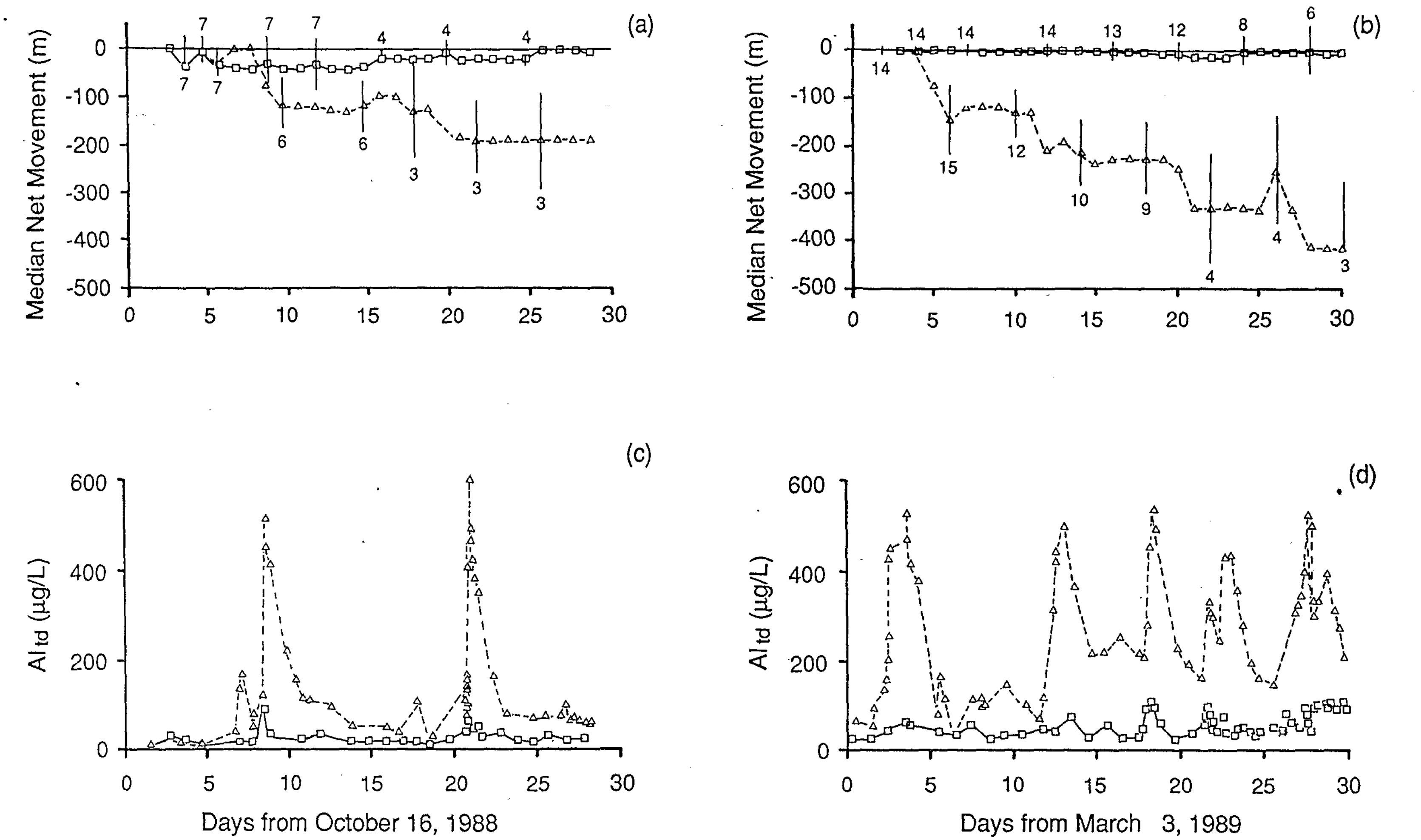


Figure 6-28. Total dissolved aluminum concentrations at continuous monitoring stations and median net movement of brook trout in Linn Run (triangles) and Baldwin Creek (squares). Negative values for movement indicate downstream relative to initial location. Sample size and ± 1 SE (vertical bars) are shown for fish movement on representative days (Source: Gagen, 1991).

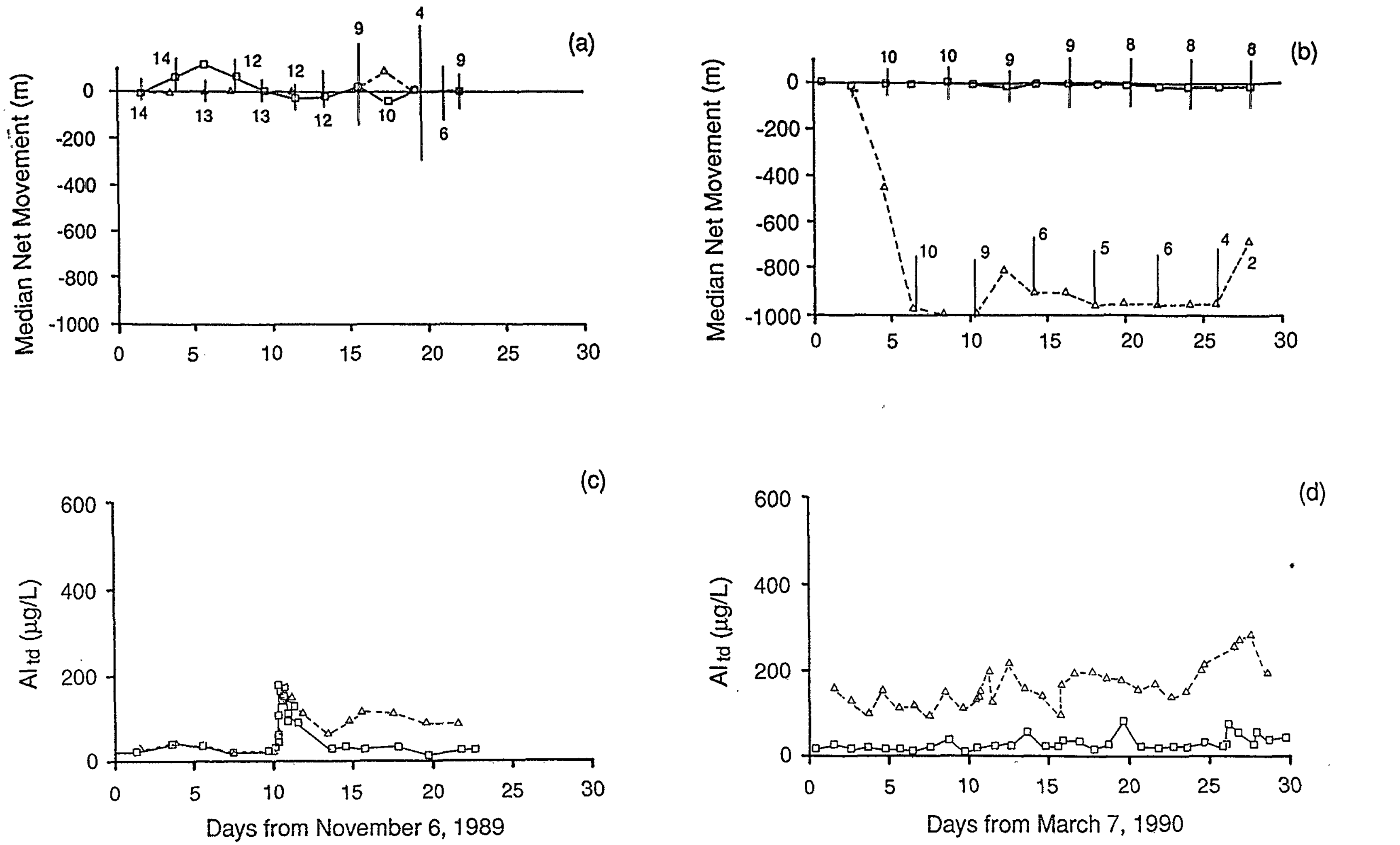


Figure 6-29. **Total dissolved aluminum concentrations at continuous monitoring stations and median net movement of brook trout in Stone Run (triangles) and Benner Run (squares). Negative values for movement indicate downstream relative to initial location. Sample size and ± 1 SE (vertical bars) are shown for fish movement on representative days (Source: Gagen, 1991).**

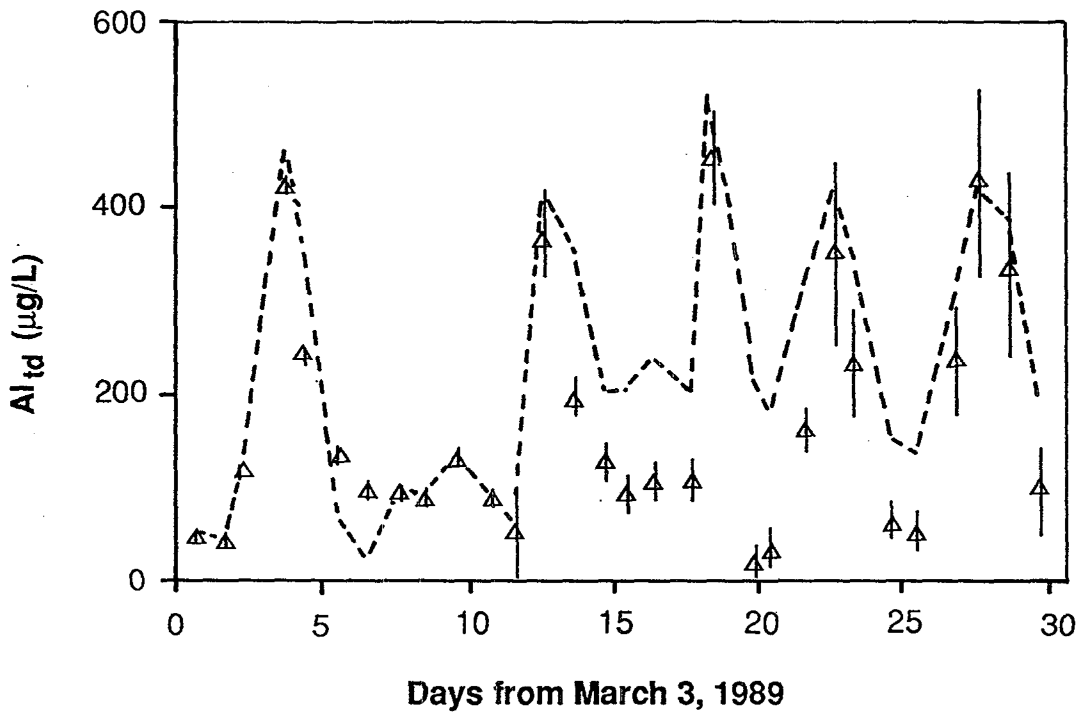


Figure 6-30. **Median stream total dissolved Al concentration at locations of transmitter-equipped fish (triangles; vertical bars = ± 1 SE) and Al_{td} concentrations of concurrent samples collected at the Linn Run continuous monitoring station (broken line) (Source: Gagen, 1991).**

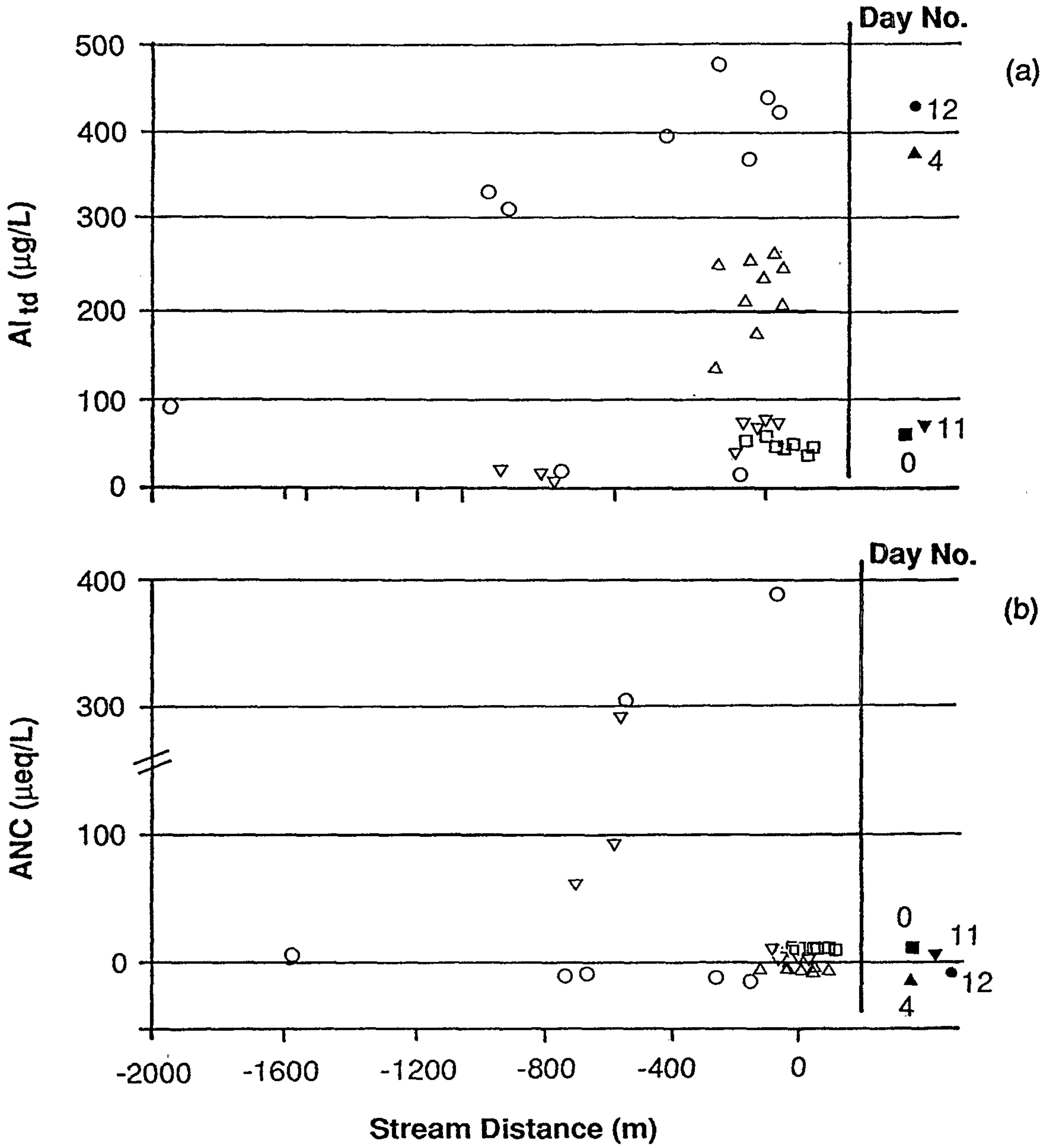


Figure 6-31. Linn Run Al_{td} concentrations and ANC at individual fish locations versus position along stream length on days 0, 4, 11, and 12. Day 0 was March 3, 1989. Solid symbols, to the right of the vertical bar, indicate concurrent data from the Linn Run continuous monitoring station. Stream distance is relative to the continuous monitoring station and negative numbers correspond to downstream (Source: Gagen, 1991).

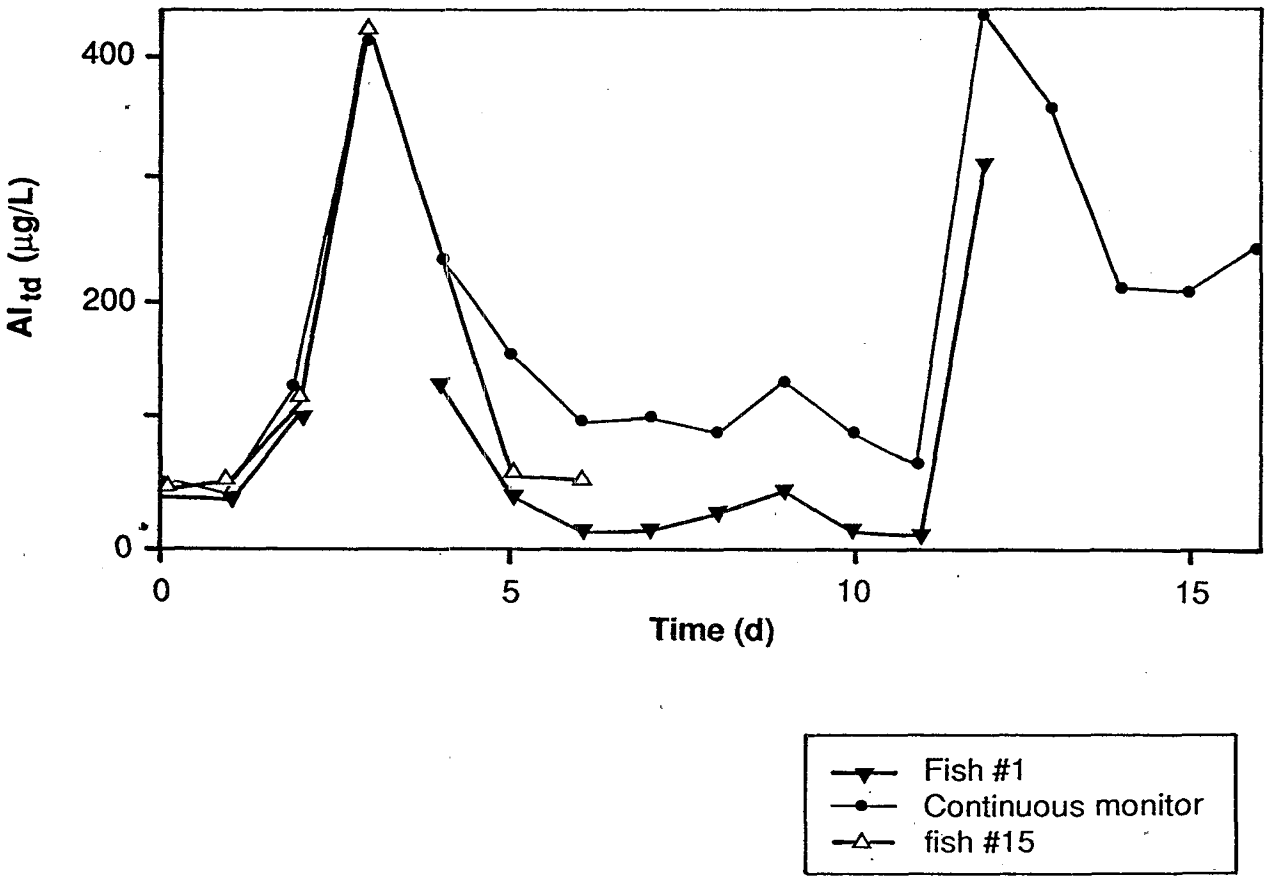


Figure 6-32. Linn Run Al_{td} concentrations during the spring 1989 telemetry study for samples collected at the continuous monitoring station versus samples collected at the locations of two radio-tagged fish that died. The last plotted Al value indicates when the fish was found dead (Source: DeWalle et al., 1991).

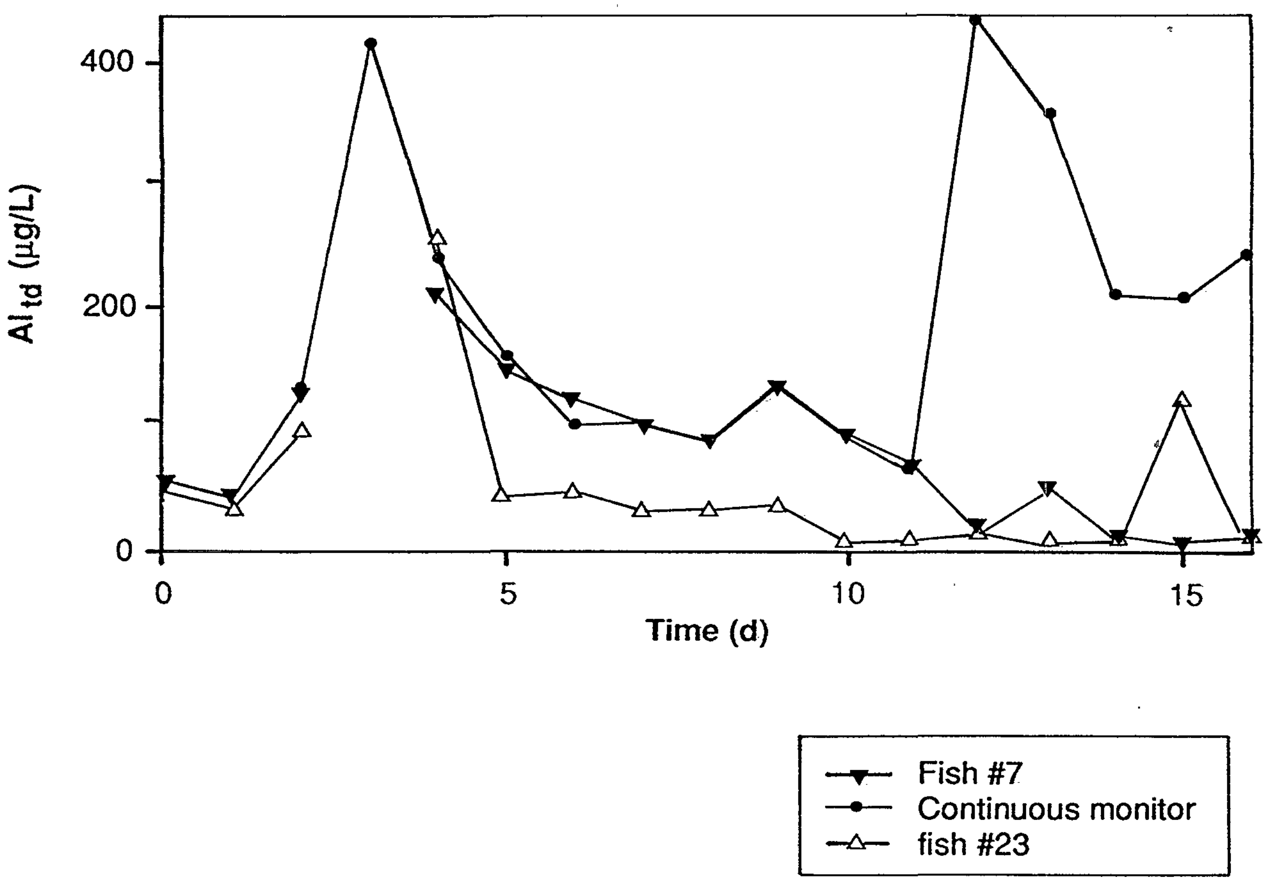


Figure 6-33. Linn Run Al_{td} concentrations during the spring 1989 telemetry study for samples collected at the continuous monitoring station versus samples collected at the locations of two radio-tagged fish that moved to microhabitats or refuges with lower Al and survived (Source: DeWalle et al., 1991).

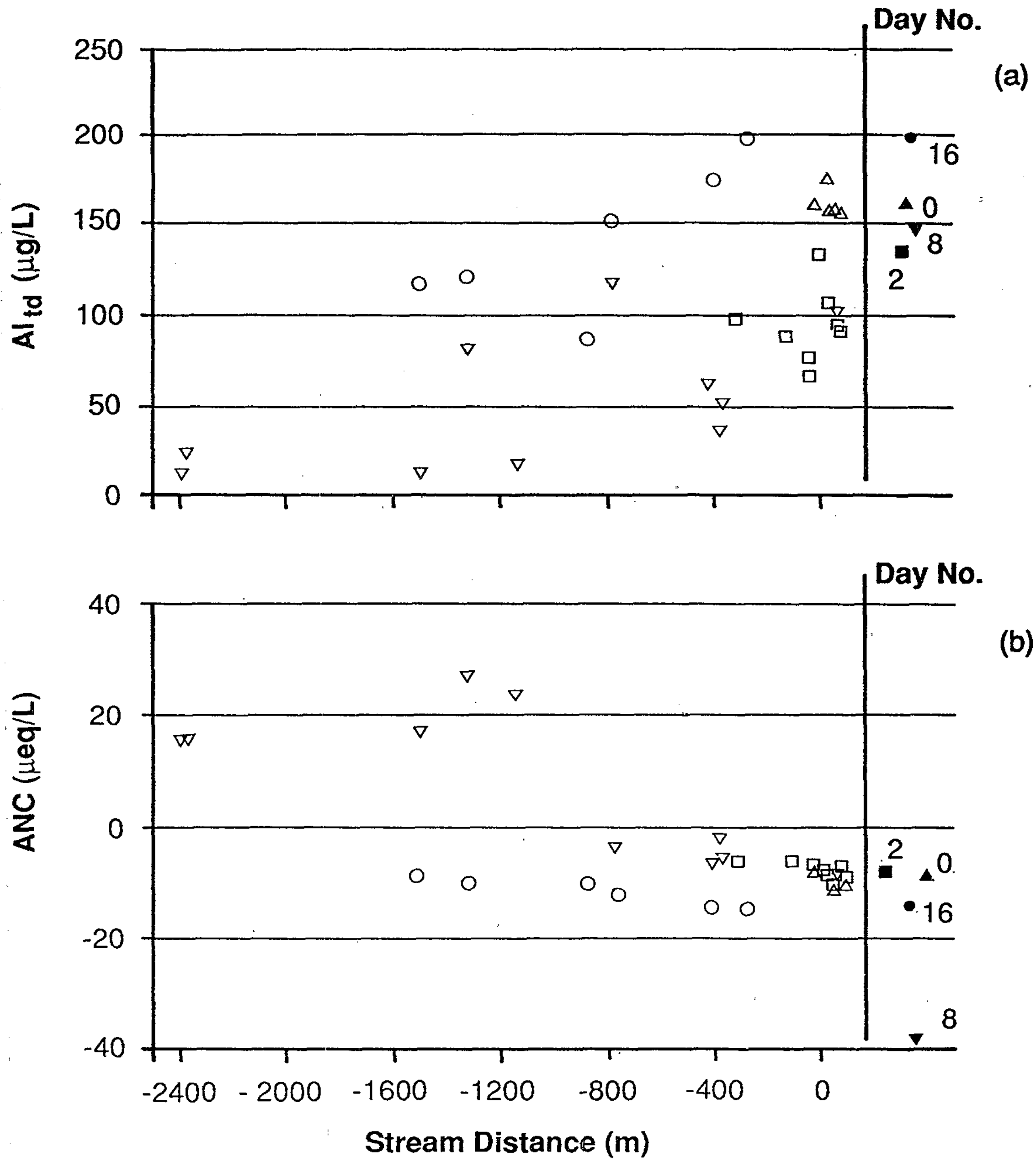


Figure 6-34. Stone Run Al_{td} concentrations and ANC at individual fish locations versus position along stream length on days 0, 2, 8, and 16 of spring 1990 telemetry study. Day 0 was March 7, 1990. Solid symbols, to the right of the vertical bar, indicate concurrent data from the Stone Run continuous monitoring station. Stream distance is relative to the continuous monitoring station; negative numbers correspond to downstream (Source: Gagen, 1991).

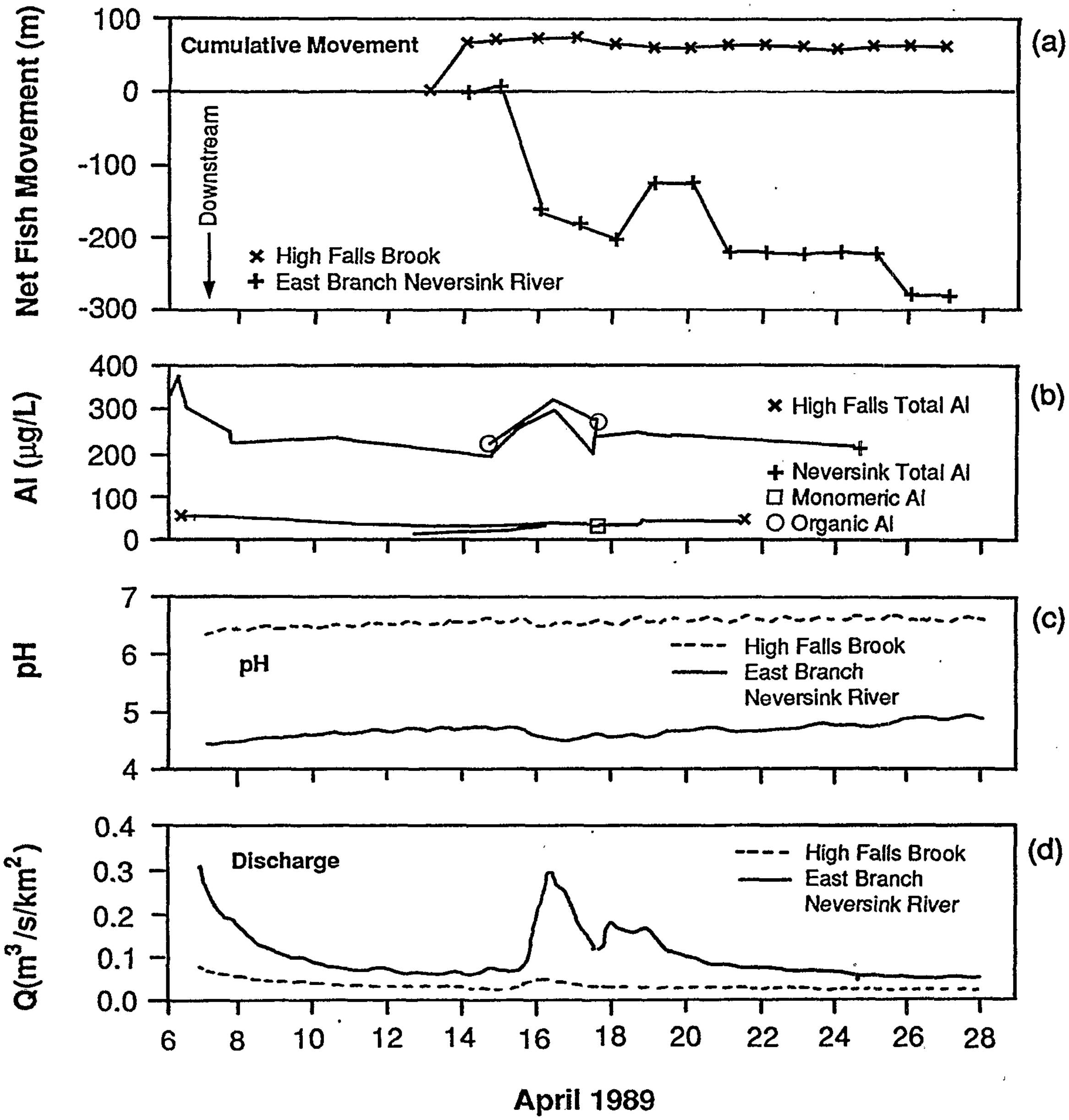


Figure 6-35. **Net downstream movement of radio-tagged fish, Al_{td} concentrations, pH, and stream discharge during the spring 1989 radiotelemetry study in High Falls Brook and East Branch Neversink River (Source: Murdoch et al., 1991).**

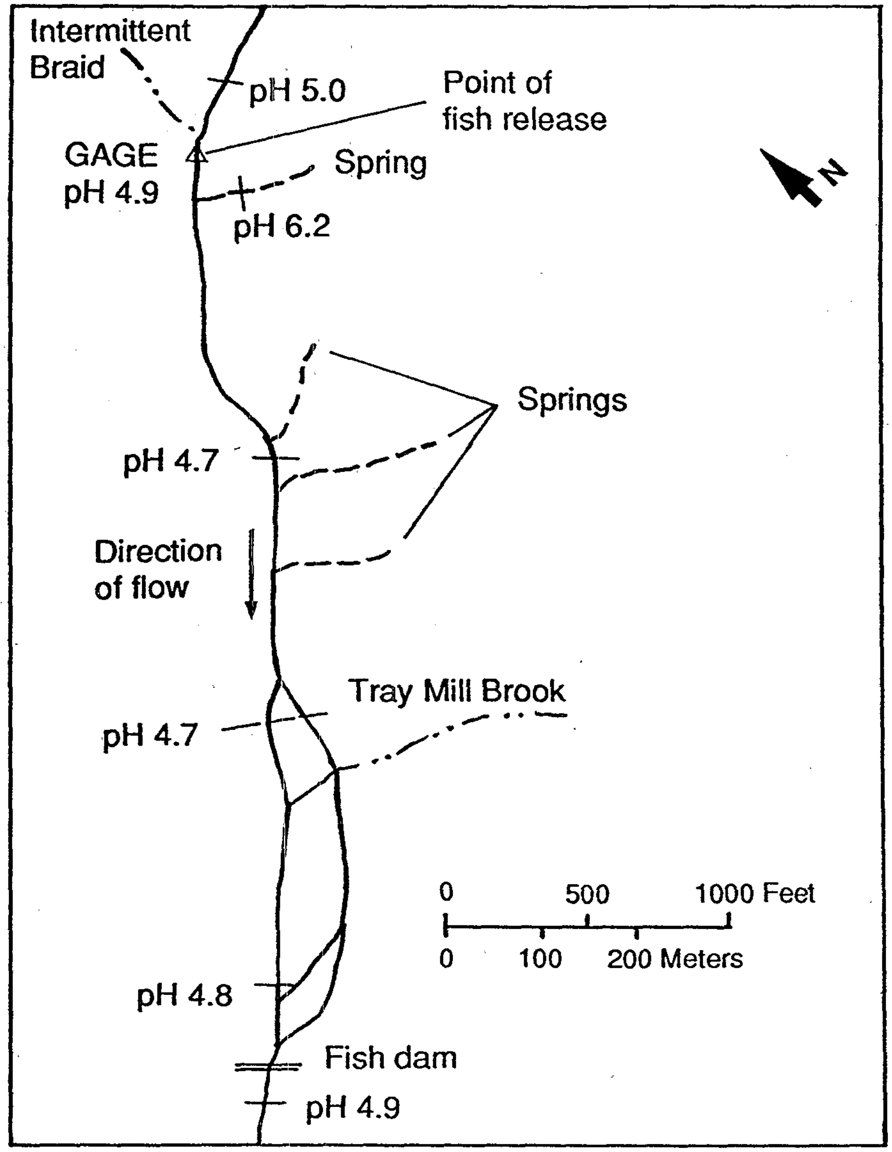


Figure 6-36. Longitudinal changes in stream pH along the East Branch Neversink River during the spring 1989 radiotelemetry study (Source: Murdoch et al., 1991).

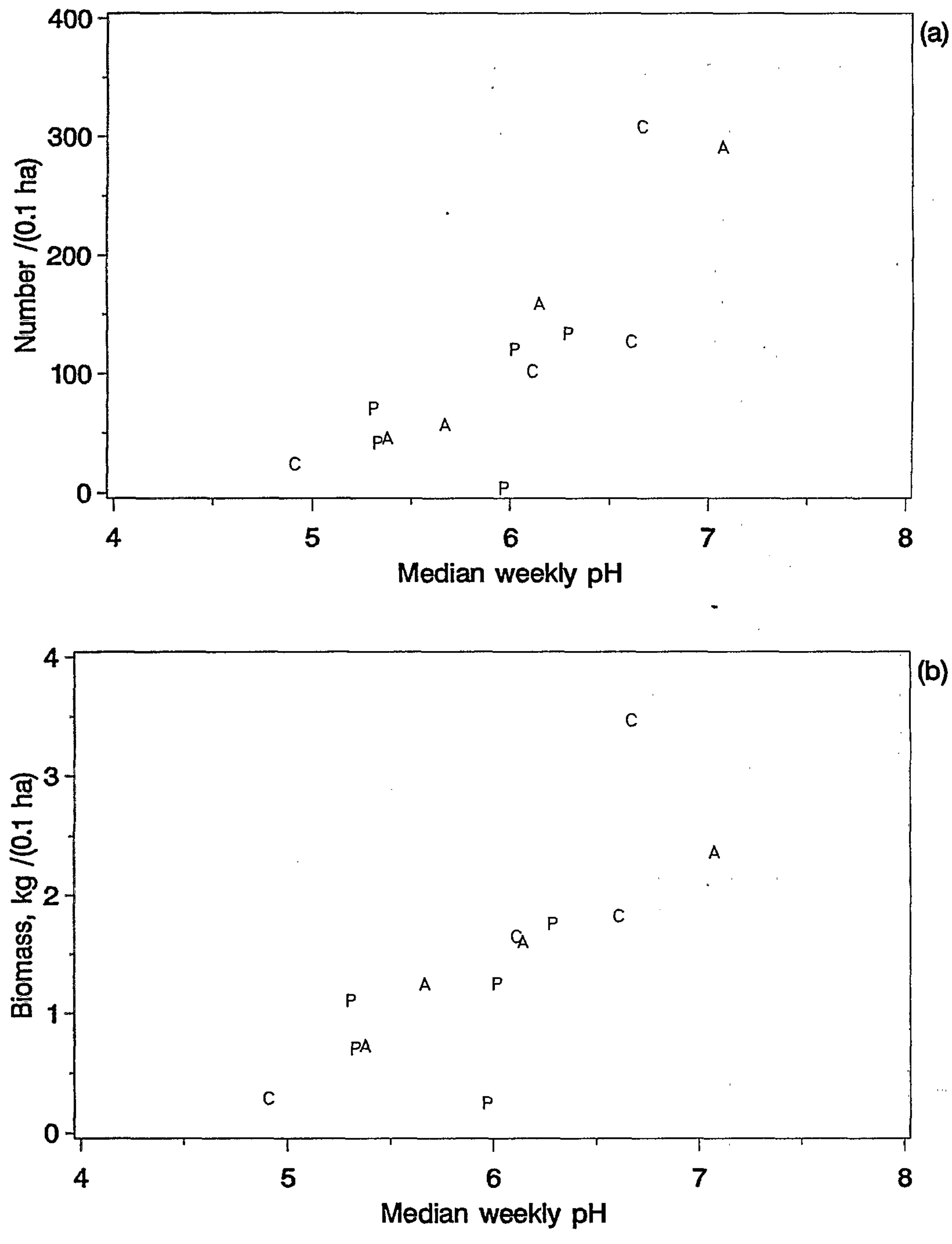


Figure 6-37. (a) Mean density (number/0.1 ha) and (b) biomass (kg/0.1 ha) of brook trout (average of fall 1988, 1989, and spring 1989, 1990 surveys) in ERP study streams as a function of median weekly pH (Tables 5-1 to 5-13). Streams labeled by region: A = Adirondacks, C = Catskills, and P = Pennsylvania.

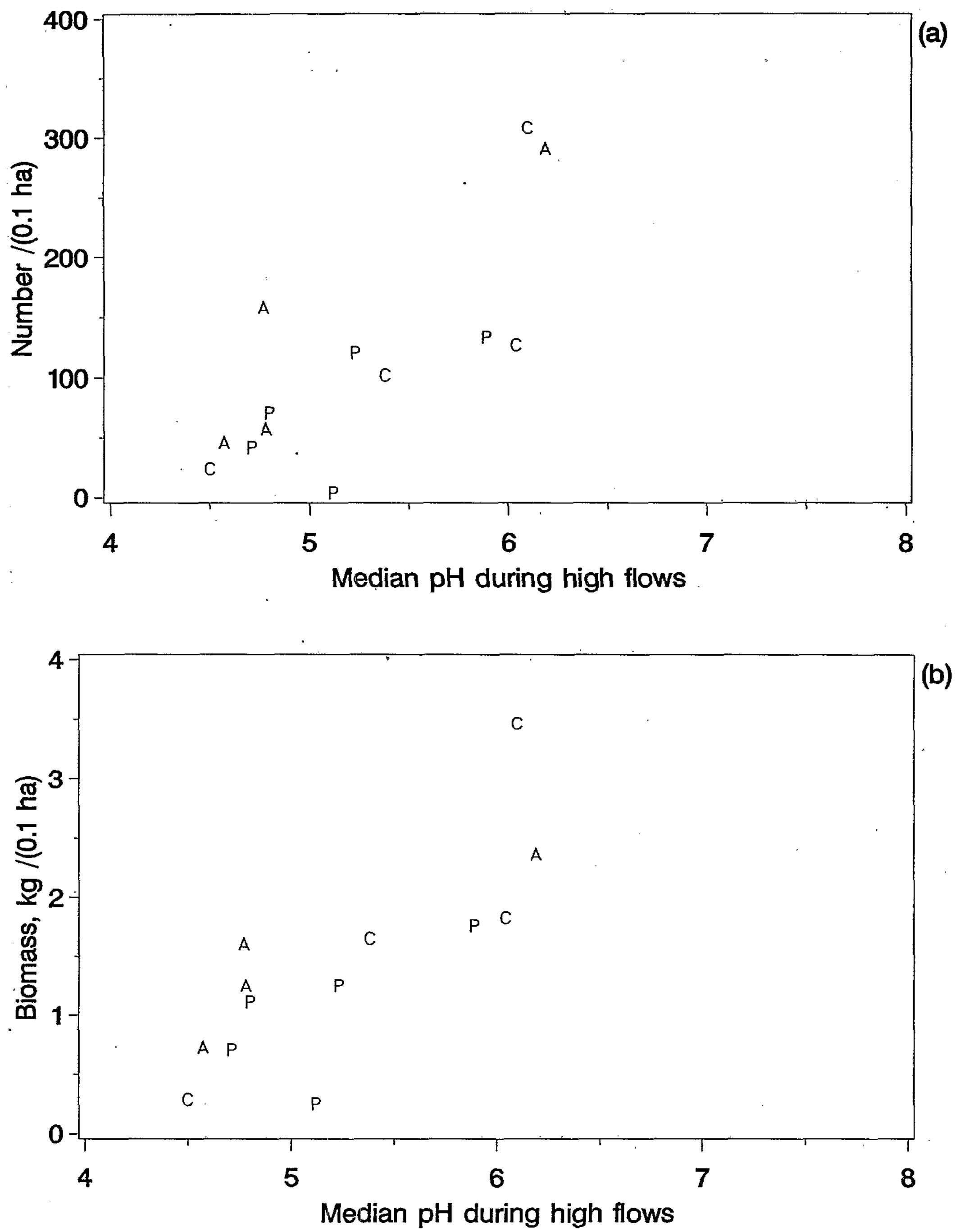


Figure 6-38. (a) Mean density (number/0.1 ha) and (b) biomass (kg/0.1 ha) of brook trout (average of fall 1988, 1989, and spring 1989, 1990 surveys) in ERP study streams as a function of median pH during the 95th percentile high flow (Table 5-15). Streams labeled by region: A = Adirondacks, C = Catskills, and P = Pennsylvania.

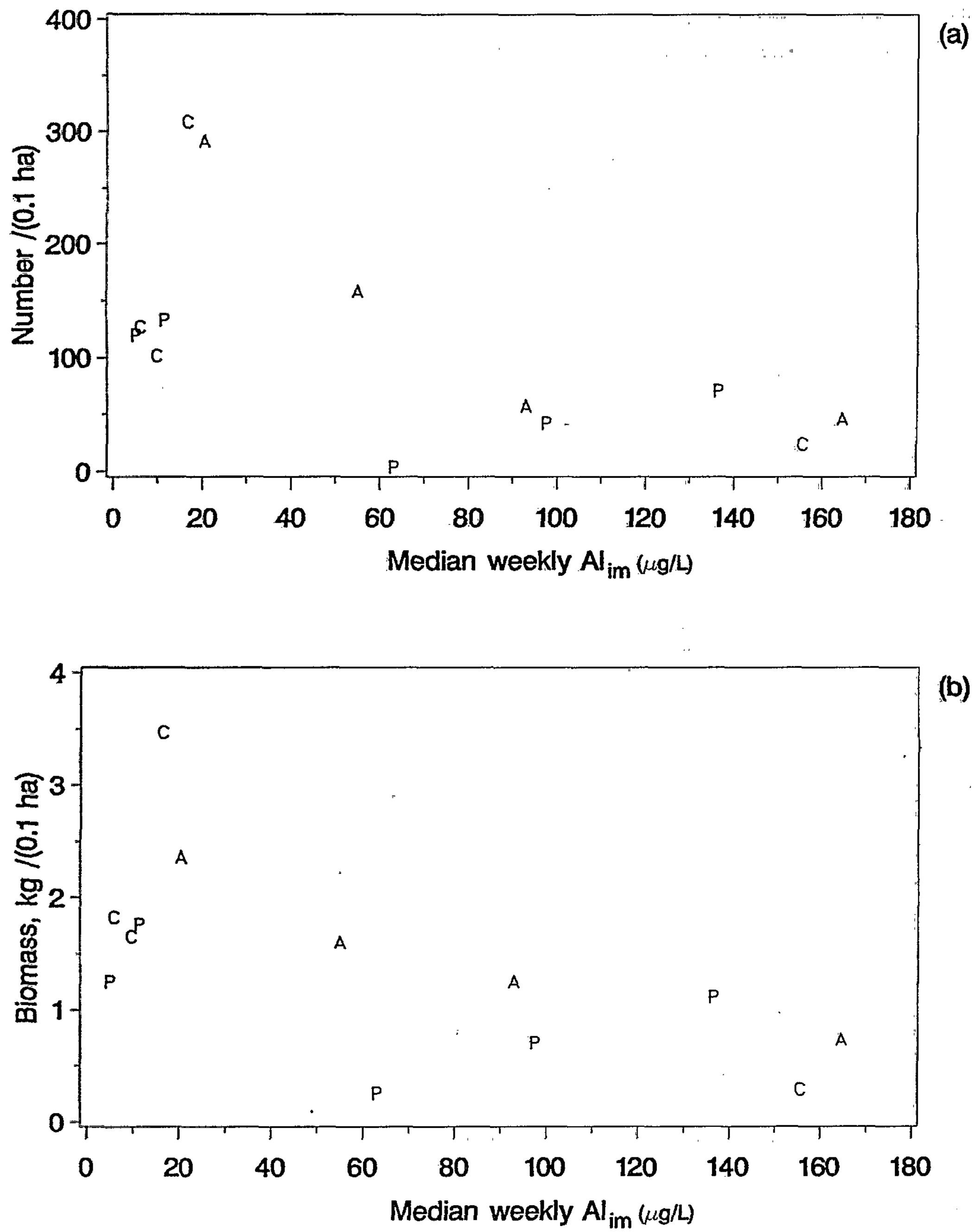


Figure 6-39. (a) Mean density (number/0.1 ha) and (b) biomass (kg/0.1 ha) of brook trout (average of fall 1988, 1989, and spring 1989, 1990 surveys) in ERP study streams as a function of median weekly inorganic Al concentration (µg/L) (Tables 5-1 to 5-13). Streams labeled by region: A = Adirondacks, C = Catskills, and P = Pennsylvania.

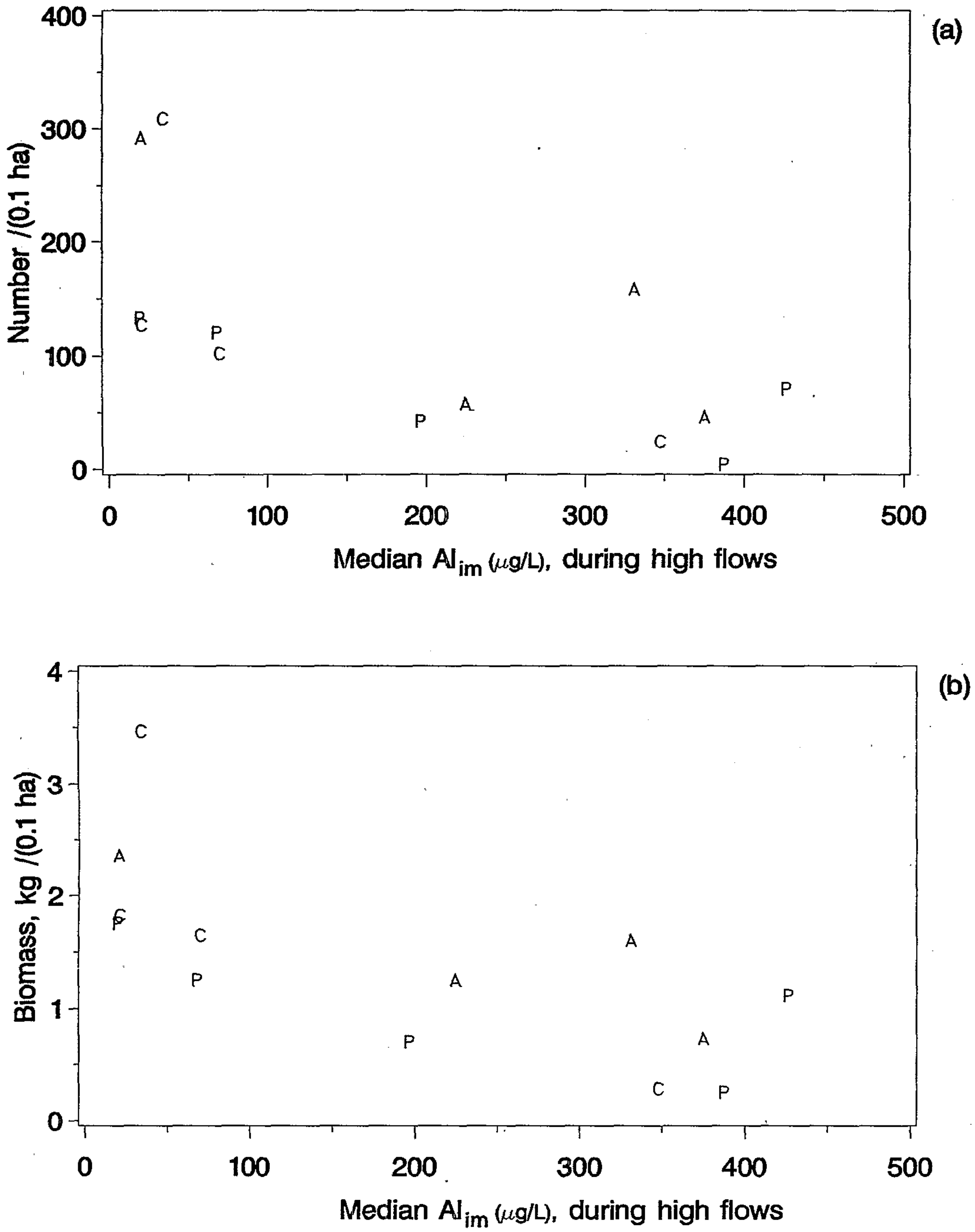


Figure 6-40. (a) Mean density (number/0.1 ha) and (b) biomass (kg/0.1 ha) of brook trout (average of fall 1988, 1989, and spring 1989, 1990 surveys) in ERP study streams as a function of median Al_{im} (µg/L) during the 95th percentile high flow (Table 5-15). Streams labeled by region: A = Adirondacks, C = Catskills, and P = Pennsylvania.

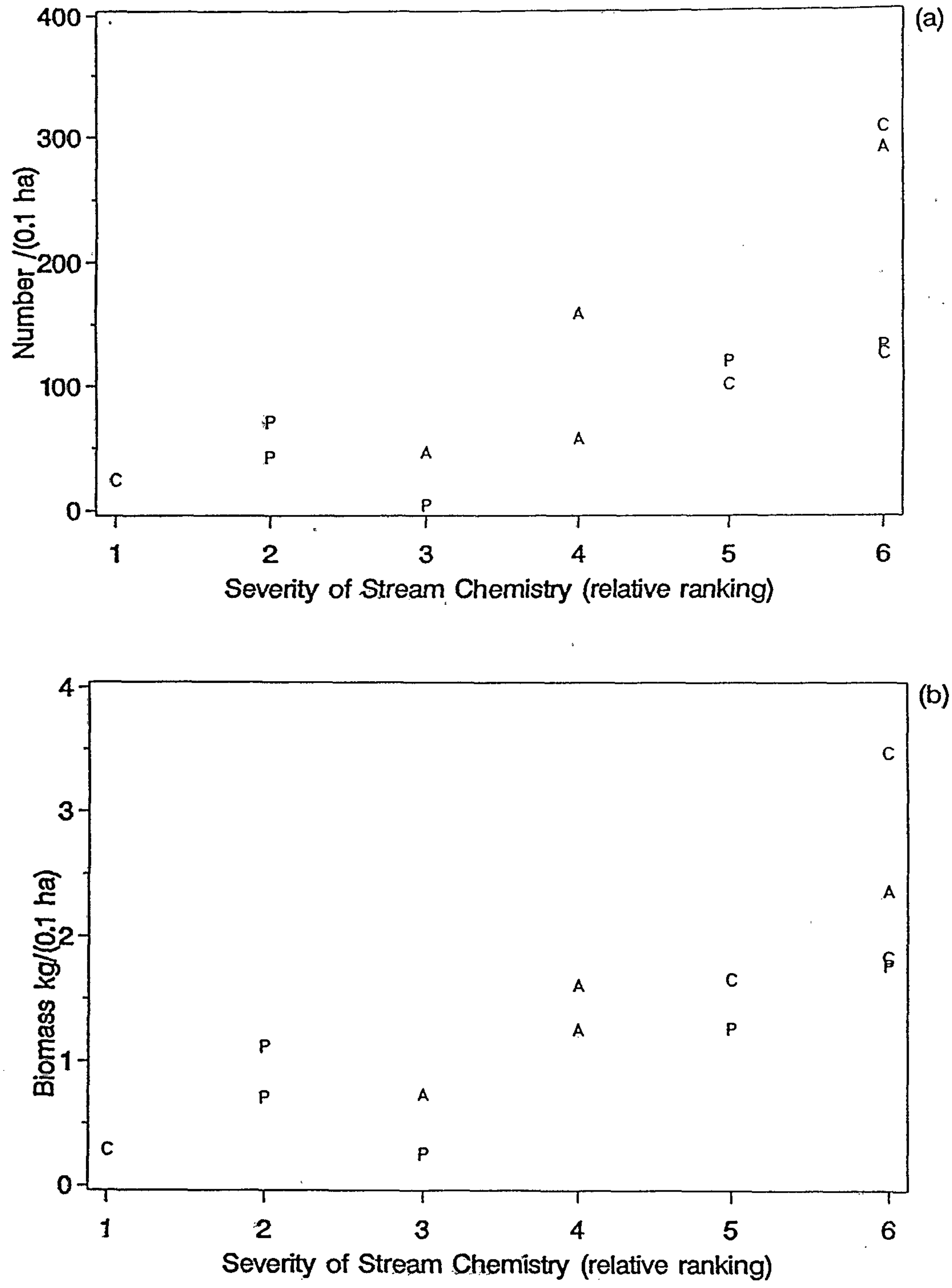


Figure 6-41. (a) Mean density (number per 0.1 ha) and (b) biomass (kg/0.1 ha) of brook trout (average of fall 1988, 1989, and spring 1989, 1990 surveys) in ERP study streams ranked according to overall severity of chemical conditions in the stream (from most severe, 1, to least severe, 6). Rankings are explained in the text; also see Section 5.2.1. Streams labeled by region: A = Adirondacks, C = Catskills, and P = Pennsylvania.

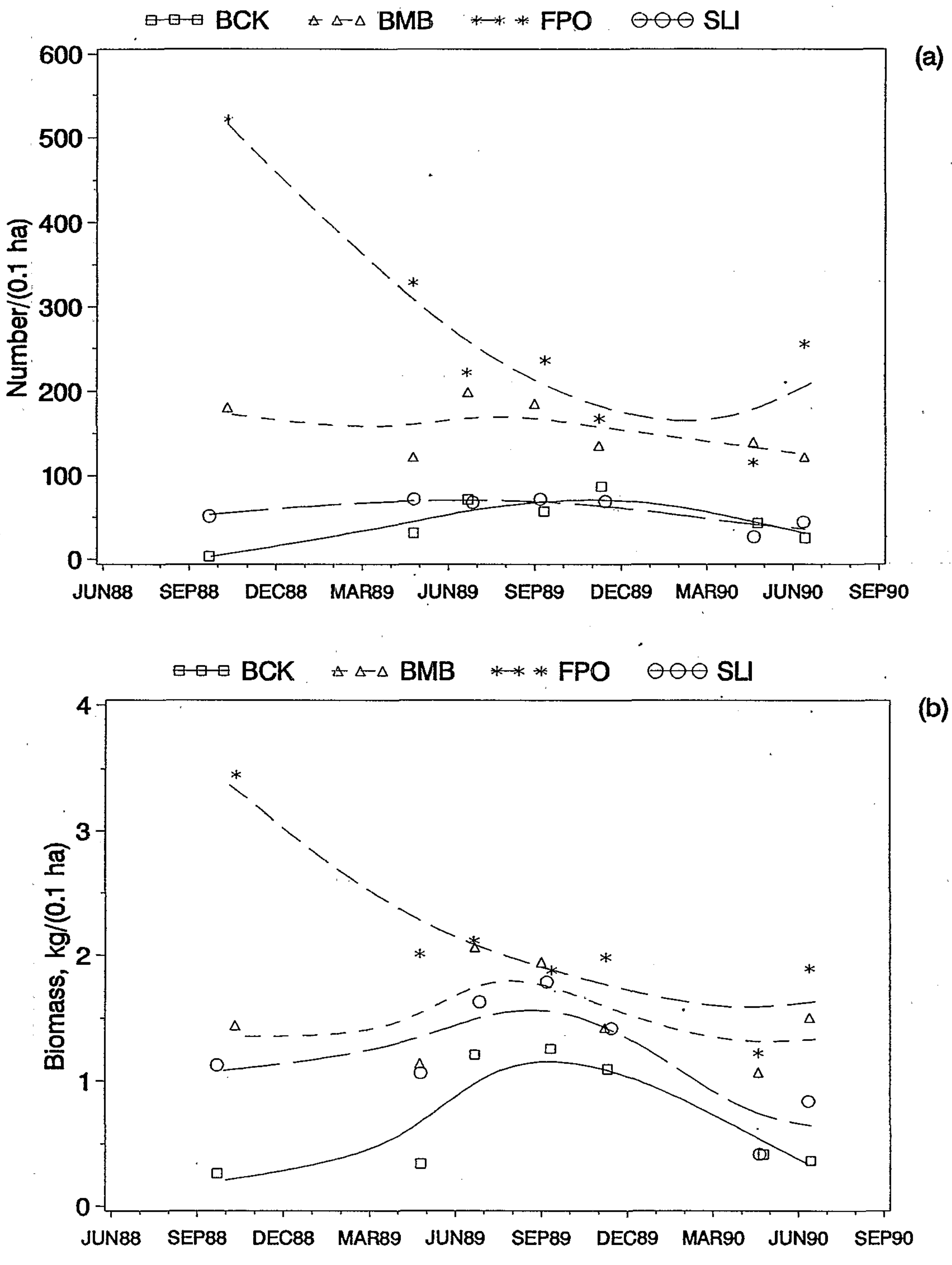
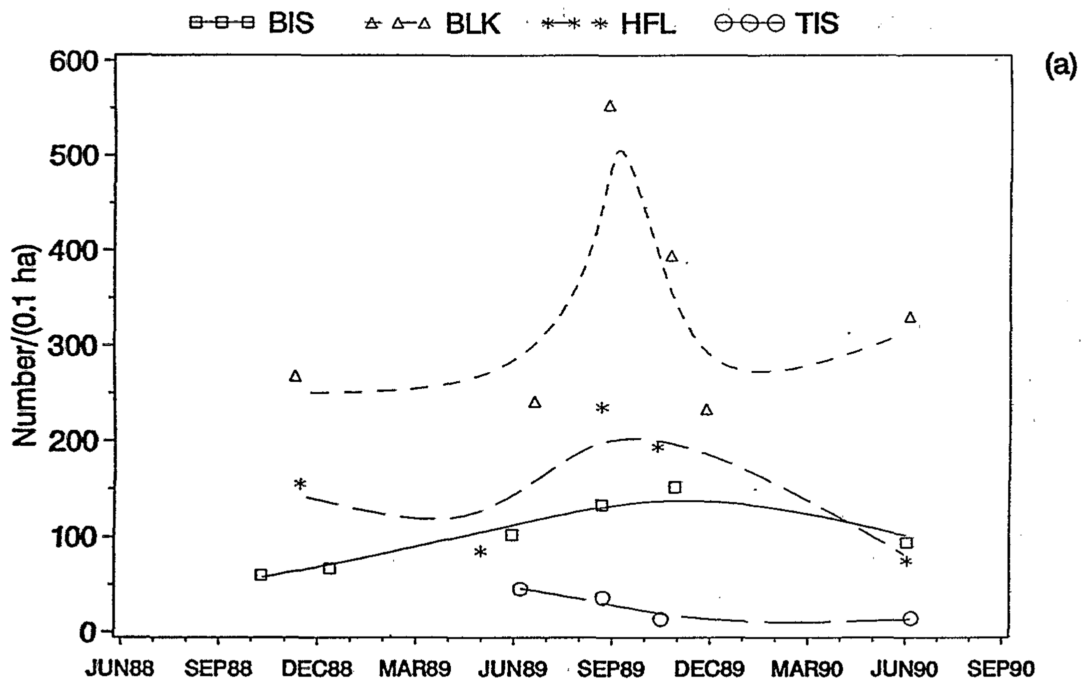


Figure 6-42. **Variations in brook trout (a) density (numbers per 0.1 ha) and (b) biomass (kg/0.1 ha) over time in Adirondack ERP streams. Cubic spline smoothing curves shown to help identify trends in brook trout population abundance. Arrows indicate approximate dates of fish transplants into ERP streams.**



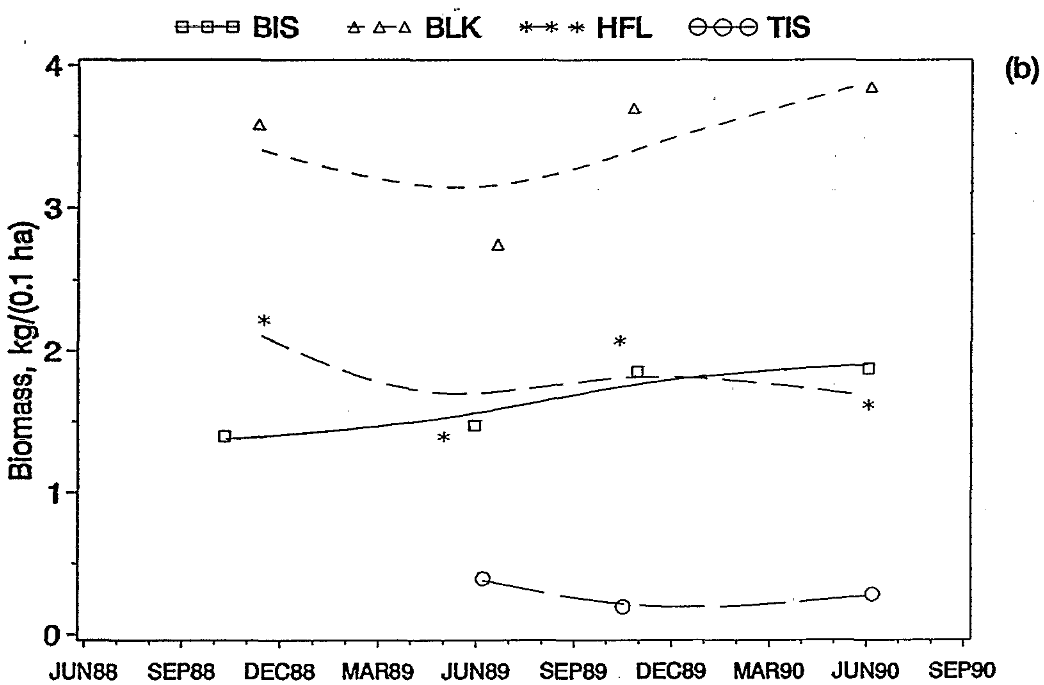


Figure 6-43. Variations in brook trout (a) density (numbers per 0.1 ha) and (b) biomass (kg/0.1 ha) over time in Catskill ERP streams. Cubic spline smoothing curves shown to help identify trends in brook trout population abundance. Arrows indicate approximate dates of fish transplants into ERP streams.

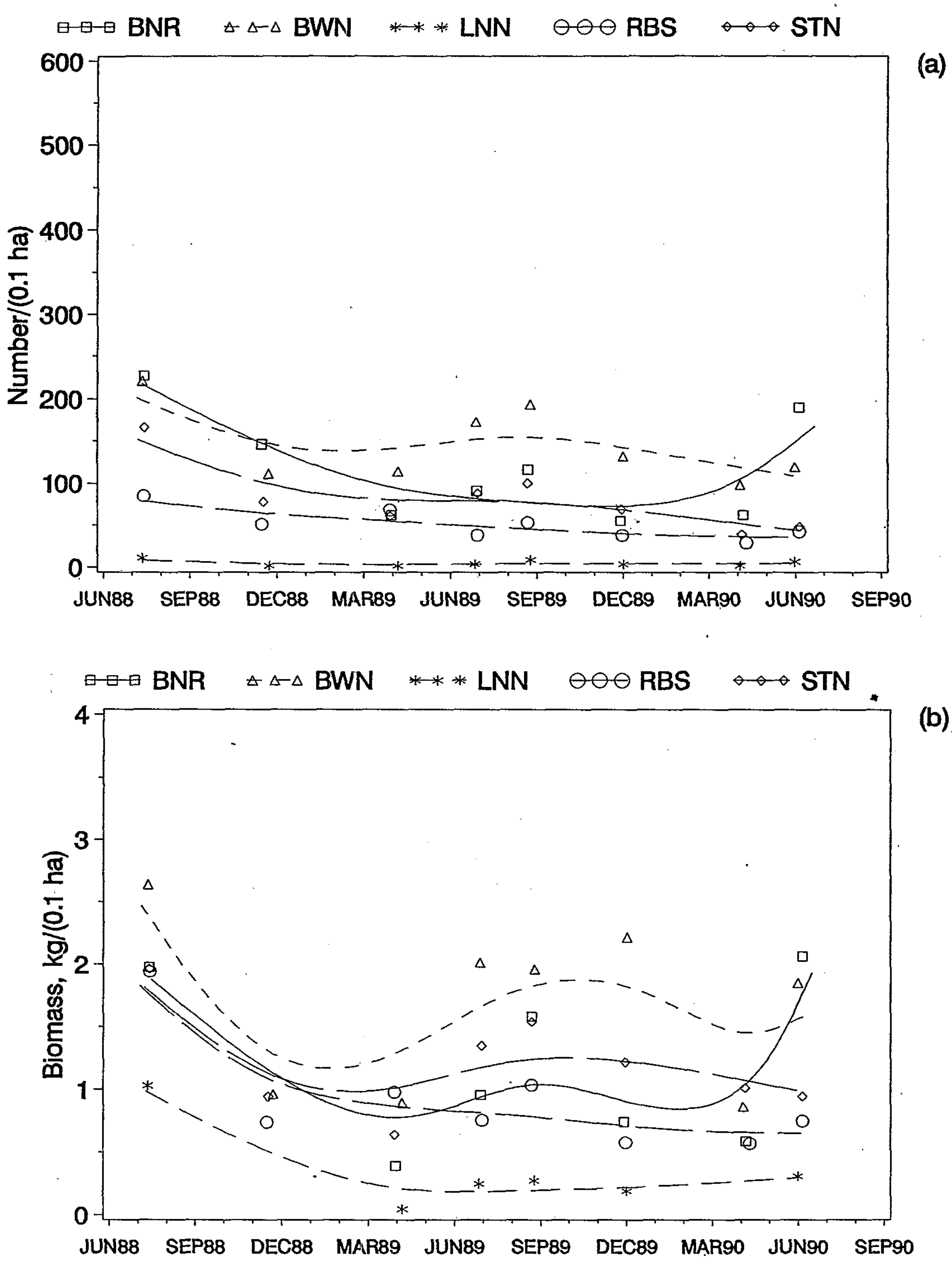


Figure 6-44. Variations in brook trout (a) density (numbers per 0.1 ha) and (b) biomass (kg/0.1 ha) over time in Pennsylvania ERP streams. Cubic spline smoothing curves shown to help identify trends in brook trout population abundance. Arrows indicate approximate dates of fish transplants into ERP streams.

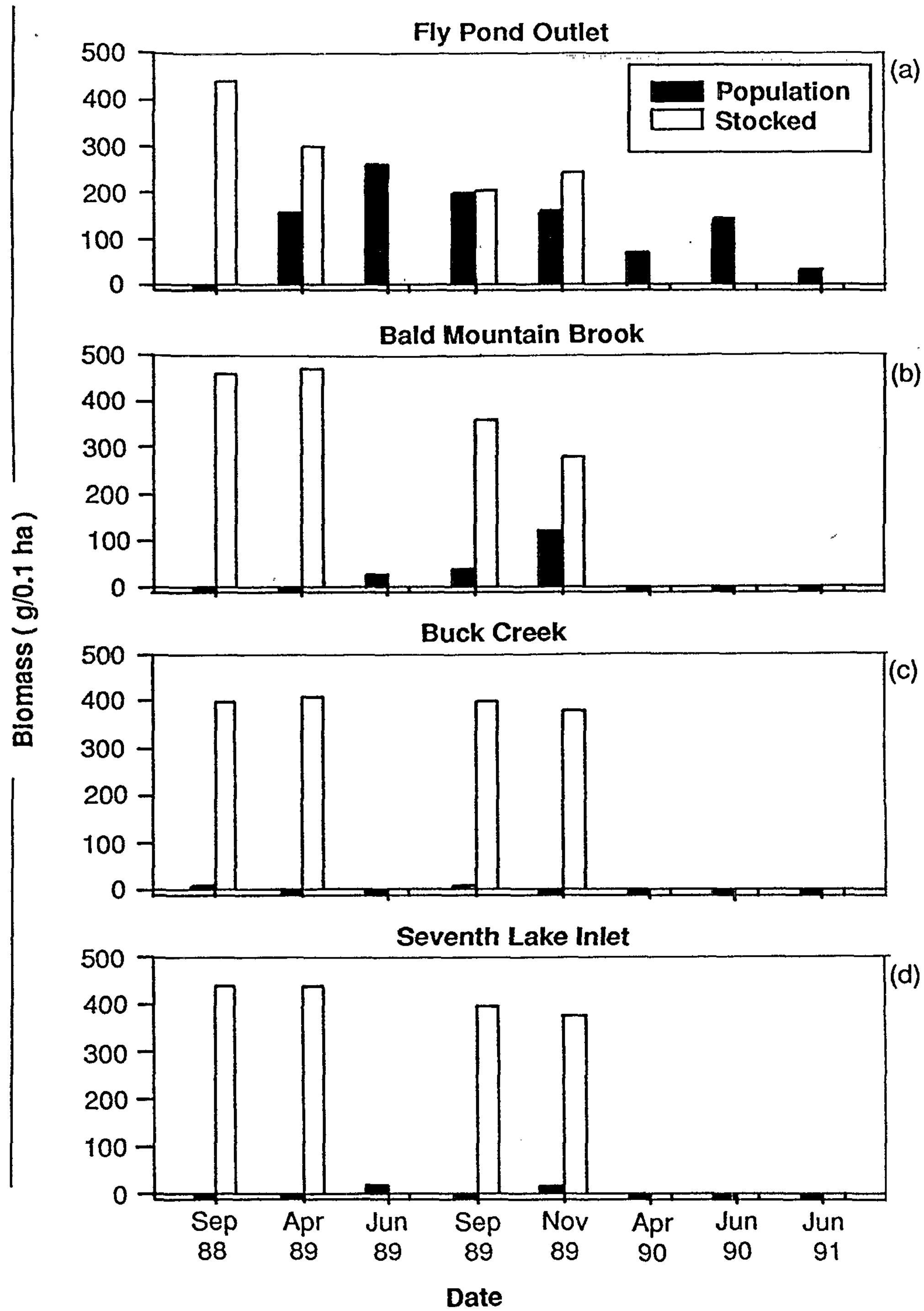


Figure 6-45. Biomass (g/m^2) of blacknose dace caught and stocked into Adirondack ERP streams. All streams sampled 8 times, September 1988 to June 1991. (Source: D. Bath, ALSC, pers. comm.).

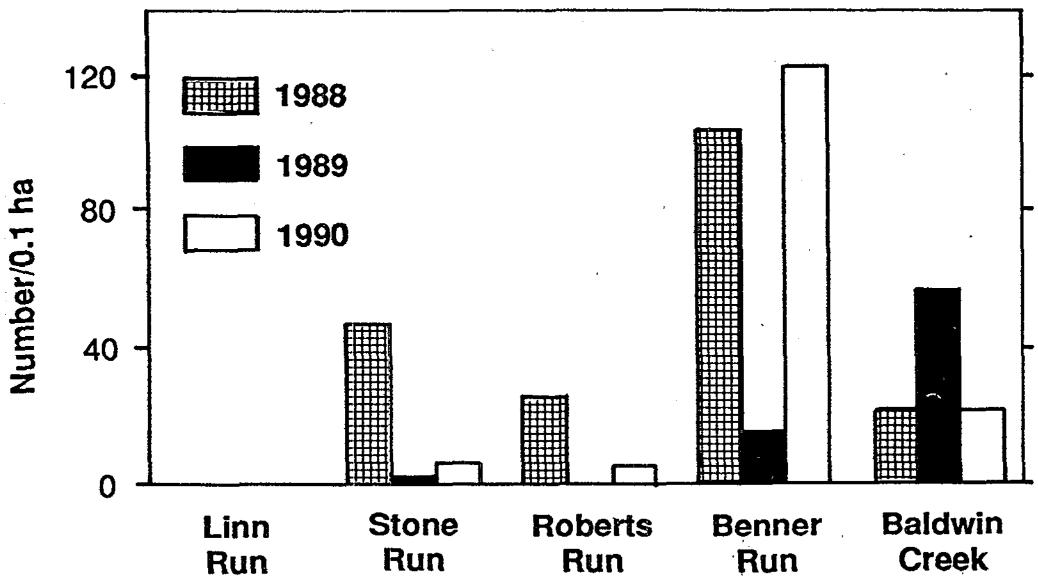


Figure 6-46. Density of age-0 (young-of-the-year) brook trout in ERP streams in Pennsylvania during May/June 1988 to 1990. No age-0 brook trout were caught in Linn Run. (Source: Gagen, 1991).

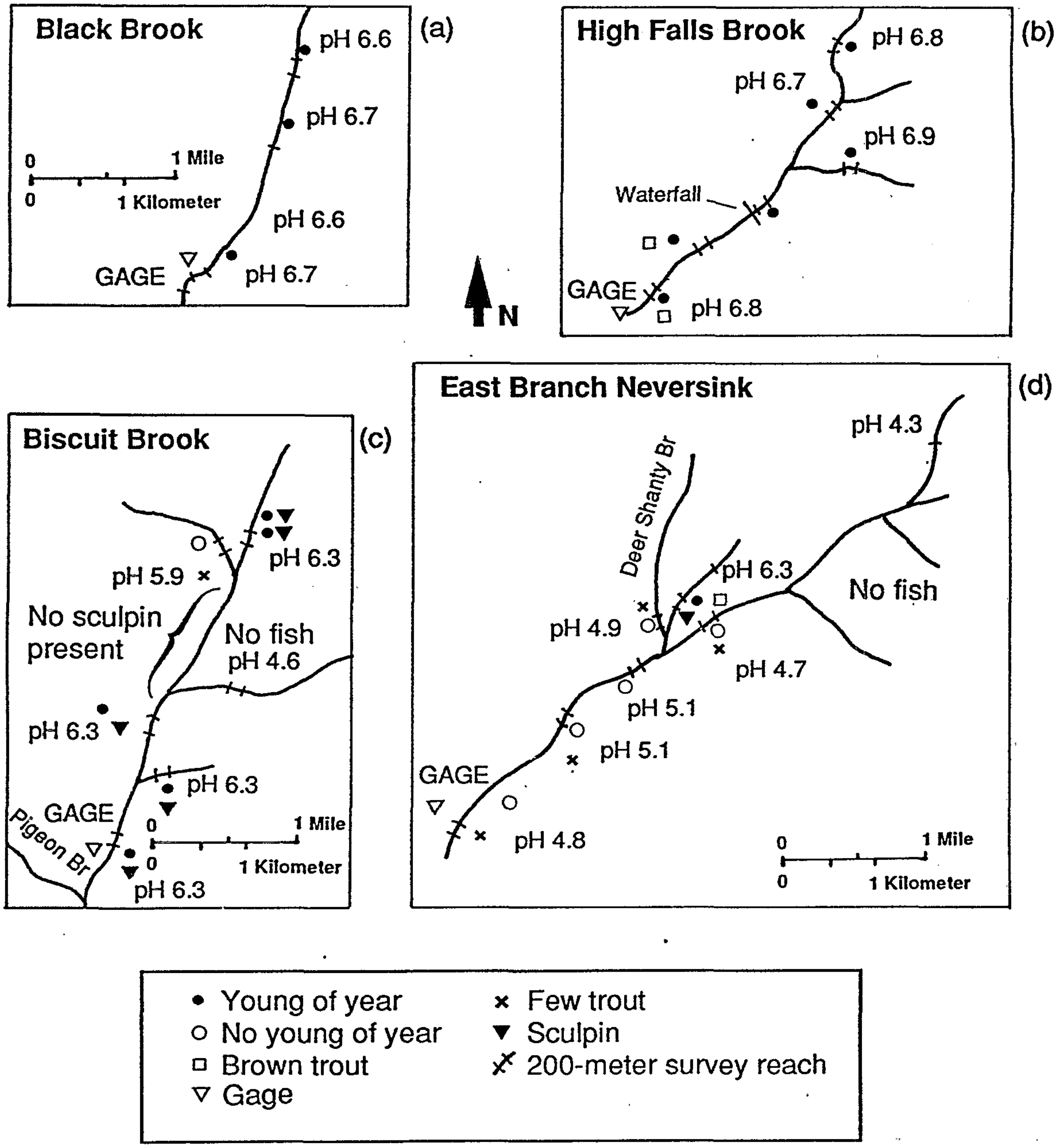


Figure 6-47. **Longitudinal profiles of fish distribution and pH along the length of the four ERP Catskill study streams during August 1989 (Source: Murdoch et al. 1991).**

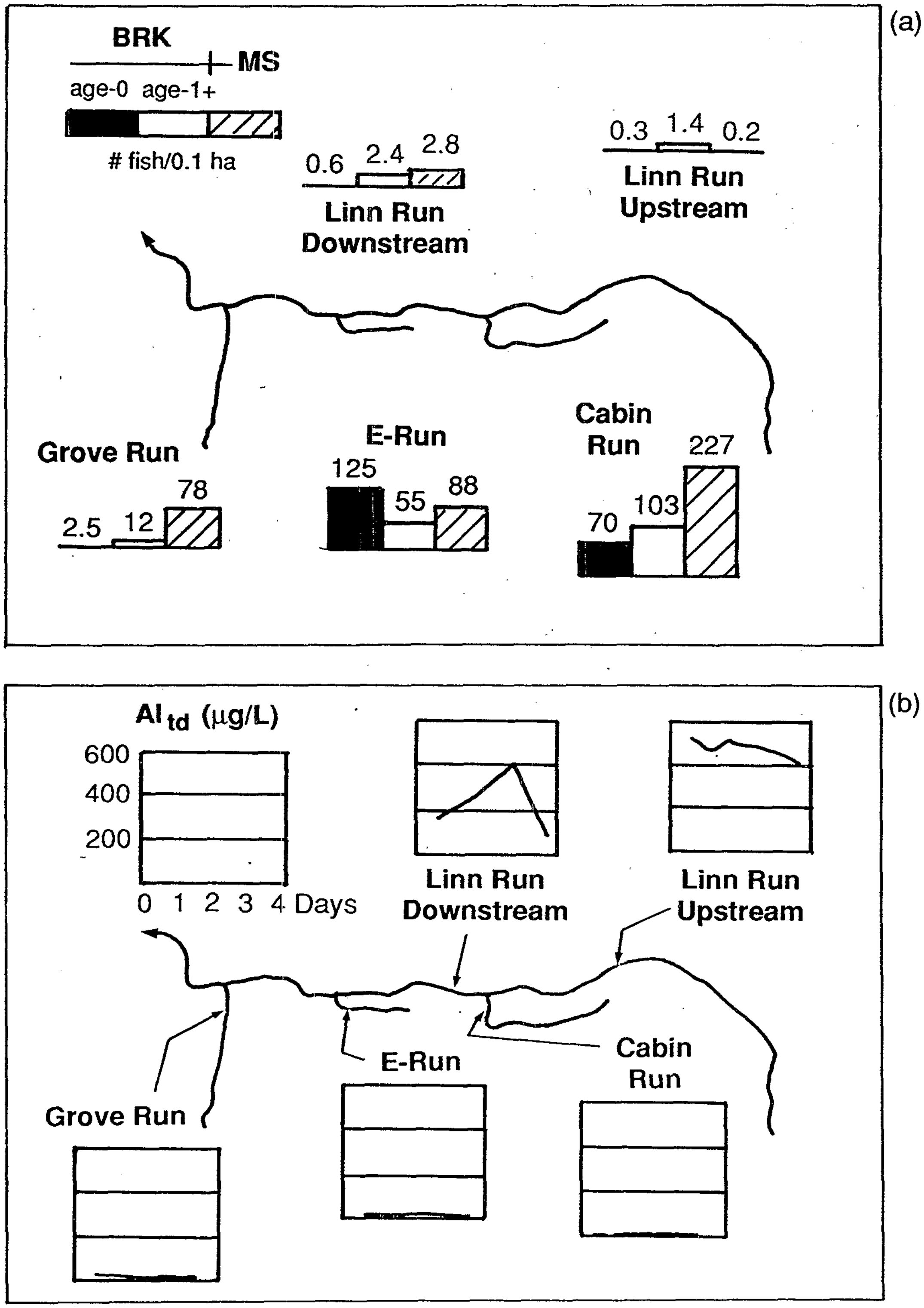


Figure 6-48. Median density of brook trout (BRK) age-0 and age-1+ and mottled sculpin (MS) captured on five sampling dates in 1987 at five sampling sites in the Linn Run drainage (a). Total dissolved aluminum concentrations during an April 1987 acidic episode (b). Arrow indicates direction of stream flow. (Source: Gagen, 1991).

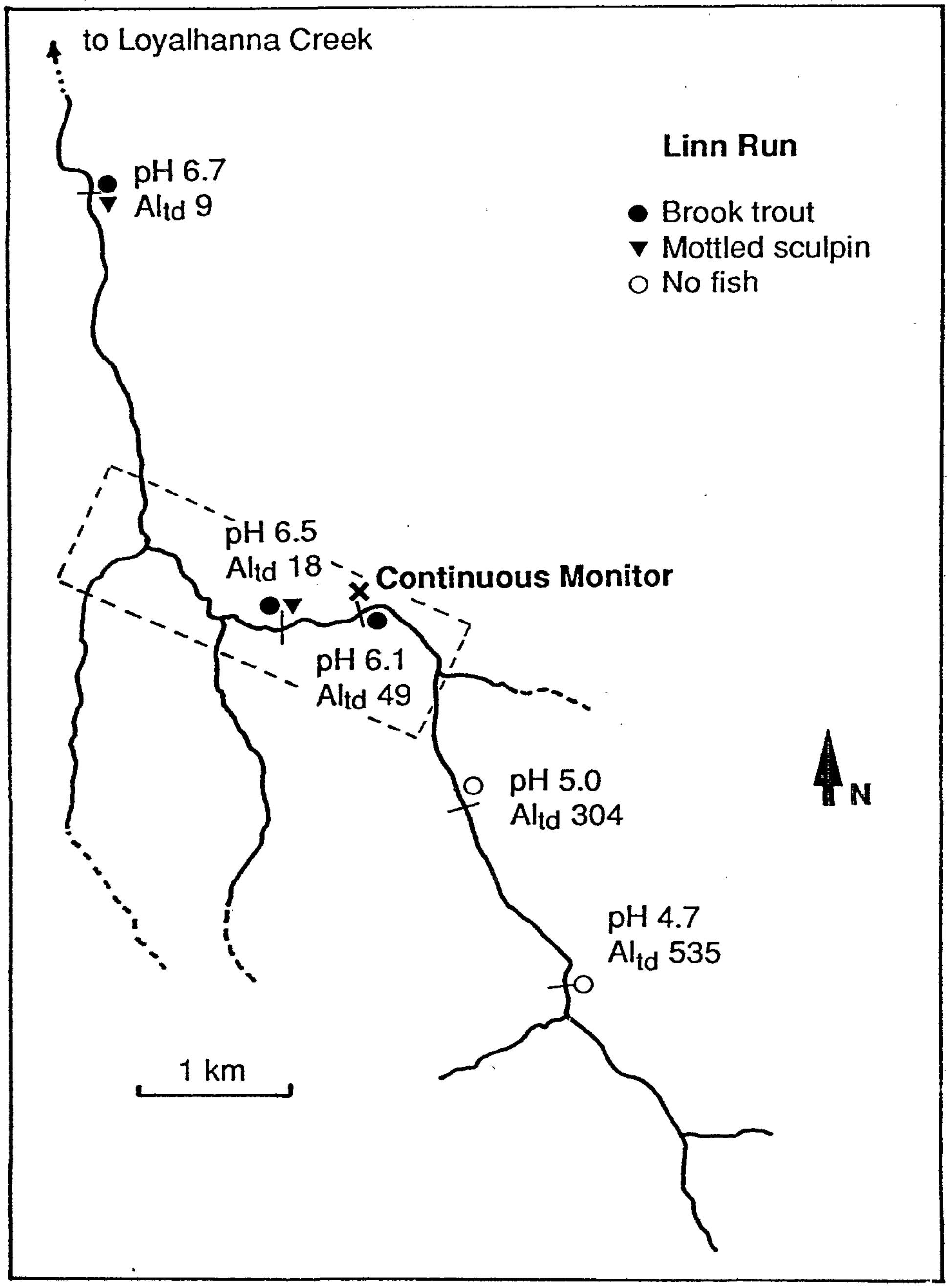


Figure 6-49. Linn Run drainage network showing fish community composition and stream pH and total dissolved aluminum concentrations. All water samples were collected on May 23, 1989, when stream discharge at the continuous monitor was 0.033 $m^3/s/km^2$. Arrow indicates direction of stream flow. Dotted box indicates area enlarged in Figure 6-48. (Source: DeWalle et al., 1991).

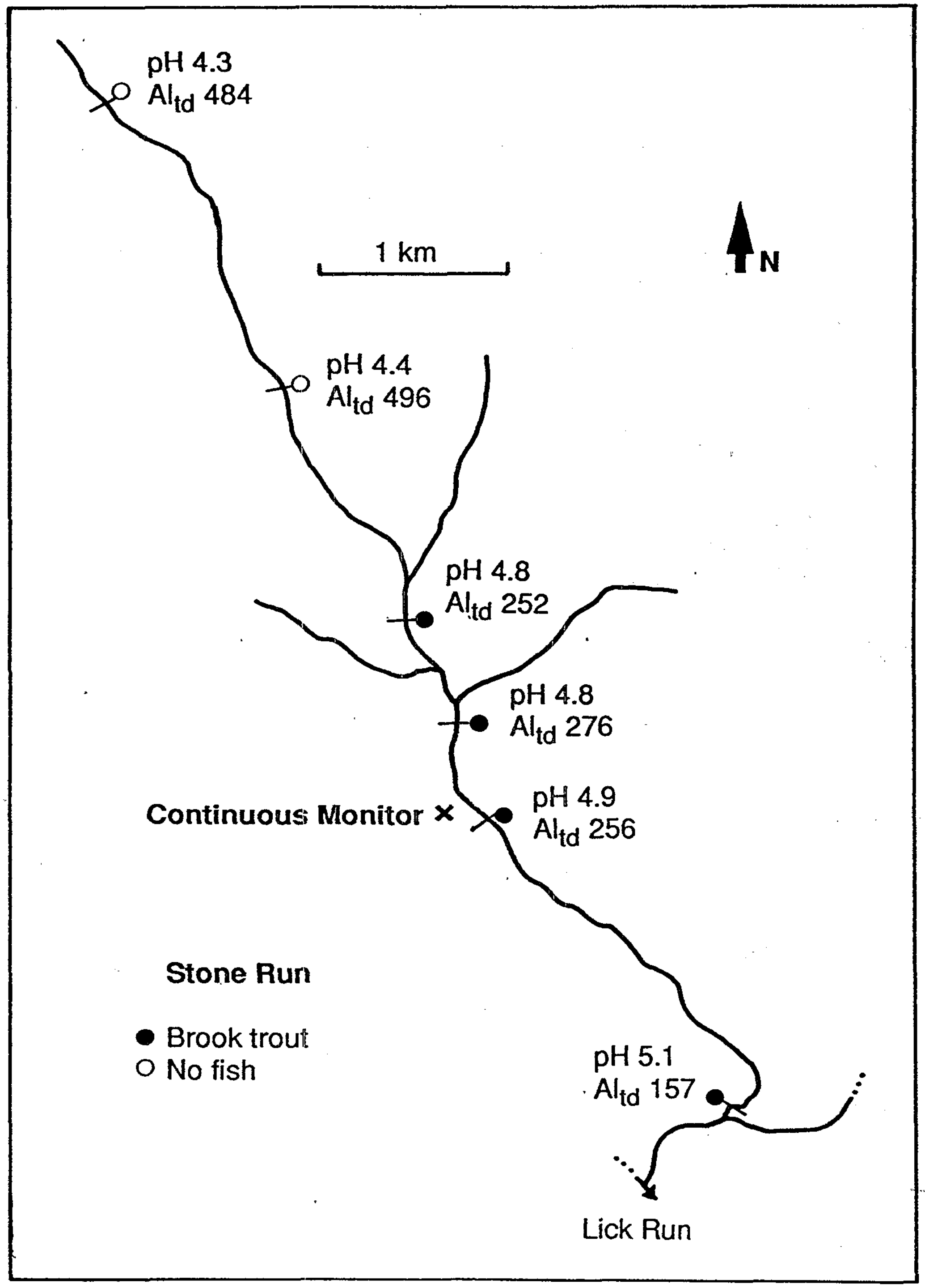


Figure 6-50. Stone Run drainage network showing fish community composition and stream pH and total dissolved aluminum concentrations. All water samples were collected on May 18, 1989 when stream discharge at the continuous monitor was 0.063 $m^3/s/km^2$. Arrow indicates direction of stream flow. (Source: DeWalle et al., 1991).

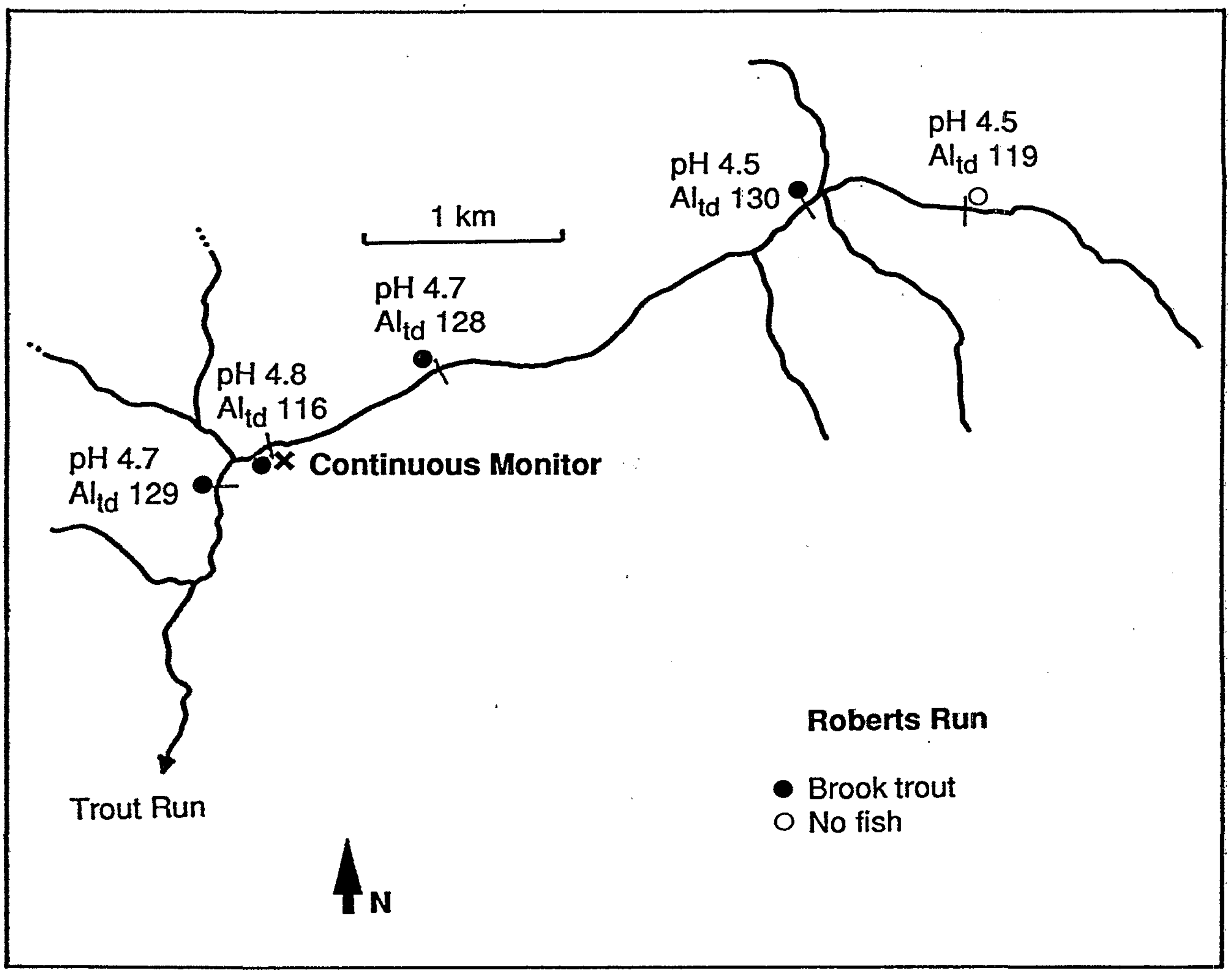


Figure 6-51. Roberts Run drainage network showing fish community composition and stream pH and total dissolved aluminum concentrations. All water samples were collected on May 18, 1989, when stream discharge at the continuous monitor was 0.072 $m^3/s/km^2$. Arrow indicates direction of stream flow. (Source: DeWalle et al., 1991).

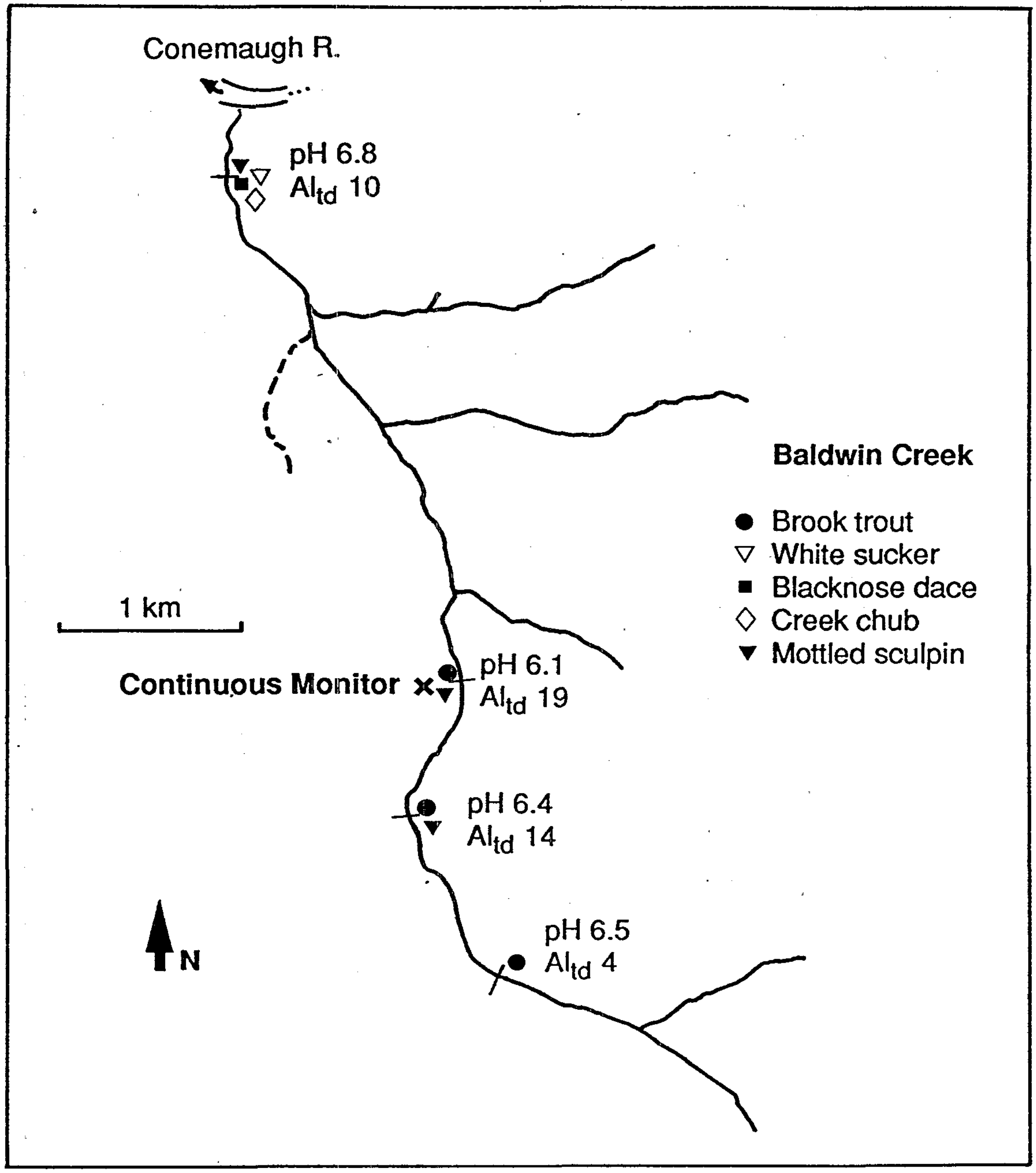


Figure 6-52. Baldwin Creek drainage network showing fish community composition and stream pH and total dissolved aluminum concentrations. All water samples were collected on May 22, 1989, when stream discharge at the continuous monitor was 0.032 $m^3/s/km^2$. Arrow indicates direction of stream flow. (Source: DeWalle et al., 1991).

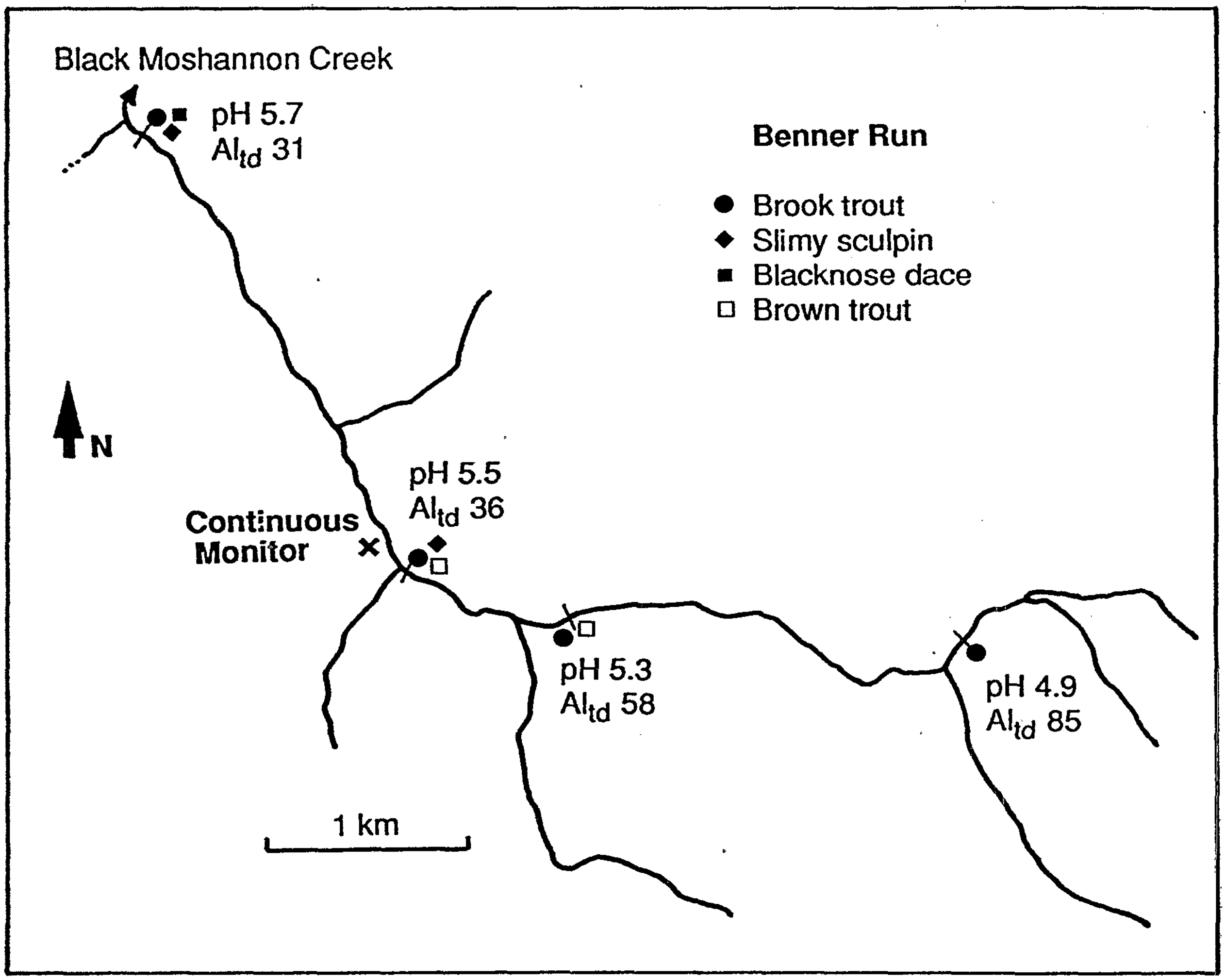


Figure 6-53. Benner Run drainage network showing fish community composition and stream pH and total dissolved aluminum concentrations. All water samples were collected on May 19, 1989, when stream discharge at the continuous monitor was 0.107 $m^3/s/km^2$. Arrow indicates direciton of stream flow. (Source: DeWalle et al., 1991).

Table 6-1. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Brook Trout in Adirondack Streams[a]

	Source of Fish[c]	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH	Al_{im}	% Mort	pH	Al_{im}	% Mort
FALL 1988									
FPO	CP	11/01/88	30	6.52 (6.20–6.84)	20 (20–20)	10.0	6.51 (6.20–6.84)	20 (20–20)	15.0
BMB	CP	11/01/88	30	4.97 (4.64–5.52)	198 (106–415)	50.0	4.97 (4.64–5.52)	198 (106–415)	50.0
BCK	CP	11/01/88	30	4.77 (4.64–5.10)	299 (192–497)	80.0	4.79 (4.64–5.10)	329 (192–497)	86.7
SLI	CP	11/01/88	30	4.95 (4.65–5.42)	210 (97–341)	20.0	4.94 (4.65–5.42)	210 (97–341)	25.0
SPRING 1989									
FPO	CP	5/26/89	25	7.06 (7.06–7.13)	10 (0–28)	0.0	7.08 (7.06–7.15)	19 (0–28)	15.0
BMB	CP	5/26/89	25	5.92 (5.83–6.33)	31 (0–72)	50.0	6.19 (5.83–6.36)	39 (0–110)	60.0
BCK	CP	5/26/89	25	5.28 (5.27–5.48)	132 (0–165)	45.0	5.38 (5.27–5.48)	100 (0–165)	45.0
SLI	CP	5/26/89	25	5.59 (5.55–5.85)	83 (9–115)	0.0	5.68 (5.55–5.85)	51 (9–115)	0.0
FALL 1989									
FPO	CP	9/27/89	40	7.07 (7.04–7.22)	42 (20–71)	20.0	7.00 (6.58–7.22)	39 (6–142)	30.0
BMB	CP	9/27/89	40	6.33 (6.15–6.51)	22 (17–33)	35.0	6.01 (5.05–6.51)	41 (17–421)	45.0
BCK	CP	9/27/89	40	5.38 (5.36–5.49)	173 (143–249)	55.0	5.20 (4.58–5.49)	200 (143–359)	60.0
SLI	CP	9/27/89	40	5.61 (5.67–5.90)	54 (31–88)	15.0	5.62 (4.84–5.90)	83 (31–250)	25.0
FPO	CP	10/06/89	31	7.04 (6.58–7.22)	35 (6–142)	10.0	7.00 (6.58–7.22)	37 (6–142)	25.0
BMB	CP	10/06/89	31	6.26 (5.05–6.51)	19 (17–421)	5.0	6.01 (5.05–6.51)	46 (17–421)	15.0
BCK	CP	10/06/89	31	5.31 (4.58–5.49)	176 (153–359)	10.0	5.20 (4.58–5.49)	199 (153–359)	15.0
SLI	CP	10/06/89	31	5.81 (4.84–5.90)	44 (31–250)	0.0	5.62 (4.84–5.90)	83 (31–250)	5.0

a Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.

b FPO = Fly Pond Outlet; SLI = Seventh Lake Inlet; BMB = Bald Mountain Brook; BCK = Buck Creek.

c CP = common pool (see Section 4.4.1 for explanation).

Table 6-1. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Brook Trout in Adirondack Streams (Continued)[a]

Stream[b]	Source of Fish[c]	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH	Al_{im}	% Mort	pH	Al_{im}	% Mort
SPRING 1990									
FPO	CP	4/30/90	30	6.58 (6.19–6.91)	25 (10–107)	0.0	6.62 (6.19–6.91)	20 (10–107)	5.0
BMB	CP	4/30/90	30	5.65 (4.74–5.87)	52 (15–277)	50.0	5.20 (4.74–5.87)	136 (15–316)	65.0
BCK	CP	4/30/90	30	4.93 (4.54–5.07)	269 (196–434)	50.0	4.82 (4.54–5.07)	296 (196–446)	70.0
SLI	CP	4/30/90	30	5.17 (4.74–5.37)	157 (87–236)	25.0	5.17 (4.74–5.41)	164 (87–280)	25.0

a Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al) in any one chemistry sample.

b FPO = Fly Pond Outlet; SLI = Seventh Lake Inlet; BMB = Bald Mountain Brook; BCK = Buck Creek.

c CP = common pool (see Section 4.4.1 for explanation).

Table 6-2. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Brook Trout in Catskill Streams[a]

Stream[b]	Source of Fish[c]	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH[d]	Al_{im}[d]	% Mort[d]	pH	Al_{im}	% Mort
FALL 1988									
Black	Black	11/10/88	35	6.22 (6.08–6.75)	19 (0–43)	5.3	6.42 (6.08–6.75)	19 (0–43)	5.3
	Black	11/10/88	35	6.22 (6.08–6.75)	19 (0–43)	0.0	6.42 (6.08–6.75)	19 (0–43)	11.1
Biscuit	Biscuit	11/03/88	41	5.91 (5.59–6.21)	13 (13–71)	4.8	5.99 (5.59–6.21)	13 (10–71)	19.0
	Biscuit	11/03/88	41	5.91 (5.59–6.21)	13 (13–71)	0.0	5.99 (5.59–6.21)	13 (10–71)	23.1
EBrNS	EBrNS	11/04/88	41	4.84 (4.59–5.05)	118 (81–207)	7.1	4.84 (4.59–5.08)	137 (81–207)	7.1
	EBrNS	11/04/88	41	4.84 (4.59–5.05)	118 (81–207)	66.7	4.84 (4.59–5.08)	137 (81–207)	83.3
Black	Black	11/30/88	15	—	—	—	6.38 (6.33–6.53)	23 (17–43)	5.0
High Falls	Black	11/30/88	15	—	—	—	6.26 (6.24–6.38)	0 (0–2)	0.0
Biscuit	Black	11/30/88	14	—	—	—	5.99 (5.98–6.01)	11 (10–16)	5.0
EBrNS	Black	11/30/88	15	—	—	—	5.03 (5.07–5.08)	134 (136–146)	15.0
SPRING 1989									
Black	PIN	4/08/89	19	—	—	—	6.42 (6.52–6.83)	12 (5–20)	23.8
High Falls	PIN	4/06/89	21	5.96 (5.86–6.77)	5 (0–17)	19.0	6.35 (5.86–6.77)	6 (0–17)	19.0
Biscuit	PIN	4/06/89	21	5.87 (5.51–6.06)	13 (6–25)	23.8	5.87 (5.51–6.28)	13 (0–25)	23.8
EBrNS	PIN	4/06/89	21	4.81 (4.56–4.96)	231 (173–312)	81.3	4.83 (4.56–4.96)	229 (173–312)	81.3
High Falls	H.Falls	4/06/89	21	5.96 (5.86–6.77)	5 (0–17)	0.0	6.35 (5.86–6.77)	6 (0–17)	0.0
EBrNS	EBrNS	4/06/89	21	4.81 (4.56–4.96)	231 (173–312)	4.8	4.83 (4.56–4.96)	229 (173–312)	4.8

[a] Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.
[b] EBrNS = East Branch Neversink River.
[c] PIN = Pigeon Creek; WBrNS = West Branch Neversink River.
[d] — = bioassay did not last 20 days; therefore, no statistics are provided for the 20-day period.

Table 6-2. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Brook Trout in Catskill Streams (Continued)[a]

Stream[b]	Source of Fish[b]	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH[d]	Al_{im}[d]	% Mort[d]	pH	Al_{im}	% Mort
SPRING 1989	(cont.)								
High Falls	WBrNS	5/04/89	13	—	—	—	6.19 (5.40–6.50)	7 (0–83)	0.0
Biscuit	WBrNS	5/04/89	13	—	—	—	5.47 (4.97–5.92)	51 (27–145)	0.0
EBrNS	WBrNS	5/05/89	20[e]	4.60 (4.43–4.78)	295 (223–505)	85.7	4.60 (4.43–4.78)	295 (223–505)	85.7
High Falls	WBrNS	5/19/89	36	6.38 (6.02–6.78)	1 (0–9)	0.0	6.55 (6.02–6.78)	0 (0–32)	4.8
EBrNS	WBrNS	5/19/89	36	4.74 (4.61–4.92)	148 (101–237)	0.0	4.67 (4.50–4.92)	177 (86–286)	47.6
High Falls	H.Falls	5/19/89	36	6.38 (6.02–6.78)	1 (0–9)	0.0	6.55 (6.02–6.78)	0 (0–32)	4.8
EBrNS	WBrNS	5/19/89	36	4.74 (4.61–4.92)	148 (101–237)	0.0	4.67 (4.50–4.92)	177 (86–286)	33.3
FALL 1989									
Black	WBrNS	10/04/89	36	6.55 (5.44–6.78)	17 (10–73)	0.0	6.55 (5.44–6.86)	20 (10–73)	0.0
High Falls	WBrNS	10/04/89	35	6.64 (5.47–6.95)	12 (0–34)	0.0	6.58 (5.47–6.95)	3 (0–34)	0.0
Biscuit	WBrNS	10/04/89	35	6.20 (5.04–6.32)	12 (7–55)	0.0	6.04 (5.04–6.34)	12 (5–55)	0.0
EBrNS	WBrNS	10/04/89	34	4.88 (4.27–5.12)	162 (138–237)	0.0	4.71 (4.27–5.12)	184 (138–243)	9.5
High Falls	H.Falls	10/05/89	34	6.65 (5.47–6.95)	4 (0–34)	9.5	6.55 (5.47–6.95)	3 (0–34)	9.5
EBrNS	EBrNS	10/07/89	31	4.86 (4.27–5.12)	162 (138–237)	4.8	4.71 (4.27–5.12)	184 (138–243)	4.8
High Falls	WBrNS	11/08/89	22	6.48 (6.00–6.73)	11 (0–28)	0.0	6.48 (6.00–6.73)	11 (0–28)	0.0
EBrNS	WBrNS	11/08/89	22	4.74 (4.52–4.90)	211 (175–264)	28.6	4.74 (4.52–4.90)	211 (175–264)	38.1
High Falls	H.Falls	11/08/89	22	6.48 (6.00–6.73)	11 (0–28)	0.0	6.48 (6.00–6.73)	11 (0–28)	0.0
EBrNS	EBrNS	11/07/89	23	4.74 (4.52–4.88)	210 (175–264)	0.0	4.74 (4.52–4.90)	211 (175–264)	4.8

a Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.
b EBrNS = East Branch Neversink River.
c PIN = Pigeon Creek; WBrNS = West Branch Neversink River.
d — = bioassay did not last 20 days; therefore, no statistics are provided for the 20-day period.
e Bioassay terminated after 11 days due to high mortality.

Table 6-2. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Brook Trout in Catskill Streams (Continued)[a]

Stream[b]	Source of Fish[c]	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH	Al_{im}	% Mort	pH	Al_{im}	% Mort
SPRING 1990									
High Falls	WBrNS	3/09/90	28	6.51 (5.95–6.66)	7 (0–60)	0.0	6.55 (5.95–6.66)	8 (0–60)	4.8
Biscuit	WBrNS	3/09/90	28	5.85 (5.30–6.44)	32 (21–117)	0.0	5.91 (5.30–6.44)	32 (6–117)	4.8
High Falls	WBrNS	4/06/90	30	6.43 (5.87–6.64)	4 (0–32)	0.0	6.54 (5.87–6.74)	2 (0–32)	0.0
Biscuit	WBrNS	4/06/90	30	5.68 (5.03–5.86)	32 (13–159)	4.8	5.76 (5.03–6.10)	25 (0–159)	4.8
EBrNS	WBrNS	4/06/90	30	4.65 (4.36–4.85)	252 (182–423)	66.7	4.68 (4.36–4.85)	213 (50–423)	66.7
High Falls	H.Falls	4/06/90	30	6.43 (5.87–6.64)	4 (0–32)	0.0	6.54 (5.87–6.74)	2 (0–32)	0.0
EBrNS	EBrNS	4/06/90	30	4.65 (4.36–4.85)	252 (182–423)	52.4	4.68 (4.36–4.85)	213 (50–423)	57.1

[a] Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.

[b] EBrNS = East Branch Neversink River.

[c] PIN = Pigeon Creek; WBrNS = West Branch Neversink River.

Table 6-3. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Brook Trout in Pennsylvania Streams[a]

Stream	Source of Fish	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH	Al_{im}	% Mort	pH	Al_{im}	% Mort
FALL 1988									
Benner	Benner	10/11/88	36	6.14 (5.96–6.53)	0 (0–10)	15.0	5.94 (5.54–6.53)	6 (0–47)	35.0
Roberts	Benner	10/05/88	36	5.69 (4.86–6.51)	28 (2–202)	9.5	5.69 (4.86–6.51)	28 (2–202)	14.3
	Roberts	10/05/88	36	5.69 (4.86–6.51)	28 (2–202)	10.3	5.69 (4.86–6.51)	28 (2–202)	10.3
	Stone	10/05/88	36	5.69 (4.86–6.51)	28 (2–202)	4.5	5.69 (4.86–6.51)	28 (2–202)	4.5
Stone	Benner	10/06/88	35	6.12 (6.02–6.26)	0 (0–9)	25.0	5.44 (5.19–6.26)	5 (0–189)	45.0
	Roberts	10/06/88	35	6.12 (6.02–6.26)	0 (0–9)	5.7	5.44 (5.19–6.26)	5 (0–189)	5.7
	Stone	10/06/88	35	6.12 (6.02–6.26)	0 (0–9)	30.3	5.44 (5.19–6.26)	5 (0–189)	30.3
Baldwin	Baldwin	10/13/88	36	6.78 (6.63–6.94)	9 (0–11)	11.1	6.69 (6.25–6.94)	9 (0–26)	19.4
Linn	Baldwin	10/13/88	36	5.92 (5.12–6.39)	55 (0–458)	2.7	5.78 (4.98–6.39)	79 (0–500)	18.9
	Benner	10/13/88	36	5.92 (5.12–6.39)	55 (0–458)	21.4	5.78 (4.98–6.39)	79 (0–500)	21.4
SPRING 1989									
Benner	Benner/ Roberts	2/21/89	42	5.82 (5.55–6.09)	15 (0–46)	0.0	5.82 (4.91–6.09)	17 (0–152)	42.9
Roberts	Roberts	2/23/89	39	5.19 (4.95–5.31)	115 (104–171)	42.9	5.21 (4.59–5.31)	117 (104–233)	52.4
Stone	Stone	2/22/89	40	5.08 (4.97–5.15)	212 (208–326)	76.2	5.18 (4.63–5.47)	173 (0–443)	90.5
Baldwin	Baldwin	2/27/89	39	5.99 (5.95–6.09)	14 (13–14)	9.5	5.99 (5.37–6.16)	14 (5–95)	52.4
Linn	Linn	2/28/89	37	5.63 (5.03–5.97)	200 (62–453)	92.9	5.38 (4.95–5.97)	208 (62–494)	97.6

[a] Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.

Table 6-3. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Brook Trout in Pennsylvania Streams (Continued)[a]

Stream	Source of Fish[b]	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH	Al_{im}	% Mort	pH	Al_{im}	% Mort
SPRING 1989	(cont.)								
Roberts	Roberts	3/14/89	20	5.10 (4.59–5.27)	127 (111–233)	28.6	5.10 (4.59–5.27)	127 (111–233)	28.6
Stone	Stone	3/14/89	20	5.22 (4.63–5.47)	149 (0–443)	19.0	5.22 (4.63–5.47)	149 (0–443)	19.0
Linn	Linn	3/20/89	17	5.30 (4.95–5.60)	208 (151–494)	85.7	5.30 (4.95–5.60)	208 (151–494)	85.7
FALL 1989									
Benner	Benner	10/30/89	21	5.96 (4.91–6.19)	11 (2–131)	14.3	5.96 (4.91–6.19)	11 (2–131)	14.3
Roberts	Stone	10/31/89	20	5.55 (4.81–5.77)	71 (48–233)	34.3	5.55 (4.81–5.77)	71 (48–233)	34.3
Stone	Stone	10/31/89	20	5.90 (5.34–6.03)	8 (0–156)	22.9	5.90 (5.34–6.03)	8 (0–156)	22.9
Baldwin	CP	11/02/89	20	6.30 (6.23–6.46)	12 (10–17)	2.9	6.30 (6.23–6.46)	12 (10–17)	2.9
Linn	CP	11/02/89	20	5.84 (4.99–6.15)	44 (19–496)	2.9	5.84 (4.99–6.15)	44 (19–496)	2.9
SPRING 1990									
Benner	CP	3/02/90	20	6.06 (5.12–6.22)	2 (0–101)	0.0	6.06 (5.12–6.22)	2 (0–101)	0.0
Stone	CP	3/02/90	20	5.18 (4.80–6.05)	204 (0–324)	91.4	5.18 (4.80–6.05)	204 (0–324)	91.4
Benner	CP	3/22/90	20	5.92 (5.16–6.17)	9 (0–90)	2.9	5.92 (5.16–6.17)	9 (0–90)	2.9
Stone	CP	3/22/90	20	5.13 (4.74–5.85)	239 (12–496)	94.3	5.13 (4.74–5.85)	239 (12–496)	94.3

a Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.

b CP = common pool (see Section 4.4.1 for explanation).

Table 6-4. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Blacknose Dace in Adirondack Streams[a]

Stream[b]	Source of Fish[c]	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH[d]	Al_{im}[d]	% Mort[d]	pH	Al_{im}	% Mort
FALL 1988									
FPO	CP	11/01/88	30	6.52 (6.20–6.84)	20 (20–20)	0.0	6.51 (6.20–6.84)	20 (20–20)	0.0
BMB	CP	11/01/88	30	4.97 (4.64–5.52)	198 (106–415)	90.0	4.97 (4.64–5.52)	198 (106–415)	90.0
BCK	CP	11/01/88	30	4.77 (4.64–5.10)	299 (192–497)	100.0	4.79 (4.64–5.10)	329 (192–497)	100.0
SLI	CP	11/01/88	30	4.95 (4.65–5.42)	210 (97–341)	95.0	4.94 (4.65–5.42)	210 (97–341)	95.0
SPRING 1989									
FPO	CP	5/08/89	10	—	—	—	6.64 (6.61–6.78)	20 (20–20)	0.0
BMB	CP	5/08/89	10	—	—	—	5.04 (5.02–5.15)	172 (151–230)	100.0
BCK	CP	5/08/89	10	—	—	—	4.76 (4.75–4.83)	334 (327–397)	100.0
SLI	CP	5/08/89	10	—	—	—	4.96 (4.93–5.08)	171 (156–224)	95.2
FPO	CP	5/18/89	41	7.03 (7.02–7.08)	14 (0–107)	0.0	7.06 (6.47–7.15)	19 (0–107)	14.3
BMB	CP	5/18/89	41	5.84 (5.67–6.11)	35 (18–163)	0.0	6.12 (5.67–6.36)	39 (0–163)	0.0
BCK	CP	5/18/89	41	5.20 (5.13–5.42)	149 (113–207)	52.4	5.38 (5.13–6.01)	92 (0–207)	66.7
SLI	CP	5/18/89	41	5.54 (5.44–5.67)	97 (72–135)	0.0	5.68 (5.44–6.11)	51 (9–135)	0.0
FALL 1989									
FPO	CP	9/27/89	40	7.07 (7.04–7.22)	42 (20–71)	0.0	7.00 (6.58–7.22)	39 (6–142)	0.0
BMB	CP	9/27/89	40	6.33 (6.15–6.51)	22 (17–30)	0.0	6.01 (5.05–6.51)	41 (17–421)	0.0
BCK	CP	9/27/89	40	5.38 (5.36–5.49)	173 (143–249)	90.0	5.20 (4.58–5.49)	200 (143–359)	100.0
SLI	CP	9/27/89	40	5.61 (5.67–5.90)	54 (31–88)	0.0	5.62 (4.84–5.90)	83 (31–250)	10.0

a Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.

b FPO = Fly Pond Outlet; BMB = Bald Mountain Brook; BCK = Buck Creek; SLI = Seventh Lake Inlet.

c CP = common pool (see Section 4.4.1 for explanation).

d — = bioassay did not last 20 days; therefore, no statistics are provided for the 20-day period.

Table 6-4. **Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Blacknose Dace in Adirondack Streams (Continued)[a]**

Stream[b]	Source of Fish[c]	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH	Al_{im}	% Mort	pH	Al_{im}	% Mort
SPRING 1990									
FPO	CP	4/30/90	30	6.58 (6.19–6.91)	25 (10–107)	0.0	6.62 (6.19–6.91)	20 (10–107)	0.0
BMB	CP	4/30/90	30	5.65 (4.74–5.87)	52 (15–277)	80.0	5.20 (4.74–5.87)	136 (15–316)	100.0
BCK	CP	4/30/90	30	4.93 (4.54–5.07)	269 (196–434)	100.0	4.82 (4.54–5.07)	296 (196–446)	100.0
SLI	CP	4/30/90	30	5.17 (4.74–5.37)	157 (87–236)	95.0	5.17 (4.74–5.41)	164 (87–280)	100.0

a Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.

b FPO = Fly Pond Outlet; BMB = Bald Mountain Brook; BCK = Buck Creek; SLI = Seventh Lake Inlet.

c CP = common pool (see Section 4.4.1 for explanation).

Table 6-5. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Slimy Sculpin in Catskill Streams[a]

Stream[b]	Source of Fish[c]	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH[d]	Al_{im}[d]	% Mort[d]	pH	Al_{im}	% Mort
FALL 1988									
Black	Black	11/10/88	35	6.22 (6.08–6.75)	19 (0–43)	0.0	6.42 (6.08–6.75)	19 (0–43)	0.0
Biscuit	Biscuit	11/03/88	41	5.91 (5.59–6.21)	13 (13–71)	0.0	5.99 (5.59–6.21)	13 (10–71)	0.0
SPRING 1989									
Black	PIN	4/08/89	19	—	—	—	6.42 (6.52–6.83)	12 (5–20)	0.0
High Falls	PIN	4/06/89	21	5.96 (5.86–6.77)	5 (0–17)	0.0	6.35 (5.86–6.77)	6 (0–17)	0.0
Biscuit	PIN	4/06/89	21	5.87 (5.51–6.06)	13 (6–25)	4.8	5.87 (5.51–6.28)	13 (0–25)	4.8
EBrNS	PIN	4/06/89	21	4.81 (4.56–4.96)	231 (173–312)	57.9	4.83 (4.56–4.96)	229 (173–312)	68.4
High Falls	WBrNS	5/04/89	13	—	—	—	6.19 (5.40–6.50)	7 (0–83)	0.0
Biscuit	WBrNS	5/04/89	13	—	—	—	5.47 (4.97–5.92)	51 (27–145)	0.0
EBrNS	WBrNS	5/04/89	9	—	—	—	4.52 (4.45–4.69)	301 (232–505)	4.8
FALL 1989									
Black	WBrNS	10/04/89	36	6.55 (5.44–6.78)	17 (10–73)	0.0	6.55 (5.44–6.86)	20 (10–73)	0.0
High Falls	WBrNS	10/04/89	35	6.64 (5.47–6.95)	12 (0–34)	0.0	6.58 (5.47–6.95)	3 (0–34)	0.0
Biscuit	WBrNS	10/04/89	35	6.20 (5.04–6.32)	12 (7–55)	4.8	6.04 (5.04–6.34)	12 (5–55)	4.8
EBrNS	WBrNS	10/04/89	34	4.88 (4.27–5.12)	162 (138–237)	4.8	4.71 (4.27–5.12)	184 (138–243)	9.5
High Falls	H.Falls	10/05/89	34	6.65 (5.47–6.95)	4 (0–34)	0.0	6.55 (5.47–6.95)	3 (0–34)	0.0
EBrNS	EBrNS	10/07/89	31	4.86 (4.27–5.12)	162 (138–237)	0.0	4.71 (4.27–5.12)	184 (138–243)	0.0

a Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.
b EBrNS = East Branch Neversink River.
c PIN = Pigeon Creek; WBrNS = West Branch Neversink River.
d — = bioassay did not last 20 days; therefore, no statistics are provided for the 20-day period.

Table 6-5. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Slimy Sculpin in Catskill Streams (Continued)[a]

Stream[b]	Source of Fish[c]	Starting Date	Total Days	20-Day Period			Full Experiment		
				pH	Al_{im}	% Mort	pH	Al_{im}	% Mort
FALL 1989									
High Falls	WBrNS	11/08/89	22	6.48 (6.00–6.73)	11 (0–28)	0.0	6.48 (6.00–6.73)	11 (0–28)	0.0
EBrNS	WBrNS	11/08/89	22	4.74 (4.52–4.90)	211 (175–264)	0.0	4.74 (4.52–4.90)	211 (175–264)	4.8
High Falls	H.Falls	11/08/89	22	6.48 (6.00–6.73)	11 (0–28)	0.0	6.48 (6.00–6.73)	11 (0–28)	0.0
EBrNS	EBrNS	11/07/89	23	4.74 (4.52–4.88)	210 (175–264)	0.0	4.74 (4.52–4.90)	211 (175–264)	4.8

a Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.
b EBrNS = East Branch Neversink River.
c PIN = Pigeon Creek; WBrNS = West Branch Neversink River.

Table 6-6. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Sculpin in Pennsylvania Streams[a]

Stream	Species	Source of Fish[b]	Starting Date	Total Days	20-Day Period			Full Experiment		
					pH	Al_{im}	% Mort	pH	Al_{im}	% Mort
FALL 1988										
Benner	Slimy	Benner	10/11/88	36	6.14 (5.96–6.53)	0 (0–10)	1.8	5.94 (5.54–6.53)	6 (0–47)	30.9
Roberts	Slimy	Benner	10/05/88	36	5.69 (4.86–6.51)	28 (2–202)	4.3	5.69 (4.86–6.51)	28 (2–202)	38.3
Stone	Slimy	Benner	10/06/88	35	6.12 (6.02–6.26)	9 (0–9)	7.4	5.44 (5.19–6.26)	5 (0–189)	7.4
Linn	Slimy	Benner	10/13/88	36	5.92 (5.12–6.39)	55 (0–458)	0.0	5.78 (4.98–6.39)	79 (0–500)	0.0
Baldwin	Mottled	Baldwin	10/13/88	36	6.78 (6.63–6.94)	9 (0–11)	0.0	6.69 (6.25–6.94)	9 (0–26)	0.0
Linn	Mottled	Baldwin	10/13/88	36	5.92 (5.12–6.39)	55 (0–458)	0.0	5.78 (4.98–6.39)	79 (0–500)	30.4
SPRING 1989										
Benner	Slimy	SixMile	2/21/89	42	5.82 (5.55–6.09)	15 (0–46)	0.0	5.82 (4.91–6.09)	17 (0–152)	0.0
Roberts	Slimy	SixMile	2/22/89	40	5.03 (4.83–5.31)	126 (104–198)	33.3	5.16 (4.59–5.31)	128 (104–233)	81.0
Stone	Slimy	SixMile	2/22/89	39	5.08 (4.97–5.15)	212 (208–326)	47.6	5.18 (4.63–5.47)	173 (0–443)	100.0
Baldwin	Mottled	Linn	2/27/89	39	5.99 (5.95–6.09)	14 (13–14)	0.0	5.99 (5.37–6.16)	14 (5–95)	33.3
Linn	Mottled	Baldwin	2/28/89	37	5.63 (5.03–5.97)	200 (62–453)	57.1	5.38 (4.95–5.97)	208 (62–494)	100.0
SPRING 1990										
Benner	Slimy	CP	3/02/90	20	6.06 (5.12–6.22)	2 (0–101)	0.0	6.06 (5.12–6.22)	2 (0–101)	0.0
Stone	Slimy	CP	3/02/90	20	5.18 (4.80–6.05)	204 (0–324)	48.6	5.18 (4.80–6.05)	204 (0–324)	48.6
Benner	Mottled	CP	3/02/90	20	6.06 (5.12–6.22)	2 (0–101)	0.0	6.06 (5.12–6.22)	2 (0–101)	0.0
Stone	Mottled	CP	3/02/90	20	5.18 (4.80–6.05)	204 (0–324)	45.7	5.18 (4.80–6.05)	204 (0–324)	45.7

a Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.

b CP = common pool (see Section 4.4.1 for explanation).

Table 6-6. Fish Mortality and Chemistry (Median, Range) During *In Situ* Bioassays with Sculpin in Pennsylvania Streams (Continued)[a]

Stream	Species	Source of Fish[b]	Starting Date	Total Days	20-Day Period			Full Experiment		
					pH	Al_{im}	% Mort	pH	Al_{im}	% Mort
SPRING 1990										
Benner	Slimy	CP	3/22/90	20	5.92 (5.16–6.17)	9 (0–90)	11.4	5.92 (5.16–6.17)	9 (0–90)	30.9
Stone	Slimy	CP	3/22/90	20	5.13 (4.74–5.85)	239 (12–496)	91.4	5.12 (4.74–5.85)	239 (12–496)	38.3
Benner	Mottled	CP	3/22/90	20	5.92 (5.16–6.17)	9 (0–90)	0.0	5.92 (5.16–6.17)	9 (0–90)	7.4
Stone	Mottled	CP	3/22/90	20	5.13 (4.74–5.85)	239 (12–496)	42.9	5.13 (4.74–5.85)	239 (12–496)	0.0

a Medians are time-weighted values, based on interpolated chemistry throughout the bioassay period. Maximum and minimum are the highest and lowest values measured (or estimated for Al_{im}) in any one chemistry sample.

b CP = common pool (see Section 4.4.1 for explanation).

Table 6-7. Fish Mortality (% Mortality after 20 Days) in *In Situ* Bioassays in Reference and Nonreference Streams

Species (Group)		% Mortality		Statistical Comparisons: Wilcoxon Rank Sums (p-value)
		Reference Stream	Nonreference Streams	
All fish	Mean	3.1	33.0	0.0001
	(Std. Dev.)	(5.6)	(33.6)	
	(n =)	(n = 46)	(n = 84)	
Brook trout (all)	Mean	4.8	30.6	0.0001
	(Std. Dev.)	(6.6)	(30.2)	
	(n =)	(n = 27)	(n = 53)	
Brook trout (common pool)	Mean	5.3	32.1	0.0009
	(Std. Dev.)	(7.2)	(30.7)	
	(n =)	(n = 17)	(n = 32)	
Blacknose dace (common pool)	Mean	0.0	58.5	0.0441
	(Std. Dev.)	(0.0)	(45.0)	
	(n =)	(n = 4)	(n = 12)	
Sculpin[a] (common pool)	Mean	1.2	26.2	0.0017
	(Std. Dev.)	(3.4)	(28.3)	
	(n =)	(n = 11)	(n = 15)	

[a] Mottled and slimy sculpin combined.

Table 6-8. Fish Mortality (% Mortality after 20 Days) in *In Situ* Bioassays Classified by ANC as Nonacidic (Reference Bioassays), Acidic Episodes, and Chronically Acidic[a]

Species (Group)		% Mortality			Statistical Comparisons: Wilcoxon Rank Sums (p-value)	
		Nonacidic	Acidic Episode	Chronically Acidic	Nonacidic vs. Acidic Episode	Acidic Episode vs. Chronically Acidic
Brook trout	Mean	8.0	31.6	31.4	0.0017	0.8769
(all)	(Std. Dev.)	(13.3)	(30.9)	(31.4)		
	(n =)	(n = 33)	(n = 14)	(n = 12)		
Brook trout	Mean	10.2	29.7	44.1	0.0257	0.4954
(common pool)	(Std. Dev.)	(15.3)	(27.9)	(36.9)		
	(n =)	(n = 23)	(n = 8)	(n = 4)		
Blacknose dace	Mean	5.8	92.0	—	0.0011	—
(common pool)	(Std. Dev.)	(17.5)	(7.6)	—		
	(n =)	(n = 9)	(n = 5)	(n = 0)		
Sculpin[b]	Mean	0.9	20.6	23.1	0.0951	0.9999
(common pool)	(Std. Dev.)	(1.9)	(31.7)	(26.5)		
	(n =)	(n = 11)	(n = 3)	(n = 6)		

[a] Nonacidic: ANC always > 0 μeq/L.
Chronically acidic: ANC always $\leq$ 0 μeq/L.
Acidic episode: Initial ANC > 0, with at least two consecutive ANC values $\leq$ 0 μeq/L during the 20-day period. Analyses were also conducted with acidic episode defined by at least one value $\leq$ 0 μeq/L. Results were similar, but in general, the differences between nonacidic and acidic episode bioassays were less distinct.

[b] Mottled and slimy sculpin combined; sample sizes too small to subset for common pool sculpin.

Table 6-9. Equations for Calculating Acidic Stress Index (from J. Baker et al. 1990a)[a]

Model based on laboratory bioassay with brook trout swim-up fry:

$$ASI_t = \frac{100}{1 + \exp[-23.49 + 5.35pH + (2.97 \times 10^{-3})Ca - (1.93 \times 10^{-3})Al_{im}]}$$

Model based on laboratory bioassay with rainbow trout fry:

$$ASI_s = \frac{100}{1 + \exp[-8.90 + 1.56pH + (4.08 \times 10^{-3})Ca - (7.04 \times 10^{-2})Al_{im}]}$$

Model based on laboratory bioassay with adult brook trout:

$$ASI_{t\text{-}ad} = 100(1 - P/0.9627), \text{ where}$$

$$P = \frac{1}{1 + \exp[-3.25 + (1.30 \times 10^{-5})(Al_{im})^2]}$$

[a] Ca units μeq/L; Al_{im} units μg/L of inorganic monomeric Al; pH as pH units.

Table 6-10. Regression Coefficients (r^2) from Single-Variable Linear and Logistic Regression of 20-Day Percent Mortality as a Function of Time-Weighted Median Values of pH, Al_{im} (μg/L), and Three Acidic Stress Indices for Brook Trout (Common Pool and All Fish), Blacknose Dace, and Slimy and Mottled Sculpin Using Both Observed and Adjusted Mortality[a]

Response Variables	Dependent Variables and Model Types							
	Linear Al_{im}	Linear Log_{10} Al_{im}	Linear pH	Linear ASI_s	Linear ASI_t	Linear $ASI_{t\text{-}ad}$	Logistic Al_{im}	Logistic pH
Trout, common, unadjusted mortality (n = 49)	0.56	0.41	0.37	0.31	0.29	0.58	0.59	0.41
Trout, common, adjusted mortality (n = 49)	0.60	0.46	0.38	0.33	0.31	0.61	0.64	0.43
All trout, unadjusted mortality (n = 74)	0.47	0.36	0.25	0.29	0.14	0.46	0.49	0.25
All trout, adjusted mortality (n = 74)	0.48	0.36	0.25	0.27	0.16	0.48	0.51	0.25
Dace, unadjusted mortality (n = 16)	0.75	0.73	0.65	0.50	0.45	0.54	0.79	0.77
All sculpin, unadjusted mortality (n = 32)	0.55	0.38	0.27	0.41	0.01	0.63	0.61	0.14
Slimy sculpin, unadjusted mortality (n = 24)	0.45	0.28	0.23	0.31	0.01	0.57	0.52	0.13

[a] ASI, see Table 6-9. Regression results presented as r^2 values for linear regression and logistic-regression analog for r^2 (Agresti, 1990). See text for definition of adjusted mortality. Measured Al_{im} is used where available; otherwise Al_{im} is estimated as described in Section 4.3.3.

Table 6-11. Logistic Regression Model Predicting 20-Day Percent Mortality of Brook Trout (Common Pool) as a Function of the Time-Weighted Median Al_{im} Concentration

Variable	Parameter Estimate	Standard Error	Pr > Chi-Square
Intercept	–2.707	0.1434	0.0001
Median Al_{im} (μg/L)	0.0136	0.0089	0.0001
Model deviance = 887.0 Variance of residuals = 323.7 r^2 = 0.592			

Table 6-12. Logistic Regression Model Predicting 20-Day Percent Mortality of Brook Trout (Common Pool): Best 3-Variable Model.

Variable	Parameter Estimate	Standard Error	Pr > Chi-Square
Intercept	–10.86	1.34	0.0001
Median Al_{im} (μg/L)	0.0191	0.0016	0.0001
Minimum pH	1.853	0.263	0.0001
Median Ca (μeq/L)	–0.0174	0.0028	0.0001
Model deviance = 826.1 Variance of residuals = 221.9 r^2 = 0.720			

Table 6-13. Logistic Regression Model Predicting 20-Day Percent Mortality of Brook Trout (Common Pool): Best 5-Variable Model.

Variable	Parameter Estimate	Standard Error	Pr > Chi-Square
Intercept	−8.334	1.32	0.0001
Median Al_{im} (μg/L)	0.0206	0.0016	0.0001
Minimum pH	1.501	0.256	0.0001
Median Ca (μeq/L)	−0.0141	0.0029	0.0001
Median DOC (mg/L)	−0.2589	0.0635	0.0001
Catskill Region	−1.3111	0.263	0.0001
Model deviance = 793.5 Variance of residuals = 166.3 $r^2 = 0.790$			

Table 6-14. Ordinary Least Squares Regression Model Predicting the Logit Transformation of the 20-Day Percent Mortality of Brook Trout (Common Pool): Best Overall Model.

Variable	Parameter Estimate	Standard Error	Pr > Chi-Square
Intercept	−6.177	1.91	0.0023
Median Al_{im} (μg/L)	0.0124	0.0022	0.0001
Minimum pH	1.085	0.367	0.0050
Median Ca (μeq/L)	−0.0136	0.0039	0.0012
Variance of residuals = 256.6[a] $r^2 = 0.651$[a]			

[a] Model statistics calculated based on predicted probability of fish mortality rather than logit transformed mortality, for comparison to logistic models.

Table 6-15. Logistic Regression Model Predicting 20-Day Percent Mortality of Blacknose Dace

Variable	Parameter Estimate	Standard Error	Pr > Chi-Square
Intercept	–7.838	2.399	0.0011
Log (integral concentration-duration for Al > 200 μg/L)	4.111	1.060	0.0001
Model deviance = 102.0 Variance of residuals = 52.9 r^2 = .975			

Table 6-16. Logistic Regression Model for Predicting 20-Day Percent Mortality of Sculpin

Variable	Parameter Estimate	Standard Error	Pr > Chi-Square
Intercept	–5.677	0.424	0.0001
Median Al (μg/L)	0.0189	0.0016	0.0001
Region	1.837	0.319	0.0001
Model deviance = 448.0 Variance of residuals = 118.1 r^2 = .799			

Table 6-17. Chemical Conditions during Telemetry Studies with Net Downstream Movement of Brook Trout

Stream	Dates	Net Movement (m)[a]	Study Period								Episode or Period Associated with Initiation of Movement[b]						Bioassay % Mortality
			pH		Al_{im} (μg/L)		Ca (μeq/L)		Discharge (cfs)		Episode/ Period	Min. pH	Max. Al_{im} (μg/L)	Duration (d)			
			Median[d]	Range	Median[d]	Range	Median[d]	Range	Median[d]	Range				Al_{im}>160	Al_{im}>200	Al_{im}>300	
Bald Mt. Brook	10/04–11/03/89	−50	6.10	5.05–6.51	28	17–421	112	102–124	1.0	0.7–12.9	Episode #13	5.05	421	1.55	0.93	0.00	5%
Buck Creek	10/04–11/03/89	−150	5.21	4.58–5.49	187	153–359	121	110–129	0.9	0.6–19.8	Initial conditions	5.41–5.49	143–153[c]	–	–	–	10%
Buck Creek	5/07–6/05/90	−200	4.82	4.54–6.16	308	22–446	105	96–162	9.1	2.2–49.0	Initial conditions	4.86	317	4.0	4.0	1.52	50%
East Br. Neversink	4/13–4/28/89	−300	4.80	4.72–4.97	186	157–284	76	74–80	38.7	18–102.8	Initial conditions	4.72	284	4.0	4.0	0.00	81%
Linn Run	10/16-11/14/88	−200	6.28	4.98–6.41	69	0–500	179	139–192	5.0	2.8–31.2	Episode #2	5.12	458	2.00	0.71	0.45	3%
Linn Run	3/03–4/02/89	−400	5.29	4.95–5.81	252	62–494	151	113–169	19.9	6.9–64.4	Episode #9	5.03	357	3.40	3.14	1.48	93%
Stone Run	3/07–4/05/90	−950	5.16	4.80–6.05	218	0–324	95	74–120	6.4	4.8–13.2	Initial conditions	5.17	211	4.0	1.09	0.00	91%

[a] From figures presented in D. Bath, Adirondack Lake Survey Corporation, Ray Brook, New York, pers. comm., 1992; Murdoch et al. (1991), and Gagen (1991).
[b] Episodes defined as described in Section 5.2.1. Initial conditions indicates that fish movement started within one to a few days after fish were released; chemistry summaries are for first four days.
[c] No chemistry samples analyzed during first four days of study; range indicates values for samples collected immediately before and after four-day period.
[d] Time-weighted median.

Table 6-18. Chemical Conditions during Telemetry Studies with Little, If Any, Net Downstream Movement of Brook Trout

Stream	Dates	pH [c]		Bioassay % Mortality	Al_{im} (μg/L)[b]		Ca (μeq/L)		Discharge (cfs)	
		Median[a]	Range		Median[a]	Range	Median[a]	Range	Median[a]	Range
Fly Pond Outlet	5/22–6/20/89	7.08	7.02–7.15	0	19	0–28	235	225–290	0.5	0.4–1.0
Fly Pond Outlet	10/05–11/03/89	6.97	6.58–7.22	10%	39	6–142	253	194–299	0.5	0.2–1.7
Fly Pond Outlet	5/05–6/05/90	6.68	6.19–7.00	0	16	10–42	197	152–241	1.2	0.8–4.7
Seventh Lake Inlet	5/23–6/20/89	5.68	5.55–5.85	0	51	9–115	124	121–128	2.5	2.3–5.1
High Falls Brook	4/13–4/27/89	6.26	5.86–6.77	19%	9	2–12	201	198–204	6.4	5.7–11.5
Baldwin Creek	10/16–11/14/88	6.44	6.28–6.94	11%	2	0–26	125	84–244	1.6	1.2–6.8
Baldwin Creek	3/03–4/02/89	5.99	5.37–6.16	9%	14	5–95	160	142–184	5.8	5.8–68.7
Benner Run	11/06–11/28/89	5.99	4.91–6.19	14%	9	0–131	66	63–109	5.9	4.3–31.6
Benner Run	3/07–4/06/90	6.03	5.12–6.22	0	3	0–101	83	61–167	4.6	4.0–10.0
Stone Run[c]	11/06–11/30/89	5.55	5.24–6.03	23%	59	0–166	116	103–132	3.2	1.4–6.4

[a] Time-weighted median.

[b] Estimated Al_{im}, as described in Section 4.3.3.

[c] Episode #15 occurred during study but resulted in no net movement: $Al_{im} > 100$ μg/L for 2.6 days; maximum $Al_{im} = 156$ μg/L.

Table 6-19. Number of Brook Trout and Blacknose Dace Caught in Fish Traps Moving Upstream and Downstream in Bald Mountain Brook and Fly Pond Outlet in Relation to Average Daily Stream Minimonitor pH[a]

Stream	Minimonitor pH	Brook Trout		Blacknose Dace	
		Upstream	Downstream	Upstream	Downstream
Bald Mountain Brook	≤ 5.0	0	0	0	16
Bald Mountain Brook	> 5.0	10	31	0	8
Fly Pond Outlet	> 6.0	23	54	2	19

[a] Source: D. Bath, ALSC, pers. comm.

Table 6-20. Number of Days Brook Trout Were Captured in Fish Traps in Bald Mountain Brook and Fly Pond Outlet in Relation to Stream Minimonitor pH[a]

Stream	Daily Minimonitor pH	No Movement	Downstream Movement	Upstream Movement	Both Directions
Bald Mountain Brook	≤ 5.0	43	0	0	0
Bald Mountain Brook	> 5.0	217	23	7	1
Fly Pond Outlet	> 6.0	233	49	23	9

[a] Fish traps were operational in both streams for 296 days; source: D. Bath, ALSC, pers. comm.

Table 6-21. Species Caught in ERP Streams[a]

Stream	Stream Chemistry					Fish Species Acid Sensitivity[d]		
	Severity Ranking[b]	Median pH		Median Al_{im} (μg/L)[c]		Acid Tolerant	Intermediate	Acid Sensitive
		Low Flow	High Flow	Low Flow	High Flow			
East Branch Neversink River	1	4.91	4.50	58	347	Brook trout		
Roberts Run	2	6.05	4.71	20	196	Brook trout	(Brown trout)[e]	
Stone Run	2	6.02	4.80	10	426	Brook trout		
Linn Run	3	6.40	5.12	0	387	Brook trout		
Buck Creek	3	6.20	4.57	47	375	Brook trout Mudminnow	Creek chub (Brown trout)[e]	Blacknose dace
Bald Mountain Brook	4	6.59	4.77	43	331	Brook trout	Creek chub	
Seventh Lake Inlet	4	6.19	4.78	59	225	Brook trout Mudminnow	Creek chub Darter sp.	
Biscuit Brook	5	6.31	5.38	3	70	Brook trout	Brown trout	Slimy sculpin
Benner Run	5	6.21	5.23	0	68	Brook trout	Brown trout	Slimy sculpin
Fly Pond Outlet	6	7.22	6.19	20	20	Brook trout White sucker Yellow perch	Creek chub	
Black Brook	6	6.82	6.10	13	34	Brook trout		Slimy sculpin
High Falls Brook	6	6.87	6.04	0	21	Brook trout	Brown trout	Slimy sculpin
Baldwin Creek	6	6.44	5.89	11	19	Brook trout		Mottled sculpin

a Streams ranked by severity of stream chemistry; fish species classified according to their acid sensitivity. Species caught using electrofishing—all sampling dates, except presence/absence of species involved in transplant experiments (brook trout, blacknose dace, and sculpin) based only on pre-transplant survey in fall 1988.

b Severity of stream chemistry ranked from 1 (most severe) to 6 (least severe); see text for explanation.

c Using measured and estimated Al_{im} combined, as described in Section 4.3.3.

d Acid sensitivity classified based on Figure 4.2 in Baker and Christensen (1991). Species classified as acid tolerant if at least some populations are expected to survive in lakes with pH $\leq$ 4.7 (i.e., lower range for critical pH $\leq$ 4.7); intermediately sensitive, with lower pH range between 4.8 and 5.0 inclusive; and acid sensitive if species is expected to occur only in waters with pH > 5.0. Mottled sculpin were not included in Figure 4.2 and were assumed to be in the same acid sensitivity class as slimy sculpin, based on their similar mortality levels in ERP *in situ* bioassays (Section 6.1). Unknown darter species caught in Seventh Lake Inlet arbitrarily classified as intermediate sensitivity.

e Only one brown trout was caught, in total, during all sampling dates. Thus, this species occurs in very low abundance.

Table 6-22. Rank Correlation Coefficients (and Associated P-Values for Test of Zero Correlation) Relating Brook Trout Density and Biomass (Mean Values from Spring and Fall Samples) to Annual Median Stream Chemistry (Weekly Samples) and Median Chemistry during Low and High Stream Discharge

Median Chemistry	Trout Density	Trout Biomass
Weekly pH	+0.852 (0.0002)	+0.890 (0.0001)
High flow pH	+0.725 (0.0050)	+0.830 (0.0005)
Low flow pH	+0.728 (0.0027)	+0.780 (0.0017)
Weekly Al_{im}	–0.610 (0.0269)	–0.687 (0.0095)
High flow Al_{im}	–0.703 (0.0073)	–0.808 (0.0008)
Low flow Al_{im}	–0.055 (0.8585)	–0.126 (0.6808)

Table 6-23. Density and Biomass of Brook Trout Measured in ERP Streams[a]

Stream	Date	Density (number/0.1 ha)			Biomass (g/0.1 ha) Caught[b]
		Caught	Estimate	95% Upper Confidence Limit	
Buck Creek	09/22/88	4	4	14	265
	04/25/89	31	31	35	344
	06/22/89	69	71	77	1208
	09/11/89	57	57	59	1255
	11/10/89	83	86	96	1092
	04/24/90	39	43	55	417
	06/14/90	26	26	28	367
	06/15/91	6	6	8	120
Bald Mountain Brook	10/11/88	162	180	216	1441
	04/24/89	117	122	140	1140
	06/22/89	194	198	212	2068
	09/01/89	171	185	212	1946
	11/07/89	135	135	140	1423
	04/19/90	135	140	158	1068
	06/13/90	113	122	144	1505
	06/15/91	90	90	104	1230
Fly Pond Outlet	10/12/88	516	522	530	3452
	04/24/89	308	329	352	2014
	06/21/89	216	222	233	2121
	09/12/89	236	236	242	1882
	11/08/89	167	167	173	1986
	04/19/90	115	115	121	1219
	06/13/90	239	256	282	1896
	06/15/91	89	89	153	1179
Seventh Lake Inlet	09/22/88	49	51	58	1125
	04/25/89	69	71	78	1063
	06/27/89	67	67	70	1629
	09/07/89	71	71	74	1788
	11/14/89	69	69	71	1418
	04/20/90	27	27	28	418
	06/12/90	43	44	49	838
	06/15/91	24	26	26	646
Biscuit Brook	10/10/88	59	60	62	—
	12/12/88	60	67	77	—
	05/30/89	87	102	116	1475
	08/22/89	126	133	141	—
	10/29/89	141	152	161	1858
	06/02/90	86	94	103	1879

[a] Data from Gagen (1991) for Pennsylvania streams; D. Bath (ALSC, pers. comm.) for Adirondack streams; B. Baldigo (USGS, pers. comm.) for Catskill streams.

[b] — = fish weights not measured.

Table 6-23. **Density and Biomass of Brook Trout Measured in ERP Streams (Continued)[a]**

Stream	Date	Density (number/0.1 ha)			Biomass (g/0.1 ha) Caught[c]
		Caught[b]	Estimate	95% Upper Confidence Limit[b]	
Black Brook	11/10/88	233	268	297	3582
	06/20/89	231	241	256	2749
	08/28/89	528	554	579	—
	10/25/89	354	395	433	3697
	11/27/89	205	233	272	—
	06/04/90	331	331	336	3849
High Falls Brook	11/15/88	147	155	165	2217
	05/01/89	82	85	92	1397
	08/22/89	197	235	277	—
	10/13/89	187	193	203	2073
	06/02/90	68	75	88	1620
East Branch Neversink River	06/07/89	28	45	71	394
	08/23/89	35	36	38	—
	10/16/89	13	14	15	195
	06/06/90	13	14	17	283
Benner Run	07/14/88	218	227	240	1976
	11/15/88	142	146	153	—
	03/30/89	60	62	72	393
	06/29/89	87	91	102	957
	08/22/89	111	116	127	1582
	11/28/89	53	55	64	744
	04/06/90	62	62	66	587
	06/05/90	180	189	202	2062
Baldwin Creek	07/12/88	84	85	87	1976
	11/22/88	111	111	116	—
	04/06/89	100	114	140	393
	06/28/89	166	172	182	957
	08/25/89	187	193	203	1582
	12/01/89	129	132	140	744
	04/03/90	92	98	112	587
	05/31/90	108	119	139	2062
Linn Run	07/12/88	—	11	—	—
	11/22/88	2	2	—	—
	04/06/89	2	2	—	50
	06/28/89	4	4	—	252
	08/25/89	9	9	—	278
	12/01/89	4	4	15	196
	04/03/90	2	2	—	—
	05/31/90	7	7	9	311

a Data from Gagen (1991) for Pennsylvania streams; D. Bath (ALSC, pers. comm.) for Adirondack streams; B. Baldigo (USGS, pers. comm.) for Catskill streams.

b — = data not obtained from regional cooperators.

c — = fish weights not measured.

Table 6-23. **Density and Biomass of Brook Trout Measured in ERP Streams (Continued)[a]**

Stream	Date	Density (number/0.1 ha)			Biomass (g/0.1 ha) Caught
		Caught	Estimate	95% Upper Confidence Limit	
Roberts Run	07/14/88	84	85	87	1942
	11/15/88	51	51	55	742
	03/29/89	64	68	80	978
	06/30/89	38	38	42	758
	08/22/89	53	53	57	1036
	11/30/89	36	38	47	578
	04/10/90	29	29	33	569
	06/05/90	42	42	45	751
Stone Run	07/14/88	159	166	178	1965
	11/17/88	71	78	92	944
	03/29/89	59	61	71	641
	06/30/89	85	88	96	1350
	08/22/89	95	100	109	1539
	11/29/89	66	69	76	1220
	04/05/90	39	39	44	1010
	06/05/90	49	48	53	945

[a] Data from Gagen (1991) for Pennsylvania streams; D. Bath (ALSC, pers. comm.) for Adirondack streams; B. Baldigo (USGS, pers. comm.) for Catskill streams.

SECTION 7

SUMMARY AND CONCLUSIONS

During the Episodic Response Project (ERP), we studied episodic acidification and the effects of episodic acidification on fish in 13 streams in the Adirondack Mountains, the Catskill Mountains, and the Northern Appalachian Plateau in Pennsylvania for approximately 20 months, starting in fall 1988 and concluding in spring 1990. Intensive field efforts were successful in collecting hydrologic, chemical, and biological data with which to accomplish project objectives. This section summarizes findings from the ERP by objective; major conclusions of the project follow.

Objective 1. Determine the magnitude, duration, frequency, and characteristics of episodic chemical changes that accompany hydrological events (snowmelt and rainstorms) in streams.

Episodes were a common phenomenon in all three regions. We recorded from 19 to 33 episodes in each of the study streams. Episode durations ranged from less than 1 day to more than 10 days. There was a direct relationship between ANC level at the beginning of episodes and the magnitude of ANC depressions that occurred during episodes. When conditions were nearly acidic at the beginning of episodes, ANC depressions tended to be smaller than during episodes in which initial ANC values were higher. However, the small ANC depressions in low ANC systems often produced acidic episodes with the lowest minimum ANC values. Acidic episodes occurred in at least some of the streams in all regions and were common where ANC values of streams immediately before the episodes were $\leq$ 50 μeq/L. When acidic episodes occurred, they were accompanied by depressed pH levels and elevated Al_{im} concentrations.

The occurrence of episodes was most common during the spring, winter, and fall months. Summer streamflow levels were low and were generally not very responsive to rainstorms. In most of the streams, three to five episodes developed much more severe chemical conditions (lower minimum ANC and pH and higher Al) than did the remainder of the episodes during the study.

In the Adirondacks, near normal snowpacks developed each winter of the study, and snowmelt, or rain on snow, produced episodes with the lowest ANC and pH values and the highest concentrations of Al_{im} recorded. For Buck Creek, Bald Mountain Brook, and Seventh Lake Inlet, minimum ANC concentrations during snowmelt were typically < -20 μeq/L; minimum pH values were < 4.6; maximum Al_{im} concentrations in Buck Creek exceeded 600 μg/L.

Snowpack accumulations were much smaller than normal in the Catskills. The majority of major episodes in the Catskills occurred in response to rainstorms. Spring rainstorms generated acidic episodes with minimum ANC values of -6 μeq/L in Biscuit Brook and -45 μeq/L in the East Branch of the Neversink River; maximum Al_{im} concentrations were 457 μg/L in the East Branch and 166 μg/L in Biscuit Brook. Episodes with similar ANC levels in the fall mobilized much less Al. The minimum episodic pH was 5.0 in Biscuit Brook and 4.3 in East Branch Neversink.

Virtually no snowpacks developed in Pennsylvania during the study period. Spring and late winter rainstorms produced most of the major episodes in the Pennsylvania streams. Benner Run and Baldwin Run were the two reference (highest ANC) streams in Pennsylvania. During the most severe episodes, Linn Run, Roberts Run, and Stone Run had minimum ANC values ranging from -17 to -52 μeq/L, minimum pH values ranging from 4.7 to 4.5, and maximum Al_{im} concentrations ranging from 270 to 707 μg/L. Similar amounts of Al mobilized in major spring and fall episodes.

Because of the small snowpacks in Pennsylvania and the Catskills, episodic conditions in these regions may not have been as severe during the ERP as during years with normal snowpack accumulations. However, large rainstorms during the spring and late winter produced high streamflows and major episodes.

The relationship between ANC and Al_{im} during episodes was fairly consistent among Adirondack streams and among Catskill streams. However, the Pennsylvania streams had distinctive Al/ANC relationships. For example, Linn Run had higher Al_{im} concentrations than did Roberts Run at a given ANC level.

Evaluation of ion change and concentration data shows that episodic ANC depressions are a result of complex interactions of multiple ions. These data also provide evidence that both natural processes and acidic deposition make important contributions to episodic acidification in the Adirondack, Catskill, and Pennsylvania study streams.

Sulfate in the streams is predominantly, if not solely, a consequence of atmospheric deposition, because the ERP watersheds do not have internal sources of S. Nitrate in the ERP watersheds probably is derived from a combination of natural N cycling and atmospheric deposition. Watersheds in the Adirondacks and Catskills, in which stream water concentrations of NO_3^- are quite high, have in all likelihood been significantly affected by atmospheric deposition of N.

For all episodes recorded (large and small) in the three ERP regions, base cation decreases were commonly the most important ion change contributing to ANC depressions. In the Catskills and Adirondacks, the largest base cation decreases occurred during nonacidic episodes. Base cation decreases were especially dominant for episodes in circumneutral streams in the study (Black Brook, Fly Pond Outlet, and High Falls Brook). However, some base cation decreases in the Pennsylvania streams were very large even during acidic episodes.

Organic acid (A^-) concentrations were greatest in the Adirondack streams, and A^- increases during episodes were commonly the second and sometimes the first ranked ion changes during major episodes. Organic acid contributions tended to be greatest in episodes with acidic or low ANC_{min} values. Organic acids were generally less important in Pennsylvania and Catskill episodes. However, A^- increases were the most important ion changes during several fall episodes in two Catskill streams. Organic acid pulses were commonly the second most important, and occasionally the most important, ion changes during episodes in the Pennsylvania streams, even though the magnitudes of A^- changes were small.

Sulfate was the dominant acid anion (C_A) virtually at all times in the study streams in all three regions. For both acidic and nonacidic episodes in the Catskills, SO_4^{2-} concentrations tended to decrease, thereby reducing ANC depressions. In the Adirondacks, SO_4^{2-} concentrations were observed to increase or decrease during episodes. However, SO_4^{2-} concentrations tended to decrease during acidic episodes. Sulfate concentrations in the Pennsylvania streams were greater than in Catskill or Adirondack streams. Based on the C_BC_A ANC definition, these large SO_4^{2-} concentrations (in all regions) provided an acidity base upon which other ion changes further modified the acid-base status of the stream waters. Another major difference between the Pennsylvania streams and the Adirondack and Catskill streams is the importance of SO_4^{2-} pulses in Pennsylvania episodes. In some major episodes, SO_4^{2-} pulses were the most important ion change contributing to ANC depressions in three of the five Pennsylvania streams (Baldwin Creek, Benner Run, and Stone Run) and were consistently the most important ion change in two of the streams.

Nitrate behavior and contributions to episodes were different in each of the three regions. Nitrate concentrations were much greater in the Catskill and Adirondack streams than in Pennsylvania streams. In the Catskills, NO_3^- concentrations typically increased during episodes, particularly during acidic episodes. In two of the Catskill streams, Biscuit Brook and East Branch Neversink River, NO_3^- was the most important ion change contributing to ANC depressions during several episodes. In the Adirondacks, NO_3^- increases were typically the third ranked ion change during episodes. The largest NO_3^- increases occurred during acidic episodes. Even though episodic changes of NO_3^- were relatively small, NO_3^- concentrations were large throughout Adirondack episodes. Nitrate pulses in Pennsylvania streams were generally small and made little contribution to ANC depressions.

Other ion changes were less important to episodes measured in the ERP. Chloride changes and concentrations usually had relatively little impact on episodes. However, for a few episodes in some Pennsylvania streams, Cl^- increases were the second most important ion change contributing to ANC depressions. In virtually all episodes, especially those that were acidic, Al increases tended to reduce ANC depressions.

From a biological perspective, we are most concerned about major episodes—those that generate low pH and ANC and high Al_{im} for relatively long periods of time (days to weeks). Ion behavior that controlled ANC depressions during major episodes recorded in each stream was not necessarily the same as the ion changes most important to smaller, more frequent episodes. In the Adirondacks, the only region to have major snowpacks, the most severe episodes generally occurred during spring snowmelt. During these episodes, base cation decreases were usually the most important contributions to ANC depressions, and A^- and NO_3^- changes positively contributed to episodes and were of similar rank (2 or 3). One Adirondack stream experienced a major snowmelt episode in which an increase in NO_3^- was the most important ion change. Three of the four Catskill streams experienced one episode influenced by snowmelt in which NO_3^- pulses were the first ranked contributor and base cation decreases were the second ranked ion change.

Within regions, the major episodes generated by rainstorms had more variable ionic controls than did snowmelt episodes. The large rain-induced Adirondack episodes occurred in the spring and fall. In these episodes, increases in A^- and decreases in base cations were the most important ion changes to ANC depressions. In major spring episodes in the Catskills, decreases in base cations or increases in NO_3^- were typically the first or second ranked ion changes contributing to ANC depressions. For the major episodes in Pennsylvania, base cation decreases and SO_4^{2-} increases were usually the most important or second most important ion changes contributing to ANC depressions. Two Pennsylvania streams experienced major rain-induced episodes in which A^- increases were the most important ion changes. In another Pennsylvania stream, NO_3^- pulses were the second ranked ion change in two major episodes.

Acidic deposition, as evidenced by stream water SO_4^{2-} and NO_3^- during episodes, contributed significantly to the occurrence of acidic episodes with low pH and high Al levels in all three study areas. Although base cation decreases are often the most important ion change that occurs during episodes, base cation decreases alone cannot create acidic stream water conditions during episodes. Organic acid pulses, a natural source of acidity, are also important contributors to ANC depressions in the Adirondack streams and, to a lesser extent, in the Catskill and Pennsylvania streams. However, SO_4^{2-} or NO_3^- pulses during episodes in study streams from all three regions augment the natural processes to create episodes with lower pH and ANC and higher Al concentrations than would have occurred from natural processes alone. In addition, large baseline concentrations of SO_4^{2-} and NO_3^- reduced episodic minimum ANC, even when these ions did not change during episodes.

We examined episodic acidification in 13 streams that were specifically selected for the ERP. It is not possible to make direct regional estimates of episodic acidification from these data. However, the results should be reasonably representative of episodic acidification responses and processes in similar streams in the Catskills, the Adirondacks, and the Northern Appalachian Plateau of Pennsylvania.

Objective 2. Evaluate the effects of episodic acidification on fish populations in streams.

Results from the ERP clearly demonstrate that episodic acidification can have long-term adverse effects on fish populations. Streams with suitable chemistry during low flow (pH > 6.0), but low pH (< 5.0–5.2) and high Al_{im} levels (> 100–200 μg/L) during high flow, supported substantially lower numbers and biomass of brook trout than nonacidic ERP streams and lacked acid-sensitive fish populations, such as blacknose dace and sculpin.

Three streams were nonacidic (ANC > 0) throughout the period of study (Fly Pond Outlet, Black Brook, High Falls Brook). Baldwin Creek had only one brief acidic episode with a minimum ANC of –1 μeq/L. These four streams had higher brook trout biomass (average values for each stream, 1.8–3.5 kg/0.1 ha) than all other ERP streams (0.3–1.6 kg/0.1 ha), and higher brook trout density (127–309 fish/0.1 ha) than in all but one other ERP stream (4–159 fish/0.1 ha).

Three streams were chronically acidic during the period of study (i.e., median weekly ANC $\leq$ 0) (East Branch Neversink River, Stone Run, Roberts Run). All three supported low numbers (24–71 fish/0.1 ha) and biomass of brook trout (0.3–1.1 kg/0.1 ha).

Two streams, Buck Creek and Linn Run, were not chronically acidic but commonly had acidic episodes lasting 10 or more days during hydrologic events. The density and biomass of trout in these streams (4–47 fish/0.1 ha and 0.25–0.73 kg/0.1 ha) were substantially less than in nonacidic ERP streams and similar to levels in the three chronically acidic ERP streams.

The four remaining ERP streams (Benner Run, Biscuit Brook, Seventh Lake Inlet, Bald Mountain Brook) had chemical conditions of intermediate severity (less frequent and shorter duration acidic episodes) and intermediate levels of brook trout density and biomass (58–158 fish/0.1 ha; 1.2–1.6 kg/0.1 ha).

As a group, streams that experienced episodic acidification had significantly ($p < 0.05$) lower levels of brook trout density and biomass than nonacidic streams. Differences in trout abundance between episodically and chronically acidic streams were not statistically significant ($p > 0.05$).

With one exception, acid-sensitive fish populations occurred only in ERP streams with median weekly pH > 6.0 (Black Brook, High Falls Brook, Biscuit Brook, Benner Run, Baldwin Run) and were absent from streams that were chronically acidic or that experienced moderate to severe episodic acidification (Bald Mountain Brook, Seventh Lake Inlet, East Branch Neversink River, Linn Run, Stone Run, Roberts Run).

Likewise, young-of-the-year brook trout were abundant (indicative of successful reproduction during the study period) in Fly Pond Outlet, Black Brook, High Falls Brook, Biscuit Brook, Benner Run, and Baldwin Creek, but were absent or rare in Bald Mountain Brook, Buck Creek, Seventh Lake Inlet, East Branch Neversink River, and Linn Run. Young-of-the-year brook trout were abundant in Stone Run and Roberts Run in 1988, associated with below normal precipitation levels in winter/spring 1988, but absent or rare in 1989, following higher than normal precipitation and presumably more severe episodes in winter/spring 1989.

In situ bioassays demonstrated that fish exposed to episodic acidification can experience significant mortality. Fish mortality during bioassays was significantly ($p < 0.05$) lower in reference streams (Fly Pond Outlet, Black Brook, High Falls Brook, Baldwin Run, Benner Run) than in non-reference streams. Mortality rates were significantly higher in bioassays with acidic episodes than in bioassays with ANC > 0 μeq/L, but similar to bioassays that had chronically acidic conditions (ANC $\leq$ 0). Results were consistent across all fish species.

Chemical conditions toxic to fish occurred at some time during the study in all ERP streams except the five reference streams. Maximum observed mortality rates were generally highest in those streams with the most severe chemical conditions: > 80% in Buck Creek, East Branch Neversink River, Stone Run, and Linn Run; between 40% and 50% in Bald Mountain Brook and Roberts Run; 20% to 30% in Seventh Lake Inlet and Biscuit Brook; and < 20% in all five reference streams. Because bioassays were not conducted during periods with the most severe chemistry in each stream, these results provide only a qualitative indicator of the toxicity of ERP streams. All streams also had at least one bioassay with low mortality (< 10%), indicating that toxic conditions do not occur throughout the year.

A net downstream movement of radio-tagged brook trout was observed in all streams and study periods that experienced stressful chemical conditions, but little to no net downstream movement occurred in streams with relatively high pH (> 5.1–5.2) and low Al_{im} (< 150–160 μg/L) throughout the study period. Downstream fish movement either was associated with chronically acidic conditions at the start of the experiment or coincided with the occurrence of one or more episodes with Al_{im} > 160 μg/L for 1.5 or more days. Radio-tagged brook trout died when exposed to high concentrations of Al during an episode in Linn Run. During the same episode, radio-tagged trout survived if they avoided exposure to peak Al levels.

Objective 3. Define key characteristics of episodes that determine the severity of effects on fish populations.

Inorganic Al was the single best predictor of fish mortality during *in situ* bioassays. Calcium, pH, and DOC were also important predictors of brook trout mortality; at a given Al_{im} concentration, lower mortality occurred in bioassays with lower minimum pH, higher Ca, and higher DOC.

Brook trout density and biomass in ERP streams were significantly ($p < 0.05$) correlated with both stream pH and Al_{im} concentrations, although rank correlations were slightly higher for pH than Al_{im}. Because pH and Ali_m are highly correlated, it is difficult, based on field data alone and given the small number of study streams ($n = 13$), to distinguish the relative importance of pH and Al_{im}.

The relationships between Al_{im} and pH, and between Al_{im} and ANC, varied among ERP streams. High levels of Al_{im} (> 200 μg/L) commonly occurred in Linn Run at pH ≤ 5.4, but only at pH ≤ 5.2 in Stone Run, Bald Mountain Brook, Buck Creek, and Seventh Lake Inlet, and at pH < 5.0 in Roberts Run and East Branch Neversink River. [No Al_{im} levels above 200 μg/L occurred in the remaining six ERP streams.] Thus, predictions of potential effects on fish based solely on pH or ANC may be misleading.

Fish exposed for longer periods of time to high Al_{im} levels, in general, had higher mortality rates. However, the single best predictor of brook trout and sculpin mortality was the time-weighted median Al_{im} concentration during the 20-day bioassay period, as opposed to more complex expressions of chemical exposure incorporating peak levels and duration.

Blacknose dace are more sensitive to high Al_{im} than brook trout or sculpin. Dace mortality was best predicted by an integrated function of duration and Al_{im} concentrations. High mortality is expected to occur with Al_{im} > 250 μg/L for two or more days.

During radiotelemetry studies, some brook trout were able to move downstream or into alkaline microhabitats and avoided exposure to low pH and high Al during episodes. However, in most cases, the majority of radio-tagged fish were exposed to relatively high, potentially lethal Al levels. Fish behavioral avoidance and the occurrence of refugia can partially, but not entirely, mitigate the adverse effects of episodic acidification on fish populations. Recolonization from groundwater seeps and more alkaline tributary streams can maintain low densities of fish in streams that experience toxic episodes, but is not sufficient to sustain fish densities or biomass at levels near those expected in the absence of adverse acid-base chemistry.

Brook trout are fairly mobile, frequently moving more than 1 km. Thus, of the fish species common in small headwater streams, brook trout are best able to take advantage of refugia. Sculpin, by contrast, generally move only short distances (e.g., < 10 m in a summer). Sculpin were as or more tolerant of high Al_{im} in bioassays than brook trout. Yet, sculpin populations are absent from streams that maintain low densities of brook trout. We hypothesize that toxic episodes have a more severe and long-lasting effect on sculpin populations, compared to brook trout populations, because of differences in fish mobility.

Better delineation of the specific characteristics of episodes and stream chemistry that are most important in controlling effects on fish and fish populations would require controlled experiments, involving specific combinations of chemical variables and exposure magnitude, duration, and timing.

Objective 4. Develop and calibrate regional models of episodic chemistry that link atmospheric deposition to biologically relevant chemistry during episodes.

We have not reported the results of modeling investigations in this report. They will be presented in future journal articles.

Major Conclusions

- Episodes were a common occurrence in the study streams of all three regions, and acidic episodes were common when ANC values were ≤ 50 µeq/L immediately before the episode. When acidic episodes occurred, they were accompanied by depressed pH levels and elevated Al_{im} concentrations.

- Acidic deposition, as evidenced by stream water SO_4^{2-} and NO_3^- during episodes, contributed significantly in two ways to the occurrence of acidic episodes with low pH and high Al levels in all three regions. Pulses of SO_4^{2-} (in Pennsylvania streams) and NO_3^- (in Catskill and Adirondack streams) during episodes augmented natural processes to create episodes with lower ANC and pH and higher Al_{im} concentrations than would have occurred from natural processes alone. In addition, large baseline concentrations of SO_4^{2-} (all regions) and NO_3^- (Catskills and Adirondacks) reduced episodic minimum ANC levels, even when these ions did not change or decreased slightly during episodes.

- Episodic acidification can have long-term adverse effects on fish populations. As a result, stream assessments based solely on chemical measurements during low flow do not accurately predict the status of fish communities in small streams.

- Fish exposed to low pH and high Al_{im} for longer periods of time experienced higher mortality. Time-weighted median Al_{im} concentration was the single best predictor of brook trout mortality.

- Fish behavioral avoidance only partially mitigated the adverse effects of episodic acidification in small streams and was not sufficient to sustain fish density or biomass at the levels expected in the absence of acidic episodes.

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APPENDIX A

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APPENDIX B

WATER CHEMISTRY PERFORMANCE EVALUATION SAMPLES AND BLANKS

B.1 PERFORMANCE EVALUATION SAMPLES

Synthetic and well-characterized natural performance evaluation (PE) samples were utilized as single-blind samples to monitor water chemistry analyses for the ERP. Natural PE samples were characterized through repeated use in a large interlaboratory round-robin program sponsored by the Long Range Transboundary Atmospheric Pollutant (LRTAP) program. For most analytes, target values for natural samples were estimated as the mean of median values reported for each round-robin study. Each sample was used in at least three rounds of the LRTAP round-robin. For synthetic samples, target values represented the theoretical concentration of analyte in the sample.

Performance objectives for precision and bias and total error were developed for each analysis, following the approach of Hunt and Wilson (1986). These objectives were used as control criteria for laboratory quality control samples, and for review of individual performance evaluation results. Two natural PE samples (FN-09 from Seventh Lake, New York, and FN-10 from Big Moose Lake, New York) were taken to the field and processed through the sample collection devices to provide information on the effects of sample collection and handling on analytical performance. Target values for these two samples were supplied to the laboratories to allow them to monitor their own performance using a consistent set of samples among all three regions throughout the entire duration of the project. Additional information about the performance evaluation sample program for the ERP is presented in the quality assurance project plan (Peck et al., 1988).

At the conclusion of the ERP, results of PE samples were reviewed for outlying observations, and those outliers that could be attributed to a definite cause (e.g., calibration problems, sample contamination, or dilution) were excluded from statistical summarization. A total of 15 data values from the Northern Appalachians region, 36 from the Adirondacks region, and 62 from the Catskills region were considered invalid and excluded. Other errors, such as reporting errors, were corrected and included in the summarization. All data (including values considered invalid) from the PE samples are included as part of the overall ERP database.

In instances where internal quality control or data verification activities indicated the need to reanalyze samples or batches of samples, associated PE samples were not reanalyzed. Thus the performance indicated from the PE samples may be conservative in some cases, because some PE sample results are no longer associated with routine sample analyses. As the results show, there were very few instances where an individual laboratory consistently achieved all performance objectives for an individual analyte. The fact that all three laboratories, each employing the same QA/QC program and utilizing identical QC samples, could not achieve the established performance objectives suggests these objectives may be too stringent for routine implementation over an extended period of time. The objectives established for the ERP were more stringent than those established for other monitoring programs, such as the National Surface Water Survey. For the ERP, project management and principal investigators considered monitoring and assessment of long-term analytical performance to be more important than performance within individual analytical batches. These objectives were based on a desire to control long-term variability in individual laboratory performance and facilitate comparability of chemical data among the three ERP regions. Thus, consistency in performance among the three regions is considered more important than the failure or success of any individual laboratory in meeting performance objectives.

Performance evaluation sample results for organic monomeric aluminum (Al_{om}), total monomeric aluminum (Al_{tm}), and total dissolved aluminum (Al_{td}) are presented in Tables B-1 and B-2[1]. For the monomeric aluminum analytes, sample sizes for most PE samples were relatively small, except for the two field-handled samples (FN-09 and FN-10). In addition, natural samples were not well characterized for monomeric aluminum species, and target values were developed based on the results of ERP analyses alone, by calculating a weighted mean value assuming unequal sample sizes and variances among laboratories, following Taylor (1987). For Al_{om} and Al_{tm}, results from the Northern Appalachians laboratory are also applicable to samples collected in the Catskills region. Organic Al and Al_{tm} data from all three regions may be subject to considerable imprecision at higher concentrations (> 0.400 mg/L; Table B-1). For Al_{tm}, data from the Adirondack region may be subject to positive bias at moderate concentrations (0.400 mg/L), whereas data from the other two regions may be subject to negative bias at very high concentrations (0.750 mg/L). For Al_{td} (Table B-2), data from all three regions may be subject to considerable imprecision at higher concentrations.

For pH (Table B-3), performance evaluation sample data indicate little bias and good precision for acidic samples (pH < 5.00), and for more circumneutral samples, based on results of natural per-

[1]All tables for this appendix follow the text.

formance evaluation samples. All three regions experienced both bias and precision problems with two synthetic samples having circumneutral target values. These samples were prepared from carbonate compounds and were subject to considerable effects from CO_2 exchange during both transport and analysis in the laboratories. These results are presented here to illustrate the effects that CO_2 can have on pH measurements of circumneutral samples of low ionic strength (if not protected from atmospheric exchange). Results from natural performance evaluation samples should be used to evaluate laboratory performance in the circumneutral range. Based on these results, data from the Northern Appalachians region are subject to more imprecision in the circumneutral range than data from the other two regions. Peck and Metcalf (1991) provide additional discussion of the problems associated with these synthetic samples.

Results for ANC analyses of PE samples (Table B-4) indicate data from the Northern Appalachians region may be subject to some negative bias and larger imprecision than data from the other two regions. Specific conductance data (Table B-5) are generally acceptable for all three regions, although some unexplained problems (possible dilution or cross-contamination) were noted with one of the field-handled samples (FN-09) from the Catskills region. As similar problems were not observed for other PE samples, this is not believed to have an impact on overall data quality. Analysis of dissolved inorganic carbon (DIC) was optional for the ERP, and thus was not subject to the same level of quality control as other analytes. Results of PE samples (Table B-6) indicate that DIC data from the Adirondacks may be subject to greater imprecision than data from the Catskills region, possible due to larger variations in atmospheric carbon dioxide concentrations in the Adirondacks laboratory affecting unprotected samples.

Results of dissolved organic carbon (DOC) analysis (Table B-7) did not indicate any major problems with performance. There were indications of possible field handling effects in PE samples from both the Northern Appalachians and the Catskills regions, and some evidence of imprecision at lower concentrations from the Northern Appalachians region.

In general, no major problems were indicated from the results of cation analyses (Tables B-8 through B-12). No problems were indicated with Ca^{2+} (Table B-8) or Mg^{2+} (Table B-9) analyses. Sodium (Table B-10) and K^+ (Table B-11) results from the Northern Appalachians and Catskills regions region show greater imprecision than data from the Adirondacks region. Ammonium was an optional analyte and was not measured in the Catskills region. Results from PE samples (Table B-12) indicate NH_4^+ data from both the Northern Appalachians and Adirondacks regions may be more imprecise than expected at higher concentrations.

Performance evaluation sample results for major anions indicate that Cl^- data from the Northern Appalachians region (Table B-13) may be more imprecise than data from the other two regions. Some imprecision was indicated at very low (0.3 mg/L) and very high (15 mg/L) concentrations in the Adirondacks region, and at very high concentrations (15 mg/L) in the Catskills region, possibly a result of dilution errors. Nitrate data from the Northern Appalachians region appear to be more imprecise than data from the other two regions (Table B-14), and there may be some influence of field handling in NO_3^- data from the Adirondacks region. No major problems were indicated for SO_4^{2-} data (Table B-15).

No major problems were identified for SiO analyses in any region (Table B-16). Results of some PE samples indicate that data from the Adirondacks may be more imprecise than data from the other two regions.

In summary, the performance evaluation sample results indicate that data from all three regions are generally comparable (with the exception of aluminum species data) and may be combined for certain types of analyses and interpretative activities. Systematic errors in the data set are not an important concern for almost all analytes, and there are only a few analytes where imprecision may affect data interpretation or its use in modeling activities. Another point of interest is that the field-handled samples did not indicate large effects of sample collection or handling on either random or systematic errors. This result indicates that the major source of measurement error is the laboratory, and that laboratory-only QC data sets can provide a reasonable assessment of data quality with respect to collection and measurement error.

B.2 BLANKS

Tables B-17 to B-19 summarize analyses of ERP field blanks. These results indicate that appropriate container cleaning and sample handling procedures were used during the project and that sample contamination was not a significant problem.

B.3 REFERENCES

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Table B-1. **Performance Evaluation Sample Summary for the Episodic Response Project: Organic Monomeric and Total Monomeric Aluminum (mg/L)**

Performance objectives: MDL[a] = 0.006; precision and bias = ±0.006 or ±3%; total error = 0.018 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Organic Monomeric Aluminum							
Adirondacks Region							
LN-14	0.001	7	0.007	0.019	+0.006	±0.040	0.030
LN-13	0.034	7	0.033	0.019	−0.001	±0.038	0.037
LN-15	0.058	4	0.068	0.027	+0.010	±0.054	0.064
FN-09	0.007	8	0.019	0.017	+0.012	±0.034	0.046
FN-10	0.042	9	0.048	0.026	+0.006	±0.052	0.058
Catskills and Northern Appalachians Regions[e]							
LN-13	0.034	6	0.035	0.018	+0.001	±0.036	0.037
FN-09	0.007	18	0.010	0.005	+0.003	±0.010	0.013
FN-10	0.042	15	0.041	0.006	−0.001	±0.012	0.013
Total Monomeric Aluminum							
Adirondacks Region							
LN-14	0.010	7	0.015	0.024	+0.005	±0.048	0.053
SYN-1	0.050	4	0.049	0.024	−0.001	±0.048	0.049
LN-13	0.058	7	0.048	0.035	−0.010	±0.070	0.080
LN-15	0.146	4	0.157	0.028	+0.011	±0.056	0.067
SYN-2	0.400	4	0.468	0.127	+17%	±54%	71%
SYN-3	0.750	4	0.755	0.062	+1%	±16%	17%
FN-09	0.041	7	0.013	0.015	±0.028	±0.030	0.002
FN-10	0.158	9	0.177	0.031	+0.019	±0.062	0.081
Catskills and Northern Appalachians Regions[e]							
LN-14	0.010	6	0.003	0.001	−0.007	±0.002	0.009
SYN-1	0.050	10	0.044	0.006	−0.006	±0.012	0.018
LN-13	0.058	6	0.059	0.009	+0.001	±0.018	0.019
SYN-2	0.400	10	0.363	0.021	−9%	±12%	21%
SYN-3	0.750	8	0.649	0.079	−14%	±24%	38%
FN-09	0.013	18	0.013	0.006	0.000	±0.012	0.012
FN-10	0.158	16	0.171	0.016	+0.013	±0.032	0.045

[a] MDL = method detection limit.
[b] Bias = Mean − Target Value. Relative bias = [(Mean − Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).
[e] Organic monomeric and total monomeric aluminum samples collected in the Catskills region were sent to the Northern Appalachian region laboratory for analysis.

Table B-2. Performance Evaluation Sample Summary for the Episodic Response Project: Total Dissolved Aluminum (mg/L)

Performance objectives: MDL[a] = 0.006; precision and bias = ±0.006 or ±3%; total error = 0.018 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
LN-14	0.010	7	0.008	0.005	-0.002	±0.010	0.008
SYN-1	0.050	7	0.040	0.007	-0.010	±0.014	0.004
LN-13	0.070	7	0.104	0.015	+0.034	±0.030	0.064
LN-15	0.183	4	0.207	0.032	+0.024	±0.064	0.088
SYN-2	0.400	7	0.382	0.025	–4%	±13%	17%
SYN-3	0.750	7	0.718	0.030	–4%	±8%	12%
FN-09	0.041	15	0.051	0.016	+0.010	±0.032	0.042
FN-10	0.187	17	0.208	0.046	+0.021	±0.092	0.113
Catskills Region							
LN-14	0.010	8	0.012	0.011	+0.002	±0.022	0.024
SYN-1	0.050	12	0.036	0.007	–0.014	±0.014	0.000
LN-13	0.070	10	0.083	0.017	+0.013	±0.034	0.047
LN-15	0.183	4	0.231	0.029	+0.048	±0.058	0.106
SYN-2	0.400	9	0.359	0.058	–10%	±32%	42%
SYN-3	0.750	8	0.718	0.099	–4%	±28%	32%
FN-09	0.041	11	0.037	0.013	–0.004	±0.026	0.030
FN-10	0.187	12	0.163	0.030	–0.024	±0.060	0.084
Northern Appalachians Region							
LN-14	0.010	10	0.014	0.009	+0.004	±0.018	0.022
SYN-1	0.050	16	0.048	0.006	–0.002	±0.012	0.014
LN-13	0.070	10	0.052	0.011	–0.018	±0.022	0.040
SYN-2	0.400	16	0.392	0.040	–2%	±20%	22%
SYN-3	0.750	13	0.759	0.122	+1%	±32%	33%
FN-09	0.041	19	0.041	0.012	0.000	±0.024	0.024
FN-10	0.187	19	0.171	0.024	–0.016	±0.048	0.064

a MDL = method detection limit.
b Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
c Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
d Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-3. Performance Evaluation Sample Summary for the Episodic Response Project: pH (pH units)

Performance objectives: MDL[a]= not appliocable; precision and bias = ±0.08; total error = 0.25.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
SYN-1	4.40	7	4.43	0.02	+0.03	±0.04	0.07
LN-15	5.52	4	5.70	0.17	+0.18	±0.34	0.52
LN-13	5.95	7	5.90	0.12	−0.05	±0.24	0.29
SYN-2	6.53	7	6.39	0.09	−0.14	±0.18	0.32
LN-14	7.07	7	6.97	0.24	−0.10	±0.48	0.58
SYN-3	7.49	7	7.33	0.22	−0.16	±0.44	0.60
FN-09	6.83	16	6.93	0.11	+0.10	±0.22	0.32
FN-10	5.15	17	5.20	0.03	+0.05	±0.06	0.11
Catskills Region							
SYN-1	4.40	11	4.42	0.04	+0.02	±0.08	0.10
LN-15	5.52	4	5.49	0.03	−0.03	±0.06	0.09
LN-13	5.95	8	5.89	0.05	−0.06	±0.10	0.16
SYN-2	6.53	10	6.08	0.21	−0.45	±0.42	−0.87
LN-14	7.07	10	7.06	0.06	−0.01	±0.12	0.13
SYN-3	7.49	11	6.99	0.16	−0.50	±0.32	−0.82
FN-09	6.83	12	6.72	0.19	−0.11	±0.38	0.49
FN-10	5.15	13	5.26	0.24	+0.11	±0.48	0.59
Northern Appalchians Region							
SYN-1	4.40	14	4.48	0.05	+0.08	±0.10	0.18
LN-15	5.52	4	5.71	0.12	+0.19	±0.24	0.43
LN-13	5.95	10	5.89	0.08	−0.06	±0.16	0.22
SYN-2	6.53	13	6.29	0.20	−0.24	±0.40	0.64
LN-14	7.07	10	6.90	0.16	−0.17	±0.32	0.49
SYN-3	7.49	14	7.10	0.24	−0.39	±0.48	0.87
FN-09	6.83	21	6.78	0.11	−0.05	±0.22	0.27
FN-10	5.15	19	5.22	0.07	+0.07	±0.14	0.21

[a] MDL = method detection limit.
[b] Bias = Mean − Target Value. Relative bias = [(Mean − Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-4. Performance Evaluation Sample Summary for the Episodic Response Project: Acid Neutralizing Capacity (μeq/L)

Performance objectives: MDL[a] = not applicable; precision and bias = ±2.5 or ±3%; total error = 7.5 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
SYN-1	–39.9	7	–37.6	4.6	+2.3	±9.2	11.5
LN-15	7.7	4	10.3	2.9	+2.6	±5.8	8.4
SYN-2	15.0	7	16.5	1.4	+1.5	±2.8	4.3
LN-13	20.5	7	24.9	5.9	+4.4	±11.8	16.2
SYN-3	140.0	7	144.3	8.7	+3%	±12%	15%
LN-14	223.3	7	228.6	16.4	+2%	±14%	16%
FN-09	152.3	16	157.0	3.8	+3%	±4%	12%
FN-10	–0.8	17	+0.9	3.9	+1.7	±7.8	9.5
Catskills Region							
SYN-1	–39.9	12	–39.2	4.1	+0.7	±8.2	8.9
LN-15	7.7	4	11.7	2.0	+4.0	±4.0	8.0
SYN-2	15.0	10	17.0	3.1	+2.0	±6.2	8.2
LN-13	20.5	10	23.3	3.5	+2.8	±7.0	9.8
SYN-3	140.0	13	133.0	7.1	–5%	±11%	16%
LN-14	223.3	10	224.5	2.4	+0.5%	±2%	2%
FN-09	152.3	12	147.0	10.4	–4%	±14%	18%
FN-10	–0.8	13	1.8	3.9	+2.6	±7.8	10.4
Northern Appalachians Region							
SYN-1	–39.9	12	–47.2	4.7	–7.3	±9.4	16.7
LN-15	7.7	4	4.8	2.2	–2.9	±4.4	7.3
SYN-2	15.0	13	9.2	6.1	–5.8	±12.2	18.0
LN-13	20.5	8	15.5	2.6	–5.0	±5.2	10.2
SYN-3	140.0	14	137.3	10.7	-2%	±16%	18%
LN-14	223.3	8	242.1	14.8	+8%	±12%	20%
FN-09	152.3	21	153.2	7.0	+1%	±9%	10%
FN-10	–0.8	19	–5.2	3.6	–4.4	±7.2	11.6

a MDL = method detection limit.
b Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
c Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
d Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-5. Performance Evaluation Sample Summary for the Episodic Response Project: Specific Conductance (μS/cm @ 25°C)

Performance objectives: MDL[a] = not applicable; precision and bias = ±1 or ±3%; total error = 3 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
SYN-1	1.4	7	2.0	0.1	+0.6	±0.2	0.8
SYN-2	17.0	7	16.7	0.6	–0.3	±1.2	1.5
LN-13	22.2	7	22.5	0.2	+0.3	±0.4	0.7
LN-15	25.9	4	25.8	0.2	–0.1	±0.4	0.5
SYN-3	45.5	7	46.7	1.8	+3%	±8%	11%
LN-14	54.1	7	54.2	0.7	+0.2%	±3%	3%
FN-09	52.1	16	50.1	0.7	–4%	±3%	7%
FN-10	23.5	17	22.8	0.5	–0.7	±1.0	1.7
Catskills Region							
SYN-1	1.4	9	2.0	0.2	+0.6	±0.4	1.0
SYN-2	17.0	10	16.3	1.2	–0.7	±2.4	3.1
LN-13	22.2	7	22.2	0.1	0.0	±0.2	0.2
LN-15	25.9	4	25.6	0.1	–0.3	±0.2	–0.5
SYN-3	45.5	10	45.2	1.4	–1%	±6%	7%
LN-14	54.1	10	53.2	0.6	–2%	±2%	4%
FN-09	52.1	12	47.8	2.2	–8%	±9%	17%
FN-10	23.5	13	22.6	0.4	–0.9	±0.8	1.7
Northern Appalachians Region							
SYN-1	1.4	13	1.9	0.2	+0.5	±0.4	0.9
SYN-2	17.0	14	16.1	1.0	–0.9	±2.0	2.9
LN-13	22.2	10	22.0	0.5	–0.2	±1.0	1.2
LN-15	25.9	4	25.4	0.3	–0.5	±0.6	1.1
SYN-3	45.5	14	44.8	2.7	–2%	±12%	14%
LN-14	54.1	10	53.1	0.8	–2%	±3%	5%
FN-09	52.1	21	48.1	1.2	–8%	±5%	13%
FN-10	23.5	19	22.3	0.5	–1.2	±1.0	-2.2

[a] MDL = method detection limit.
[b] Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-6. Performance Evaluation Sample Summary for the Episodic Response Project: Dissolved Inorganic Carbon (mg C/L)

Performance objectives: MDL[a] = 0.05; precision and bias = ±0.05 or ±3%; total error = 0.15 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
SYN-1	0.12	7	0.19	0.23	+0.07	±0.46	0.53
SYN-2	0.30	7	0.41	0.12	+0.11	±0.24	0.35
LN-15	0.37	4	0.34	0.16	-0.03	±0.32	0.35
LN-13	0.46	7	0.56	0.18	+0.10	±0.36	0.46
SYN-3	1.80	5	2.05	0.23	+14%	±22%	36%
LN-14	2.82	7	3.18	0.20	+13%	±13%	26%
FN-09	2.06	12	2.21	0.13	+7%	±12%	19%
FN-10	0.49	13	0.38	0.10	–0.11	±0.20	0.31
Catskills Region							
SYN-1	0.12	7	0.15	0.02	+0.03	±0.04	0.07
SYN-2	0.30	7	0.37	0.04	+0.07	±0.08	0.15
LN-15	0.37	0					
LN-13	0.46	6	0.61	0.01	+0.15	±0.02	0.17
SYN-3	1.80	6	1.80	0.05	0%	±6%	6%
LN-14	2.82	6	3.10	0.04	+10%	±3%	13%
FN-09	2.06	6	2.20	0.19	+7%	±17%	24%
FN-10	0.49	5	0.58	0.12	+0.09	±0.24	0.33

Northern Appalachians Region

Dissolved inorganic carbon was not measured at this laboratory.

[a] MDL = method detection limit.
[b] Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-7. Performance Evaluation Sample Summary for the Episodic Response Project: Dissolved Organic Carbon (mg C/L)

Performance objectives: MDL[a] = 0.1; precision and bias = ±0.1 or ±5%; total error = 0.3 or 15%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
SYN-1	2.5	7	2.6	0.1	+4%	±8%	12%
LN-14	3.8	7	4.2	0.1	+11%	±5%	16%
LN-15	3.9	4	4.2	0.1	+8%	±5%	13%
SYN-2	5.0	7	5.2	0.2	+4%	±8%	12%
LN-13	6.1	7	6.4	0.1	+5%	±3%	8%
SYN-3	10.0	7	10.1	0.3	+1%	±6%	7%
FN-09	4.4	16	4.1	0.2	–7%	±10%	17%
FN-10	3.3	17	3.5	0.2	+6%	±11%	17%
Catskills Region							
SYN-1	2.5	14	2.7	0.1	+8%	±7%	15%
LN-14	3.8	7	4.3	0.2	+13%	±9%	22%
LN-15	3.9	0					
SYN-2	5.0	14	4.9	0.2	–2%	±8%	10%
LN-13	6.1	8	6.2	0.1	+2%	±3%	5%
SYN-3	10.0	13	10.0	0.3	0%	±6%	6%
FN-09	4.4	11	4.2	0.3	–5%	±14%	19%
FN-10	3.3	12	3.9	0.3	+18%	±15%	33%
Northern Appalachians Region							
SYN-1	2.5	13	2.9	0.3	+16%	±21%	37%
LN-14	3.8	10	4.3	0.4	+13%	±19%	32%
LN-15	3.9	4	4.0	0.2	+3%	±10%	13%
SYN-2	5.0	13	5.4	0.3	+8%	±11%	19%
LN-13	6.1	10	6.1	0.3	0%	±10%	10%
SYN-3	10.0	13	10.3	0.4	+3%	±8%	11%
FN-09	4.4	21	4.2	0.5	–5%	±24%	29%
FN-10	3.3	19	3.6	0.5	+9%	±28%	37%

[a] MDL = method detection limit.
[b] Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-8. Performance Evaluation Sample Summary for the Episodic Response Project: Calcium (mg/L)

Performance objectives: MDL[a] = 0.01; precision and bias = ±0.01 or ±3%; total error = 0.03 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
LN-13	2.08	7	2.15	0.06	+3%	±6%	9%
LN-15	2.31	4	2.26	0.09	–2%	±8%	10%
SYN-1	2.50	7	2.58	0.07	+3%	±5%	8%
SYN-2	4.50	6	4.60	0.08	+2%	±3%	5%
LN-14	5.59	7	5.23	1.30	–6%	±50%	56%
SYN-3	7.00	7	7.10	0.08	+1%	±2%	3%
FN-09	5.02	16	5.09	0.23	+1%	±9%	10%
FN-10	1.82	17	1.81	0.06	–1%	±7%	8%
Catskills Region							
LN-13	2.08	8	2.05	0.04	–1%	±4%	5%
LN-15	2.31	4	2.22	0.14	–4%	±13%	17%
SYN-1	2.50	10	2.53	0.09	+1%	±7%	8%
SYN-2	4.50	10	4.57	0.19	+2%	±8%	10%
LN-14	5.59	8	5.51	0.19	–1%	±7%	8%
SYN-3	7.00	10	7.04	0.18	+1%	±5%	6%
FN-09	5.02	12	4.51	0.44	–10%	±20%	30%
FN-10	1.82	13	1.78	0.05	–2%	±6%	8%
Northern Appalachians Region							
LN-13	2.08	10	2.08	0.11	0%	±11%	11%
LN-15	2.31	4	2.38	0.17	+3%	±14%	17%
SYN-1	2.50	13	2.48	0.16	–1%	±13%	14%
SYN-2	4.50	14	4.54	0.23	+1%	±10%	11%
LN-14	5.59	10	5.48	0.14	–2%	±5%	7%
SYN-3	7.00	14	7.01	0.25	0%	±7%	7%
FN-09	5.02	21	4.87	0.24	–3%	±10%	13%
FN-10	1.82	19	1.74	0.13	–4%	±15%	19%

[a] MDL = method detection limit.
[b] Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-9. **Performance Evaluation Sample Summary for the Episodic Response Project: Magnesium (mg/L)**

Performance objectives: MDL[a] = 0.01; precision and bias = ±0.01 or ±3%; total error = 0.03 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
LN-15	0.36	4	0.37	0.01	+3%	±5%	8%
LN-13	0.48	7	0.48	0.01	0%	±4%	4%
SYN-1	0.50	7	0.52	0.04	+4%	±15%	19%
SYN-2	0.80	7	0.83	0.04	+4%	±10%	14%
LN-14	1.47	7	1.46	0.04	–1%	±5%	6%
SYN-3	1.50	7	1.51	0.04	+1%	±5%	6%
FN-09	0.78	16	0.82	0.06	+5%	±15%	20%
FN-10	0.29	17	0.30	0.02	+0.01	±0.04	0.05
Catskills Region							
LN-15	0.36	4	0.35	0.02	–3%	±11%	14%
LN-13	0.48	8	0.48	0.02	0%	±8%	8%
SYN-1	0.50	10	0.52	0.01	+4%	±4%	8%
SYN-2	0.80	11	0.82	0.02	+2%	±5%	7%
LN-14	1.47	8	1.46	0.04	–1%	±5%	6%
SYN-3	1.50	11	1.52	0.05	+1%	±7%	8%
FN-09	0.78	12	0.73	0.06	–6%	±16%	22%
FN-10	0.29	12	0.29	0.02	0.00	±0.04	0.04
Northern Appalachians Region							
LN-15	0.36	4	0.34	0.02	–6%	±12%	18%
LN-13	0.48	10	0.47	0.02	–2%	±8%	10%
SYN-1	0.50	12	0.51	0.01	+2%	±4%	6%
SYN-2	0.80	14	0.82	0.03	+2%	±7%	9%
LN-14	1.47	10	1.42	0.04	–3%	±6%	9%
SYN-3	1.50	13	1.46	0.16	–3%	±22%	25%
FN-09	0.78	20	0.78	0.02	0%	±5%	5%
FN-10	0.29	19	0.28	0.02	–0.01	±0.04	0.05

[a] MDL = method detection limit.
[b] Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-10. Performance Evaluation Sample Summary for the Episodic Response Project: Sodium (mg/L)

Performance objectives: MDL[a] = 0.01; precision and bias = ±0.01 or ±3%; total error = 0.03 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
LN-13	0.54	7	0.54	0.02	0%	±7%	7%
LN-15	0.70	4	0.69	0.01	−1%	±3%	4%
SYN-1	0.80	7	0.82	0.10	+3%	±24%	27%
LN-14	1.56	7	1.57	0.02	+1%	±3%	4%
SYN-2	3.50	7	3.55	0.23	+1%	±13%	14%
SYN-3	6.00	7	6.04	0.21	+1%	±7%	8%
FN-09	2.59	16	2.59	0.05	0%	±4%	4%
FN-10	0.57	17	0.56	0.06	−2%	±21%	23%
Catskills Region							
LN-13	0.54	8	0.53	0.02	−2%	±8%	10%
LN-15	0.70	4	0.67	0.01	−4%	±3%	7%
SYN-1	0.80	11	0.80	0.03	0%	±8%	8%
LN-14	1.56	8	1.56	0.04	0%	±5%	5%
SYN-2	3.50	11	3.47	0.06	−1%	±3%	4%
SYN-3	6.00	10	5.85	0.14	−3%	±5%	8%
FN-09	2.59	12	2.41	0.20	−7%	±17%	24%
FN-10	0.57	13	0.57	0.03	0%	±11%	11%
Northern Appalachians Region							
LN-13	0.54	8	0.55	0.01	2%	±4%	6%
LN-15	0.70	4	0.54	0.16	−23%	±59%	82%
SYN-1	0.80	13	0.81	0.08	1%	±20%	21%
LN-14	1.56	10	1.41	0.23	−10%	±33%	43%
SYN-2	3.50	14	3.43	0.37	−2%	±22%	24%
SYN-3	6.00	13	6.08	0.15	1%	±5%	6%
FN-09	2.59	21	2.44	0.31	−6%	±25%	31%
FN-10	0.57	19	0.56	0.10	−2%	±36%	38%

[a] MDL = method detection limit.
[b] Bias = Mean − Target Value. Relative bias = [(Mean − Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-11. Performance Evaluation Sample Summary for the Episodic Response Project: Potassium (mg/L)

Performance objectives: MDL[a] = 0.01; precision and bias = ±0.01 or ±3%; total error = 0.03 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
SYN-1	0.25	7	0.25	0.02	0.00	±0.04	0.04
LN-13	0.32	7	0.31	0.01	–0.01	±0.02	0.03
SYN-2	0.35	7	0.34	0.07	–3%	±41%	44%
LN-15	0.42	4	0.42	0.01	0.00	±5%	5%
SYN-2	0.60	7	0.59	0.04	–2%	±14%	16%
LN-14	0.73	7	0.72	0.01	–1%	±3%	4%
FN-09	0.47	16	0.44	0.01	–6%	4%	10%
FN-10	0.32	17	0.31	0.03	–0.01	±0.06	0.07
Catskills Region							
SYN-1	0.25	10	0.25	0.02	0.00	±0.04	0.04
LN-13	0.32	8	0.32	0.01	0.00	±0.02	0.02
SYN-2	0.35	11	0.36	0.04	+3%	±22%	25%
LN-15	0.42	4	0.41	0.02	–2%	±10%	12%
SYN-2	0.60	11	0.60	0.02	0%	±7%	7%
LN-14	0.73	8	0.74	0.04	+1%	±11%	12%
FN-09	0.47	12	0.42	0.05	–11%	24%	35%
FN-10	0.32	13	0.30	0.02	–0.02	±0.04	0.06
Northern Appalachians Region							
SYN-1	0.25	13	0.24	0.02	–0.01	±0.04	0.05
LN-13	0.32	8	0.33	0.01	0.01	±0.02	0.03
SYN-2	0.35	13	0.36	0.03	+3%	±17%	20%
LN-15	0.42	4	0.38	0.04	–10%	±21%	31%
SYN-2	0.60	14	0.59	0.04	–2%	±14%	16%
LN-14	0.73	10	0.71	0.05	–3%	±14%	17%
FN-09	0.47	21	0.44	0.04	–6%	18%	24%
FN-10	0.32	19	0.30	0.06	–0.02	±0.12	0.14

[a] MDL = method detection limit.
[b] Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-12. Performance Evaluation Sample Summary for the Episodic Response Project: Ammonium (mg/L)

Performance objectives: MDL[a] = 0.01; precision and bias = ±0.01 or ±5%; total error = 0.03 or 15%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
LN-14	0.01	7	0.00	0.02	–0.01	±0.04	0.05
LN-15	0.03	4	0.04	0.01	+0.01	±0.02	0.03
LN-13	0.04	7	0.06	0.01	+0.02	±0.02	0.04
SYN-1	0.10	7	0.10	0.01	0.00	±0.02	0.02
SYN-2	0.25	7	0.24	0.03	–4%	±25%	29%
SYN-3	0.50	6	0.48	0.08	–4%	±33%	37%
FN-09	0.01	15	0.02	0.03	+0.01	±0.06	0.07
FN-10	0.04	16	0.04	0.02	0.00	±0.04	0.04
Catskills Region							
Ammonium was not determined for this region.							
Northern Appalachians Region							
LN-14	0.01	10	0.01	0.005	0.00	±0.01	0.01
LN-15	0.03	4	0.03	0.003	0.00	±0.01	0.01
LN-13	0.04	10	0.05	0.01	+0.01	±0.02	0.03
SYN-1	0.10	13	0.10	0.02	0.00	±0.04	0.04
SYN-2	0.25	13	0.23	0.02	–8%	±17%	25%
SYN-3	0.50	14	0.46	0.04	–8%	±17%	25%
FN-09	0.01	21	0.01	0.01	0.00	±0.02	0.02
FN-10	0.04	18	0.03	0.01	–0.01	±0.02	0.03

[a] MDL = method detection limit.
[b] Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-13. Performance Evaluation Sample Summary for the Episodic Response Project: Chloride (mg/L)

Performance objectives: MDL[a] = 0.01; precision and bias = ±0.01 or ±3%; total error = 0.03 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
LN-13	0.36	7	0.32	0.02	−11%	±13%	24%
LN-15	0.50	4	0.49	0.03	−2%	±12%	14%
SYN-1	0.80	7	0.75	0.02	−6%	±5%	11%
LN-14	2.09	7	1.99	0.04	−5%	±4%	9%
SYN-2	5.00	7	4.77	0.13	−5%	±5%	10%
SYN-3	15.0	7	14.7	1.1	−2%	±15%	17%
FN-09	3.96	16	3.93	0.13	−1%	±7%	8%
FN-10	0.30	17	0.32	0.05	+7%	±31%	38%
Catskills Region							
LN-13	0.36	7	0.37	0.01	+3%	±5%	8%
LN-15	0.50	4	0.50	0.003	0%	±1%	1%
SYN-1	0.80	10	0.79	0.02	−1%	±5%	6%
LN-14	2.09	7	2.04	0.05	−2%	±5%	7%
SYN-2	5.00	13	5.09	0.19	+2%	±7%	9%
SYN-3	15.00	12	15.55	1.48	+4%	±19%	23%
FN-09	3.96	11	3.92	0.23	−1%	±12%	13%
FN-10	0.30	12	0.35	0.04	+17%	±23%	40%
Northern Appalachians Region							
LN-13	0.36	10	0.36	0.03	0%	±17%	17%
LN-15	0.50	4	0.49	0.06	−2%	±24%	26%
SYN-1	0.80	15	0.74	0.09	−8%	±24%	32%
LN-14	2.09	10	2.04	0.11	−2%	±11%	13%
SYN-2	5.00	14	4.78	0.59	−4%	±25%	29%
SYN-3	15.00	12	15.26	1.02	+2%	±13%	15%
FN-09	3.96	21	3.82	0.55	−4%	±29%	33%
FN-10	0.30	19	0.33	0.03	+10%	±18%	28%

a MDL = method detection limit.
b Bias = Mean − Target Value. Relative bias = [(Mean − Target Value) ÷ Target Value] × 100.
c Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
d Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-14. Performance Evaluation Sample Summary for the Episodic Response Project: Nitrate (mg/L)

Performance objectives: MDL[a] = 0.006; precision and bias = ±0.006 or ±3%; total error = 0.018 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
LN-14	0.055	7	0.019	0.047	–0.036	±0.094	0.140
LN-13	0.126	7	0.142	0.053	+0.016	±0.106	0.122
SYN-1	0.300	7	0.309	0.017	+3%	±11%	14%
LN-15	1.415	4	1.442	0.080	+2%	±11%	13%
SYN-2	3.000	7	2.980	0.118	–1%	±8%	9%
SYN-3	6.000	7	5.960	0.360	–1%	±12%	13%
FN-09	1.063	16	0.979	0.062	–8%	±13%	21%
FN-10	0.886	17	0.945	0.069	+7%	±15%	22%
Catskills Region							
LN-14	0.055	7	0.050	0.000	–0.005	±0.000	–0.005
LN-13	0.126	7	0.120	0.014	–0.006	±0.028	0.034
SYN-1	0.300	10	0.312	0.034	+4%	±22%	26%
LN-15	1.415	4	1.438	0.016	+2%	±2%	4%
SYN-2	3.000	12	2.918	0.104	–3%	±7%	10%
SYN-3	6.000	12	5.722	0.289	–5%	±10%	15%
FN-09	1.063	11	0.925	0.057	–13%	±12%	25%
FN-10	0.886	12	0.899	0.023	+2%	±5%	7%
Northern Appalachians Region							
LN-14	0.055	10	0.046	0.034	–0.009	±0.068	0.077
LN-13	0.126	10	0.120	0.053	–0.006	±0.106	0.106
SYN-1	0.300	15	0.313	0.034	+4%	±22%	26%
LN-15	1.415	4	1.147	0.021	–19%	±4%	23%
SYN-2	3.000	13	2.985	0.166	–0.5%	±11%	12%
SYN-3	6.000	12	6.019	0.867	+0.3%	±29%	29%
FN-09	1.063	19	0.898	0.091	–16%	±20%	36%
FN-10	0.886	19	0.855	0.102	–4%	±24%	28%

[a] MDL = method detection limit.
[b] Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-15. Performance Evaluation Sample Summary for the Episodic Response Project: Sulfate (mg/L)

Performance objectives: MDL[a] = 0.06; precision and bias = ±0.06 or ±3%; total error = 0.18 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
SYN-1	2.00	7	1.96	0.04	–2%	±4%	6%
LN-13	5.60	7	5.54	0.08	–1%	±3%	4%
SYN-2	6.00	7	5.87	0.06	–2%	±2%	4%
LN-15	6.45	4	6.32	0.08	–2%	±2%	4%
LN-14	8.80	7	8.80	0.18	0%	±4%	4%
SYN-3	10.00	7	9.87	0.14	–1%	±3%	4%
FN-09	6.36	16	6.45	0.07	+1%	±2%	3%
FN-10	5.65	17	5.87	0.17	+4%	±6%	10%
Catskills Region							
SYN-1	2.00	12	2.02	0.03	+1%	±3%	4%
LN-13	5.60	7	5.63	0.08	0.5%	±3%	4%
SYN-2	6.00	13	5.92	0.08	–1%	±3%	4%
LN-15	6.45	4	6.30	0.39	–2%	±12%	14%
LN-14	8.80	7	8.94	0.15	+2%	±4%	6%
SYN-3	10.00	10	9.93	0.09	–1%	±2%	3%
FN-09	6.36	11	6.35	0.32	–0.2%	±10%	10%
FN-10	5.65	13	5.90	0.10	+4%	±3%	7%
Northern Appalachians Region							
SYN-1	2.00	11	1.78	0.09	–11%	±10%	21%
LN-13	5.60	10	5.38	0.20	–4%	±7%	11%
SYN-2	6.00	14	5.60	0.34	–7%	±12%	19%
LN-15	6.45	4	6.11	0.12	–5%	±4%	9%
LN-14	8.80	10	8.71	0.37	–1%	±8%	9%
SYN-3	10.00	15	9.67	0.60	–3%	±12%	15%
FN-09	6.36	21	6.26	0.48	–2%	±15%	17%
FN-10	5.65	19	5.67	0.34	+0.4%	±12%	12%

[a] MDL = method detection limit.
[b] Bias = Mean – Target Value. Relative bias = [(Mean – Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-16. Performance Evaluation Sample Summary for the Episodic Response Project: Silica (mg/L)

Performance objectives: MDL[a] = 0.05; precision and bias = ±0.05 or ±3%; total error = 0.15 or 10%.

Lot	Target Value	n	Mean	Std. Dev.	Bias[b]	Precision[c]	Total Error[d]
Adirondacks Region							
SYN-1	0.70	7	0.66	0.04	−0.04	±0.08	0.12
LN-13	1.10	7	1.10	0.08	0.00	±0.16	0.16
LN-14	2.15	7	2.24	0.19	+4%	±17%	21%
SYN-2	3.00	7	3.05	0.13	+2%	±8%	10%
LN-15	4.16	4	4.32	0.30	+4%	±14%	18%
SYN-3	7.00	7	7.06	0.47	+1%	±13%	14%
FN-09	4.07	15	4.33	0.34	+6%	±16%	22%
FN-10	3.47	17	3.74	0.23	+8%	±12%	20%
Catskills Region							
SYN-1	0.70	8	0.76	0.07	0.06	±0.14	0.20
LN-13	1.10	8	1.19	0.08	0.09	±0.16	0.25
LN-14	2.15	8	2.35	0.07	+9%	±6%	15%
SYN-2	3.00	8	3.15	0.13	+5%	±8%	13%
LN-15	4.16	0					
SYN-3	7.00	7	6.70	0.15	−4%	±5%	9%
FN-09	4.07	11	4.18	0.29	+3%	±14%	17%
FN-10	3.47	13	3.74	0.22	+8%	±12%	20%
Northern Appalachians Region							
SYN-1	0.70	11	0.72	0.07	+0.02	±0.14	0.16
LN-13	1.10	10	1.06	0.07	−0.04	±0.14	0.18
LN-14	2.15	10	2.00	0.10	−7%	±10%	17%
SYN-2	3.00	16	2.88	0.16	−4%	±11%	15%
LN-15	4.16	4	3.65	0.18	−12%	10%	22%
SYN-3	7.00	13	6.72	0.31	−4%	±9%	13%
FN-09	4.07	21	4.02	0.27	−1%	±13%	14%
FN-10	3.47	19	3.34	0.28	−4%	±17%	21%

[a] MDL = method detection limit.
[b] Bias = Mean − Target Value. Relative bias = [(Mean − Target Value) ÷ Target Value] × 100.
[c] Precision = 2 × standard deviation. Relative precision = 2 × [(Standard deviation ÷ Mean) × 100].
[d] Total error = |bias (or relative bias)| + precision (or relative precision), following Hunt and Wilson (1986).

Table B-17. Field Blank Sample Results for Measured Variables for the Adirondacks

Constituent characteristics	Number of Observations	Mean	Minimum	Maximum	Standard Deviation	Lower 95% CI	Upper 95% CI
Aluminum, organic monomeric (mg/L)	69	-0.0003	-0.0340	0.0480	0.0171	-0.0344	0.0338
Aluminum, total dissolved (mg/L)	128	-0.0019	-0.0228	0.0299	0.0078	-0.0173	0.0135
Aluminum, total monomeric (mg/L)	71	0.0007	-0.0360	0.0490	0.0165	-0.0321	0.0335
ANC (μeq/L)	128	2.7480	-5.8300	68.0900	7.0736	-11.2483	16.7443
Calcium (mg/L)	105	0.0845	-0.0470	5.6040	0.5637	-1.0332	1.2022
Chloride (mg/L)	107	0.0364	-0.0990	0.5160	0.0766	-0.1153	0.1881
Specific conductance (μS)	128	1.6581	0.7600	18.4200	2.1185	-2.5338	5.8499
Dissolved inorganic carbon (mg/L)	74	0.1421	-0.1320	0.9950	0.1435	-0.1439	0.4280
Dissolved organic carbon (mg/L)	106	0.2539	-0.2200	1.4100	0.3928	-0.5248	1.0326
Potassium (mg/L)	105	0.0113	-0.0510	0.8870	0.0909	-0.1690	0.1916
Magnesium (mg/L)	105	0.0084	-0.0160	0.3000	0.0332	-0.0574	0.0742
Sodium (mg/L)	105	0.0076	-0.0530	0.3160	0.0526	-0.0967	0.1119
Ammonium (mg/L)	107	0.0111	-0.0150	0.2770	0.0326	-0.0536	0.0757
Nitrate (mg/L)	107	0.0016	-0.0538	0.1448	0.0259	-0.0498	0.0530
pH (pH units)	128	5.6928	5.1800	6.8200	0.1930	5.3109	6.0748
Silica (mg/L)	107	0.0238	-0.1780	2.3660	0.2626	-0.4967	0.5444
Sulfate (mg/L)	107	0.0718	0.0300	1.0830	0.1207	-0.1675	0.3111

Table B-18. Field Blank Sample Results for Measured Variables for the Catskills

Constituent characteristics	Number of Observations	Mean	Minimum	Maximum	Standard Deviation	Lower 95% CI	Upper 95% CI
Aluminum, organic monomeric (mg/L)	6	0.0217	0.0030	0.091	0.03426	-0.0622	0.1055
Aluminum, total dissolved (mg/L)	52	0.0189	-0.0010	0.411	0.06786	-0.1173	0.1550
Aluminum, total monomeric (mg/L)	8	0.0581	0.0020	0.420	0.14631	-0.2793	0.3955
ANC (μeq/L)	60	1.4810	-9.0500	10.650	4.16079	-6.8418	9.8038
Calcium (mg/L)	64	0.0484	0.0050	0.700	0.09195	-0.1353	0.2321
Chloride (mg/L)	3	0.1197	0.0890	0.174	0.04718	-0.0305	0.2698
Specific conductance (μS)	65	1.1620	0.6900	2.430	0.34633	0.4703	1.8537
Dissolved inorganic carbon (mg/L)	45	0.2320	0.0700	0.940	0.15938	-0.0890	0.5530
Dissolved organic carbon (mg/L)	61	0.7367	0.1800	10.400	1.29975	-1.8623	3.3357
Potassium (mg/L)	62	0.0134	0.0100	0.100	0.01280	-0.0122	0.0390
Magnesium (mg/L)	63	0.0116	0.0100	0.040	0.00515	0.0013	0.0219
Sodium (mg/L)	64	0.0377	0.0100	0.840	0.10804	-0.1782	0.2535
Nitrate (mg/L)	2	0.0440	0.0430	0.045	0.00141	0.0379	0.0501
pH (pH units)	66	5.6941	5.1900	6.370	0.21218	5.2705	6.1177
Silica (mg/L)	41	0.3098	0.0100	6.920	1.07605	-1.8634	2.4829

Table B-19. Field Blank Sample Results for Measured Variables for Pennsylvania

Constituent characteristics	Number of Observations	Mean	Minimum	Maximum	Standard Deviation	Lower 95% CI	Upper 95% CI
Aluminum, organic monomeric (mg/L)	4	0.0060	0.0000	0.0220	0.0107	-0.0237	0.0357
Aluminum, total dissolved (mg/L)	24	0.0022	-0.0010	0.0070	0.0021	-0.0021	0.0065
Aluminum, total monomeric (mg/L)	4	0.0008	0.0000	0.0030	0.0015	-0.0034	0.0049
ANC (μeq/L)	24	-5.4025	-12.3300	4.6100	3.5674	-12.7653	1.9603
Calcium (mg/L)	9	0.0308	0.0080	0.0640	0.0196	-0.0136	0.0752
Chloride (mg/L)	9	0.0243	0.0000	0.0510	0.0190	-0.0186	0.0673
Specific conductance (μS)	9	1.4211	1.0200	3.2100	0.6844	-0.1270	2.9693
Dissolved organic carbon (mg/L)	8	0.6500	0.0900	1.5100	0.4663	-0.4253	1.7253
Potassium (mg/L)	9	-0.4418	-2.0000	0.0120	0.8834	-2.4403	1.5567
Magnesium (mg/L)	9	0.0034	0.0000	0.0070	0.0023	-0.0018	0.0086
Sodium (mg/L)	9	0.0132	0.0010	0.0650	0.0203	-0.0328	0.0592
Ammonium (mg/L)	9	0.0060	0.0000	0.0120	0.0030	-0.0008	0.0128
Nitrate (mg/L)	9	0.0182	0.0000	0.0440	0.0173	-0.0208	0.0573
pH (pH units)	25	5.5996	4.7800	5.8400	0.2237	5.1389	-
Silica (mg/L)	9	0.1111	0.0500	0.200	0.0547	-0.0125	0.2347
Sulfate (mg/L)	8	0.0256	0.0000	0.039	0.0125	-0.0033	0.0545

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