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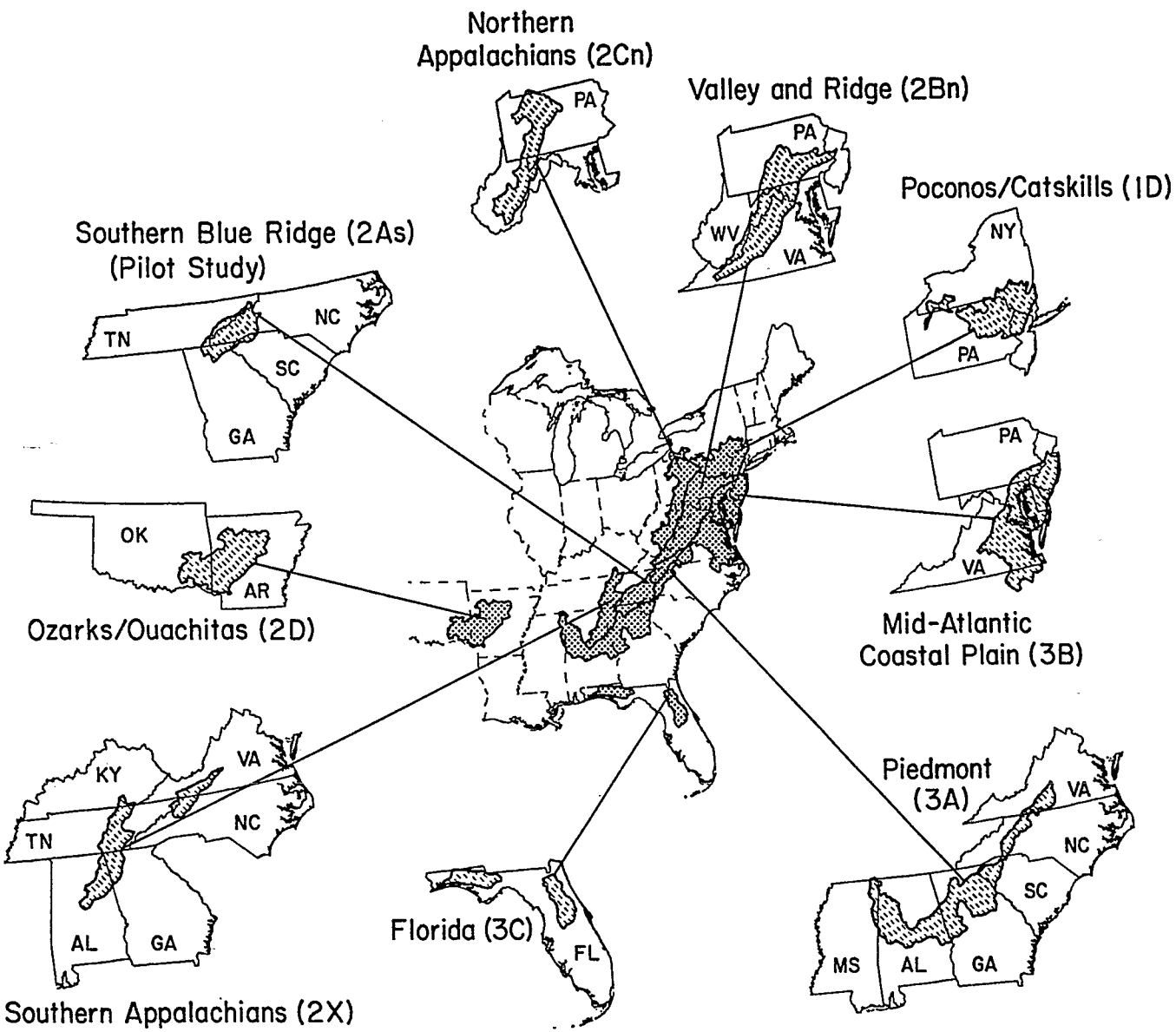
Chemical Characteristics of Streams in the Mid-Atlantic and Southeastern United States (National Stream Survey-Phase I)

Volume I: Population Descriptions and Physico-Chemical Relationships

Aquatic Effects Research Program

SUBREGIONS OF THE NATIONAL STREAM SURVEY - PHASE I



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Chemical Characteristics of Streams in the Mid-Atlantic and Southeastern United States

(Results of the National Stream Survey - Phase I)

Volume I: Population Descriptions and Physico-Chemical Relationships

A Contribution to the
National Acid Precipitation Assessment Program

U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

Environmental Research Laboratory - Corvallis, OR 97333
Environmental Monitoring Systems Laboratory - Las Vegas, NV 89119

NOTICE

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Sale, M.J.[2], P.R. Kaufmann[1], H.I. Jager[8], J.M. Coe[2], K.A. Cougan[5], A.J. Kinney[7], M.E. Mitch[1], and W.S. Overton[3]. 1988. Chemical Characteristics of Streams in the Mid-Atlantic and Southeastern United States. Volume II: Streams Sampled, Descriptive Statistics, and Compendium of Physical and Chemical Data. EPA/600/3-88/021b. U.S. Environmental Protection Agency, Washington, D.C.

Inquiries regarding the availability of the National Stream Survey - Phase I Mid-Atlantic and Southeast data base should be directed in writing to:

Chief, Watershed Branch
U.S. Environmental Protection Agency
Environmental Research Laboratory
200 SW 35th Street
Corvallis, Oregon 97333

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[1] Utah State University, Utah Water Research Laboratory, Logan, Utah 84322. Present address: U.S. Environmental Protection Agency, Environmental Research Laboratory, 200 SW 35th Street, Corvallis, Oregon 97333.
[2] Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box X, Bldg. 1505, Oak Ridge, Tennessee 37831. Operated by Martin Marietta Energy Systems, Inc., under Contract No. DE-AC05-84OR21400 for the U.S. Department of Energy.
[3] Oregon State University, Department of Statistics, Kidder Hall No. 8, Corvallis, Oregon 97331.
[4] Utah State University, Utah Water Research Laboratory, Logan, Utah 84332. Present address: U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Mail Drop 39, Research Triangle Park, North Carolina 27711.
[5] Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada, 89119.
[6] Duke University School of Forestry, 105 Biological Sciences Bldg., Durham, North Carolina 27706.
[7] Northrop Services, Inc., U.S. Environmental Protection Agency, 200 SW 35th Street, Corvallis, Oregon 97333.
[8] Science Applications International Corporation, Environmental Science Division, Oak Ridge National Laboratory, P.O. Box X, Bldg. 1505, Oak Ridge, Tennessee 37831.

PREFACE

The National Surface Water Survey (NSWS) was initiated in 1983 by the U.S. Environmental Protection Agency (EPA) under the National Acid Precipitation Assessment Program (NAPAP), a federal interagency task force mandated by Congress in 1980. The NSWS is a phased, systematic study designed to: (1) characterize the present chemistry of surface waters in the United States and classify them for more intensive study, (2) describe chemical temporal variability and biological resources in subsets of surface waters, and (3) provide a foundation for documenting trends in surface water chemistry through long-term monitoring. The NSWS is one of several major projects in the Acid Deposition Aquatic Effects Research Program (AERP). This program, one of many research programs investigating acidic deposition, is administered by the Acid Deposition and Atmospheric Research Division: Office of Acid Deposition, Environmental Monitoring and Quality Assurance, in the U.S. EPA Office of Research and Development.

The AERP addresses four primary assessment questions:

1. How extensive is the change in aquatic resources as a result of current levels of acidic deposition?
2. What is the anticipated extent and rate of change to these resources in the future?
3. What levels of change in sensitive surface waters are associated with various rates of acidic deposition?
4. What is the rate of change or recovery of affected systems, given decreases in acidic deposition rates?

Five major research projects within the AERP specifically address these assessment questions from a regional perspective. These projects and their goals are:

1. **National Surface Water Survey (NSWS):** To determine the present chemistry, characterize the chemical temporal variability, and determine the key biological resources of lakes and streams in potentially sensitive regions of the United States.

2. **Direct/Delayed Response Project (DDRP):** To predict changes in these aquatic resources at various levels of acidic deposition, considering the terrestrial and aquatic variables that influence these changes.

3. **Watershed Manipulation Project (WMP):** To verify that predictions of future change are reasonably sound by manipulating watershed catchments or system components.

4. **Episodic Response Project (ERP):** To evaluate the regional importance of short-term acidification resulting from episodic hydrologic events and its effect on the quality of the biological environment.

5. **Temporally Integrated Monitoring of Ecosystems Project (TIME):** To test the validity of predicted changes through long-term monitoring of regionally characteristic lakes and streams.

The NSWS, including surveys of lakes and streams, addresses the first goal of the AERP. Understanding the national-scale effects of acidic deposition on aquatic resources requires that

the present chemical status of surface waters be understood on large geographical scales. The National Stream Survey - Phase I (NSS-I), conducted in the mid-Atlantic and southeastern United States, was designed to describe, statistically, the present surface water chemistry on a regional scale. Although cause-and-effect relationships between acidic deposition and surface water response cannot be determined on the basis of NSS-I data alone, analysis of correlative relationships within the NSS-I data base and other information do further our understanding (and will continue to do so) of the extent to which mid-Atlantic and southeastern streams are at risk due to acidic deposition. Determining the relationship between acidic deposition and surface water chemistry is the goal of future activities within the AERP.

The National Stream Survey is funded and administered by the U.S. EPA, Office of Acid Deposition, Environmental Monitoring, and Quality Assurance (OADEMQA) in Washington, D.C. The Environmental Research Laboratory - Corvallis (ERL-C), with cooperating contracts with Utah State University, Oregon State University, and Northrop Environmental Services, is responsible for coordinating the activities of the Survey and for project design, data validation, geographic analysis, and data interpretation. The Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV) is responsible for quality assurance and quality control, logistics, and analytical support. Oak Ridge National Laboratory (ORNL) is responsible for developing and maintaining the data base management system for the Survey. ORNL also participated in data interpretation, provided statistical programming to implement the target population characterizations, and did mapping and other geographic analysis.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL RESEARCH LABORATORY
200 S.W. 35TH STREET
CORVALLIS, OREGON 97333

August 3, 1988

We are pleased to provide you with a complimentary copy of the enclosed report entitled:

"Chemical Characteristics of Streams in the Mid-Atlantic and Southeastern United States (Results of the National Stream Survey-Phase I)"

Volume I: Population Descriptions and Physico-Chemical Relationships
Volume II: Streams Sampled, Descriptive Statistics, and Compendium of Physical and Chemical Data

This report is a product from our National Surface Water Survey (NSWS), first implemented by the U.S. EPA in 1984 under the auspices of the National Acid Precipitation Assessment Program with a survey of Eastern lakes. The enclosed report describes the design and results of National Stream Survey field activities in the Mid-Atlantic and Southeastern U.S. during the spring of 1986 and summarizes our current interpretation of these results. Data obtained during the 1985 National Stream Survey pilot in the Southern Blue Ridge Mountains are also included in this data analysis and interpretation.

We hope that you will find the report useful and look forward to receiving any comments you may wish to share with us. The availability of the National Stream Survey database will be announced in the AERP status, a publication of the Aquatic Effects Research Program, in the fall of 1988. To obtain copies of the AERP status, contact:

Wes Kinney
U.S. EPA Environ. Monit. Systems Lab.
P.O. Box 93478
Las Vegas, Nevada 89193-3478
(702)798-2358 (FTS 545-2358)

or

Deb Chaloud
Lockheed Engr. and Sci. Co.
1050 E. Flamingo Rd., Suite 209
Las Vegas, Nevada 89119
(702)734-3227

Sincerely,

Dixon H. Landers
Research Director
National Surface Water Survey

ERRATA August 29, 1988

Please note the following changes to the two-volume EPA report, "Chemical Characteristics of streams in the Mid-Atlantic and Southeastern United States (National Stream Survey-Phase I)":

Volume I

1. On p. 31, Table 2-3, the subtotal of the number of site exclusions in subregion 2X should be 90, **NOT** 91.

2. pp. 224, 308, 322, 330, and 388 are missing page numbers and should be labelled "THIS PAGE INTENTIONALLY LEFT BLANK"

Volume II

1. On p. 61, section 5.1.2, W_{ij} is the inverse of the joint inclusion probability. The equation for calculating W_{ij} should read:

$$W_{ij} = [2nW_iW_j - (W_i+W_j)] / 2(n-1).$$

2. An incorrect subregion prefix has been used in the stream identification code (STRM_ID) in some of the data listings for the special interest stream North Fork of Ben's Creek. This stream is located in subregion 2Cn, **NOT** 2Bn. The correct STRM_ID for the North Fork of Ben's Creek is 2C035913L, as given in Tables 4-4 and 4-5 on pp. 56 and 57. It has been INCORRECTLY labelled as STRM_ID 2B035913L in the special interest site physical and chemical data listings in Tables 6-2, 7-5, 7-6, 7-7, and 7-8 (pp. 430, 586, 588, 590, and 592). The data in the tables is correct. The site map in Fig. 3-4 shows the correct location of the North Fork of Ben's Creek (#35913) in subregion 2Cn. However, it should have been put on the subregion 2Cn map page (Fig. 3-3, p. 14) rather than on the subregion 2Bn map page (fig. 3-4, p. 15).

3. pp. 22, 394, 432, and 594 are missing page numbers and should be labelled "THIS PAGE INTENTIONALLY LEFT BLANK"

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Supplemental information on the National Stream Survey - Phase I (NSS-I) can be found in the series of ancillary manuals and reports. These publications include:

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ERL-C (Northrop Services, Oregon State University, and Utah State University)

Statistical and Technical Support

Charles Ariss
D. James Blick
Mark Dehaan
Keith Eshleman
Mary Kay Hernandez
Randy Hjort
Kathy Hurley
Robert McCleod
Avis Newell
Gina O'Brien
Roze Royce
Sharmon Stambaugh
George Weaver
Anthony Zagar
Sharon Ziminski

Geographical Support

Anastasia Allen
Darrel Downs
Jeff Irish
Suzanne Pierson

Oak Ridge National Laboratory (U.S. DOE and Martin-Marietta Energy Systems, Inc.)

Data Base Management and Analysis

Jan Coe
Mary Alice Faulkner
Barbara Jackson

Systems Applications, Inc.

Statistical Consulting

Steven Edland
Stella Grosser
Thomas Permutt
Alison Pollack

EMSL-LV (U.S. EPA and Lockheed-EMSCO)

Field Sampling and Logistical Support

David Anthony
John Baker
Barry Baldigo
Jeffrey Bielling
John Campbell
James Crawford
David Crouse
Betsy Dickes
Jacqueline DiMauro
Richard Easton
Elizabeth Floyd
Elizabeth Hill
Mark Hodgkins
Rainer Hoenicke
Paul Hook
David Horton
Michael Hoppus
Frederick Kirschner
C. Mel Knapp
Christopher LaFlash
Lou Lunte
Lesa Madison
Cindy Mayer
Celeste McCuish
Diane McDonald
Anne Neale
Donald Osborne
Mike Parker
Peggy Perman
Steve Pierett
Robert Rice
Gary Roecker
John Schutt
Monica Schwalbach
Karen Short
Eugene Smith
Brad Teague
Timothy Zebuske

Processing Laboratory Support

Barney Akuna
John Alston
Lori Arent
Mary Balogh
Christina Borror
Deb Chaloud
Hal Coleman
Betsy Dickes
Robert Heine
Herb Herpolsheimer
Robert Hughes
Valerie Miller
Molly Morison
James Nitteraurer
Roxanne Parks
James Pendleton
Carla Schuman
Sally Snell
Carl Whitfield
Brenda Whitfield
Jeffrey Wolfe

Statistical and Technical Support

Byron Blasdell
Brian Cordova
Robert Corse
John Curtis
Ramon Denby
Jerry Dugas
Robert Enwall
Annalisa Hall
John Henshaw
Daniel Hillman
John Lau
Tim Lewis
Jeff Love
Linda Marks
Richard Maul
Richard Metcalf
Mohammed Miah
John Nicholson
Mick Reese
Valerie Sheppe
Paula Showers
Lynn Stanley
Martin Stapanian
Donna Sutton
Mark Sweeney
John Teberg
John Wengert

Quality Assurance and Quality Control

Sevda Drouse
Marianne Faber
Daniel Heggem
Wesley Kinney
Carol MacLeod
Dean Mericas
T. Mitchell-Hall
James Pollard
Robert Schonbrod
Donna Sutton

CONTRIBUTIONS OF NSS-I AUTHORS

The National Stream Survey - Phase I (NSS-I) and this document represent the efforts of many individuals. The primary contributors to this report are noted here.

Section 1: Introduction
- P.R. Kaufmann, Utah State University
- J.J. Messer, Utah State University

Section 2: Survey Design
- W.S. Overton, Oregon State University
- J.J. Messer, Utah State University
- A.J. Kinney, Northrop Services, Inc.
- P.R. Kaufmann, Utah State University

Section 3: Methods
- M.E. Mitch, Utah State University
- K.A. Cougan, Lockheed-EMSCO, Inc.
- C.A. Hagley, Lockheed-EMSCO, Inc.

Section 4: Data Quality Assessment
- D.V. Peck, Lockheed-EMSCO, Inc.
- A.T. Herlihy, Utah State University
- J.W. Elwood, Oak Ridge National Laboratory
- P.R. Kaufmann, Utah State University

Section 5: Target Population--Physical Characteristics
- P.R. Kaufmann, Utah State University
- M.J. Sale, Oak Ridge National Laboratory
- M.E. Mitch, Utah State University

Section 6: Target Population Regional Chemistry
- P.R. Kaufmann, Utah State University
- W.S. Overton, Oregon State University
- M.J. Sale, Oak Ridge National Laboratory
- M.E. Mitch, Utah State University
- H.I. Jager, Science Applications International, Inc.
- J.J. Messer, Utah State University

Section 7: Temporal Variability in Baseflow Chemistry
- A.T. Herlihy, Utah State University
- P.R. Kaufmann, Utah State University
- K.H. Reckhow, Duke University

Section 8: Ion Relationships
- J.W. Elwood, Oak Ridge National Laboratory
- H.I. Jager, Science Applications International, Inc.

Section 9: Nature and Distribution of Acidic and Low ANC Streams
A.T. Herlihy, Utah State University
P.R. Kaufmann, Utah State University
D.D. Brown, Northrop Services, Inc.

Section 10: Evidence of Acidification
P.R. Kaufmann, Utah State University
J.W. Elwood, Oak Ridge National Laboratory
A.T. Herlihy, Utah State University

Section 11: Summary and Conclusions
P.R. Kaufmann, Utah State University
A.T. Herlihy, Utah State University
J.W. Elwood, Oak Ridge National Laboratory

Editing: S.J. Christie, Northrop Services, Inc.

NSS-I Technical Directors:
Design and Implementation - Jay J. Messer
Data Analysis and Interpretation - Philip R. Kaufmann

NSS-I Statistical Design: W. Scott Overton

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EXECUTIVE SUMMARY

Background

National Stream Survey - Phase I (NSS-I) field activities were conducted in the mid-Atlantic and southeastern United States in the spring of 1986 by the U.S. Environmental Protection Agency (EPA) as part of the National Surface Water Survey (NSWS). The first phase of the NSWS was designed to determine the present chemical status of surface waters in regions of the United States containing the majority of streams and lakes considered to be at risk as a result of acidic deposition. The NSS-I was conducted as part of the National Acid Precipitation Assessment Program (NAPAP). Like the previous EPA NSWS activities (Eastern and Western Lake Surveys), it contributes directly to one of NAPAP's principal objectives: the quantification of the extent, location, and characteristics of acidic and potentially sensitive streams and lakes in the United States.

The NSS-I was conducted in four Mid-Atlantic and five Southeast subregions of the United States (Figure E-1), identified on the basis of similar physiographic characteristics:

- <u>Mid-Atlantic (MA) Region</u>

  - Interior Mid-Atlantic (IMA) Subregions
    -- Poconos/Catskills (1D)
    -- Northern Appalachians (2Cn)
    -- Valley and Ridge (2Bn)

  - Mid-Atlantic Coastal Plain Subregion (3B)

- <u>Southeastern (SE) Region</u>

  - Interior Southeast (ISE) Subregions
    -- Southern Blue Ridge (2As) - Pilot Survey in 1985
    -- Piedmont (3A)
    -- Southern Appalachians (2X)
    -- Ozarks/Ouachitas (2D)

  - Florida Subregion (3C)

These subregions of the United States were expected, on the basis of geology, deposition rates, and previous water quality data, to contain a substantial number of streams that have low acid neutralizing capacity (ANC) or that are acidic (ANC $\leq$ 0). Furthermore, NSS-I efforts during 1986 were concentrated in areas where acidic deposition rates are relatively high, but where lakes are not abundant. We do not have synoptic information from the National Lake Survey (NLS) on surface water chemistry in these areas. A Pilot Survey was conducted in the Southern Blue Ridge subregion one year earlier than field activities in the remainder of the NSS-I subregions. This NSS-I Pilot Survey was designed to assess the logistic and scientific feasibility of the full-scale NSS-I Survey.

NSS-I field activities to date have not included areas of the Northeast, Upper Midwest, and West. Though these regions are expected to contain low ANC or acidic streams potentially

SUBREGIONS OF THE NATIONAL STREAM SURVEY - PHASE I

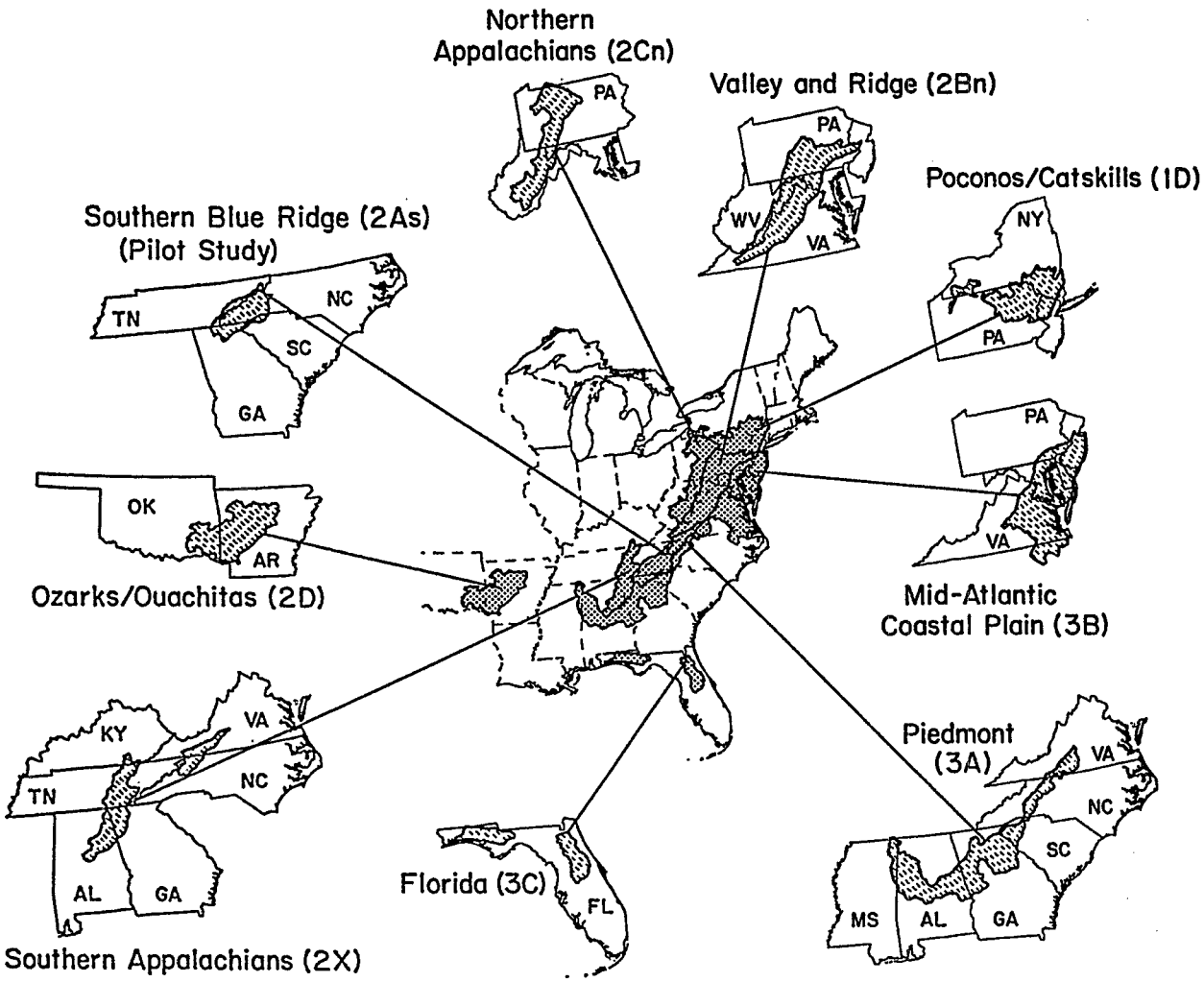

Figure E-1. NSS-I subregions.

sensitive to acidic deposition, they also contain numerous lakes that were sampled as part of EPA's Eastern and Western Lake Surveys. Furthermore, NSS-I field activities thus far have not included synoptic stream chemistry sampling in parts of the South Atlantic and Gulf Coastal Plains expected to contain predominantly low ANC surface waters--but where deposition rates are comparatively lower than in most of the Survey area, and where organic acidity is expected to play an important role. Field activities in the Florida subregion test the utility of NSS-I logistical and design protocols in lowland stream networks of the Southeast Coastal Plain.

Objectives

The objectives of the NSS-I in the Mid-Atlantic and Southeast were to:

- Determine the percentage, extent (number, length, and drainage area), location, and chemical characteristics of streams in the Mid-Atlantic and Southeast that are presently acidic, or that have low ANC and thus might become acidic in the future.

- Identify streams representative of important classes in each region that might be selected for more intensive study or long-term monitoring.

Methods

Within the NSS-I subregions, the stream resource of interest (the target resource) was identified as those streams that have drainage areas less than 155 square kilometers (60 square miles), but that are large enough to be represented as blue lines on 1:250,000-scale U.S. Geological Survey (USGS) topographic maps. Reviewers accepted this size range as a reasonable compromise that would include streams large enough to be important for fish habitat, yet still small enough to be susceptible to the impacts of acidic deposition.

Unlike lakes, which can be counted and sampled as discreet entities, streams form a hierarchical network in which small streams are tributaries to large streams. The NSS-I sampled stream reaches defined as segments of the stream network, as represented by blue lines on the 1:250,000-scale maps. These segments, or reaches, were identified as mapped blue-line segments between two tributary confluences. Sampling points on each of these reaches were just above the downstream point of confluence (lower node) and just below the upstream point of confluence (upper node). The upper node of each reach represented as a headwater was defined as the farthest upstream extent of the mapped blue line representation.

Because not all stream reaches in the mid-Atlantic and southeastern United States could be sampled, a statistical procedure was developed for selecting a subset of streams as a probability sample from which the characteristics of the total reach population could be extrapolated. A two-stage sampling procedure was used to obtain a randomized, systematic sample of approximately 500 reaches with good spatial distribution over each of the nine NSS-I subregions (50 to 80 reaches per subregion). Reaches were excluded if they were too large (drainage area > 155 km^2), were located within metropolitan areas or tidal zones, or were affected by oil field brine, acid mine drainage, or point-source pollution.

The NSS-I used index values to describe the chemical status of each stream sampled. This index value was measured during baseflow of the spring season between snowmelt and leafout (approximately March 15 to May 15). The choice of the spring index sampling period involved a trade-off between minimizing within-season and episodic chemical variability and maximizing the probability of sampling chemical conditions potentially limiting for aquatic organisms.

As a result of Pilot Survey experience, two spring season samples were judged sufficient to index chemical characteristics of streams in the Mid-Atlantic subregions. In the Southeast, where acidic deposition effects were expected to be less probable, one spring sample was taken at each site. To quantify and incorporate the variability between upstream and downstream ends of reaches, chemical and physical variables were measured at both ends.

Chemical variables measured at each sampling site included those related to biological effects (e.g., pH, extractable aluminum, and competing ligands such as fluoride and dissolved organic carbon), other variables related to potential sensitivity and related geochemistry (ANC, base cations, acid anions, and silica), and others indicative of anthropogenic disturbances or nutrient status (phosphorus, iron, ammonium, and turbidity). Samples were stabilized within 12 to 24 hours of collection and standardized quality control and quality assurance protocols were followed during sample handling, analyses, data reporting, data storage and analysis. Population frequency distributions (with 95% confidence bounds) were calculated for selected chemical and physical variables.

Selected Results

Overview

The basic results of the NSS-I are population descriptions of the location, number, length, and percentage of streams within referenced ranges of chemical concentration. The most important of these descriptions are those concerning ANC and pH. Further data interpretation includes an examination of regional patterns in the relationships among the chemical constituents within stream waters in an effort to infer the possible geochemical factors and anthropogenic impacts controlling stream chemistry. Lastly, a high-interest segment of the stream population with low ANC was examined and classified according to probable sources of acidity.

Survey data such as that collected by the NSS-I cannot in itself be used to prove causal relationships (e.g., the effect of acidic deposition on stream chemistry). However, the lines of correlative evidence we present can be examined to determine whether or not they support hypotheses concerning the true controls on streamwater chemistry.

Regional Chemical Characteristics

Target Population of Interest--

Physical and chemical characteristics of an estimated 57,000 stream reaches with a combined length of approximately 200,000 km (124,000 mi) were extrapolated from a probability sample of approximately 450 stream reaches in the stream population of interest within the nine NSS-I subregions. (An additional 54 reaches were visited in the field, but were found to have characteristics such as acid mine drainage or tidal effects that classified them as noninterest sites for this particular assessment.) The population of streams targeted by the NSS-I is best described as small to mid-sized streams in the low end of the size range typically managed by state fishery agencies. Stream reaches sampled by the NSS-I are typically about 3 km long. At their upstream ends, approximately half of these stream reaches are classified as headwater reaches on 1:24,000-scale topographic maps. At their downstream ends, most reaches (67%) are of Strahler Order 2 and 3. Median drainage areas at the upstream and downstream ends of the population of NSS-I target stream reaches are 1.5 km^2 and 8.1 km^2. Twenty percent of these

reaches have drainage areas less than 0.18 km^2 at their upstream ends. For perspective, the majority of these streams have widths between 1 and 6 m and depths between 0.1 and 0.5 m.

Types of Population Descriptions--

All regional population descriptions of the NSS-I target population are based on spring baseflow index chemistry (see Methods). The "index" is a representative value for each chemical constituent based on spring baseflow samples. It is important to understand the limitations as well as the strengths of the chemical index approach. For example, the number of stream reaches that are acidic due to episodic pH depressions during storm runoff cannot be obtained or inferred directly from the distribution of index chemistry provided by the NSS-I. The number of streams experiencing acidic episodes may be much greater than the number estimated to be acidic during spring baseflow. Further studies of short-term and seasonal variability are expected to demonstrate a useful predictive relationship between index chemistry and chemistry during other times of the season or year.

We present two types of population descriptions expressing the distribution of the population of target streams over the range of ANC and pH. One type of description (Table E-1) is based on enumerating reaches with upstream and downstream chemistry in reference ranges. The population distribution estimates based on upstream and downstream sampling comprise two spring baseflow "snapshots" focusing at different positions within the streamflow network represented by blue lines on 1:250,000-scale topographic maps.

Separate distributions of chemistry at the upstream and downstream ends of target stream reaches provide a fairly complex picture of their status. It is perhaps of greater interest to combine upstream and downstream chemical measurements by interpolation along the length of reaches and to report the status of the stream resource in a second type of population estimate expressed in terms of the combined length of streams within reference categories of pH and ANC (Table E-2; Figures E-2 and E-3). We have focused our presentation on these length distributions because they may have more utility for fish habitat quality assessment. However, the tables in this Executive Summary show, separately, the upstream and downstream estimates discussed above.

Reference Values for ANC and pH--

Population proportions are reported within ranges of ANC and pH defined by reference values. ANC, a measure of the amount of acid that can be neutralized by a sample of water, is probably the most important variable measured in the NSS-I. The value of ANC = 0 is of significance because waters at or below this level have no capacity to neutralize acid inputs--they are acidic by definition.

The 50 $\mu eq\ L^{-1}$ ANC reference value forms the upper bound of a range of aquatic systems between 0 and 50 $\mu eq\ L^{-1}$ that may be considered to have very low ANC. Although there may be no special significance to the 50 $\mu eq\ L^{-1}$ level, some scientists term surface waters with ANC $< 50\ \mu eq\ L^{-1}$ as "extremely acid sensitive"[1]. There is some evidence that streams and lakes with spring baseflow ANC (streams) or fall turnover ANC (lakes) below this level may be prone to acidic episodes during storm events or snowmelt. Low ANC is probably a necessary condition predisposing acidic episodes, although certainly not a sufficient one. Streams or lakes that

[1]Schindler, D.W. 1988. Effects of acid rain on freshwater ecosystems. Science 239:149-157.

Table E-1. Population Estimates of the Percentage of NSS-I Target Stream Lower (L) and Upper (U) Reach Nodes with Spring Baseflow Index ANC and pH Below Reference Values

	ANC (μeq L^{-1}) ≤ 0		≤ 50		≤ 200		Total (No. of Reaches)	
Region	L	U	L	U	L	U	L	U
Interior MA	1.3	5.4	8.6	20.4	40.6	49.1	25,715	24,945
MA Coastal Plain	6.8	11.8	19.5	30.2	41.0	55.8	11,287	11,284
Interior SE	*	0.6	5.8	7.5	46.4	51.6	18,720	18,686
Florida	14.5	39.2	57.5	70.0	81.2	77.6	1,555	1,727
Total NSS-I Area	2.3	6.1	11.2	19.6	43.7	52.1	57,277	56,642

	pH ≤ 5.0		≤ 5.5		≤ 6.0		Total (No. of Reaches)	
Region	L	U	L	U	L	U	L	U
Interior MA	1.1	3.9	2.0	8.5	5.1	15.4	25,715	24,945
MA Coastal Plain	6.8	11.8	13.2	23.5	21.6	49.3	11,287	11,284
Interior SE	*	*	*	1.9	2.7	8.6	18,720	18,686
Florida	14.5	31.2	23.8	49.9	61.9	71.8	1,555	1,727
Total NSS-I Area	2.2	5.0	4.1	10.6	9.1	21.6	57,277	56,642

*No samples observed in this range; estimated percentage is less than 1%.

MA = Mid-Atlantic
SE = Southeast

Table E-2. Population Estimates of the Combined Length (km) and Percentage of NSS-I Target Stream Reaches with Spring Baseflow ANC and pH less than Reference Values

Region	ANC (μeq L^{-1}) ≤ 0	≤ 50	≤ 200	Total Length (km)
Interior MA	2,324 (3.3)	7,431 (10.7)	31,235 (44.9)	69,569
MA Coastal Plain	2,527 (6.3)	9,636 (23.9)	21,091 (52.3)	40,296
Interior SE	117 (0.1)	4,064 (4.7)	41,860 (48.1)	86,939
Florida	461 (12.0)	2,356 (61.2)	2,939 (76.4)	3,848
Total NSS-I Area	5,429 (2.7)	23,487 (11.7)	97,125 (48.4)	200,652

Region	pH Ranges ≤ 5.0	≤ 5.5	≤ 6.0	Total Length (km)
Interior MA	2,231 (3.2)	4,712 (6.8)	8,514 (12.2)	69,569
MA Coastal Plain	3,147 (7.8)	9,565 (23.7)	18,707 (46.4)	40,296
Interior SE	* (*)	723 (0.8)	5,747 (6.6)	86,939
Florida	522 (13.6)	1,708 (44.4)	2,828 (73.5)	3,848
Total NSS-I Area	5,900 (2.9)	16,708 (8.3)	35,796 (17.8)	200,652

*No samples observed in this range; estimated percentage is less than 1%.

MA = Mid-Atlantic
SE = Southeast

NSS-I INTERPOLATED LENGTH DISTRIBUTION – ANC

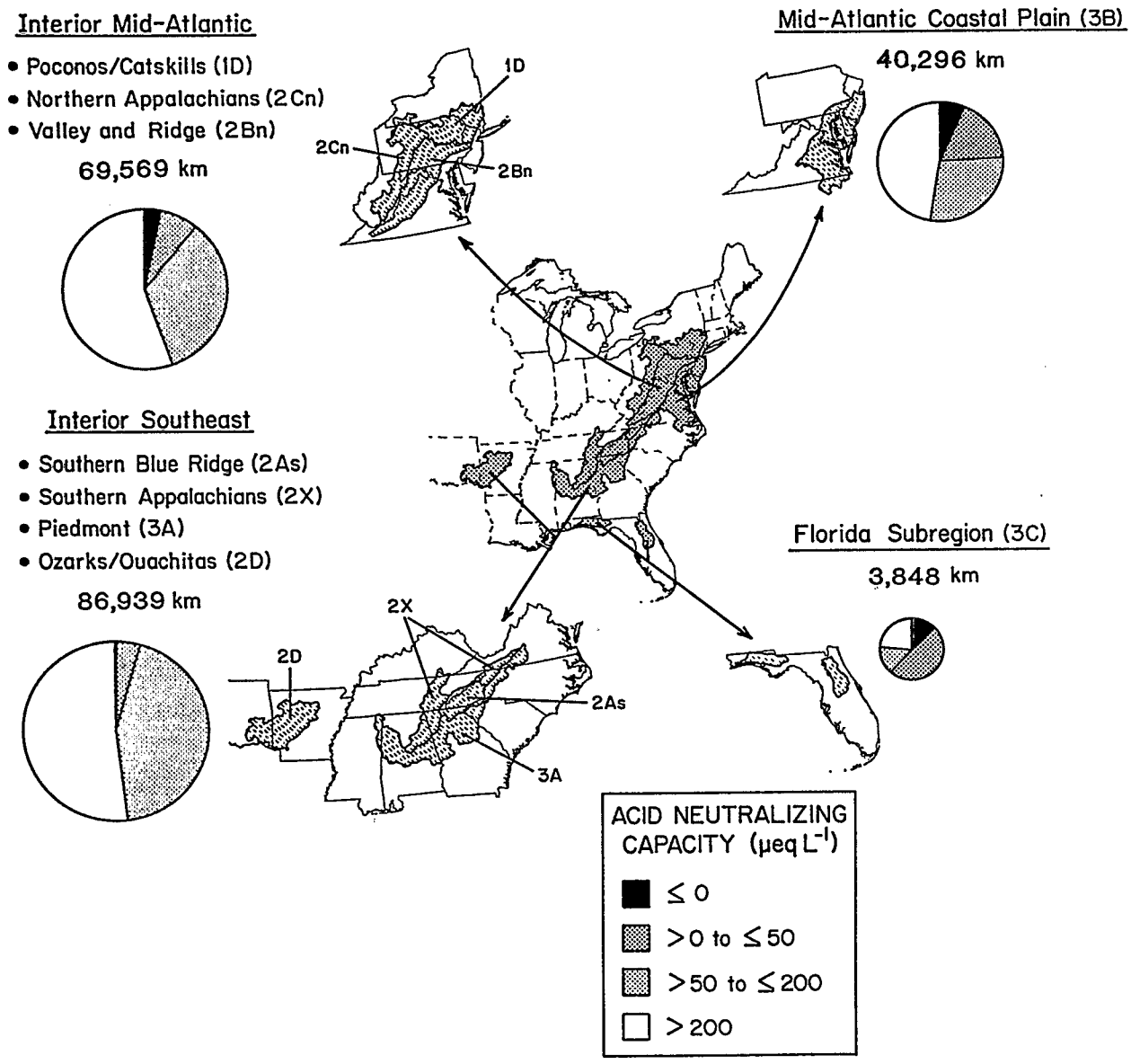

Figure E-2. Population estimates for ANC in eastern United States streams. Pie diagram area is proportional to the combined length of target streams in each region.

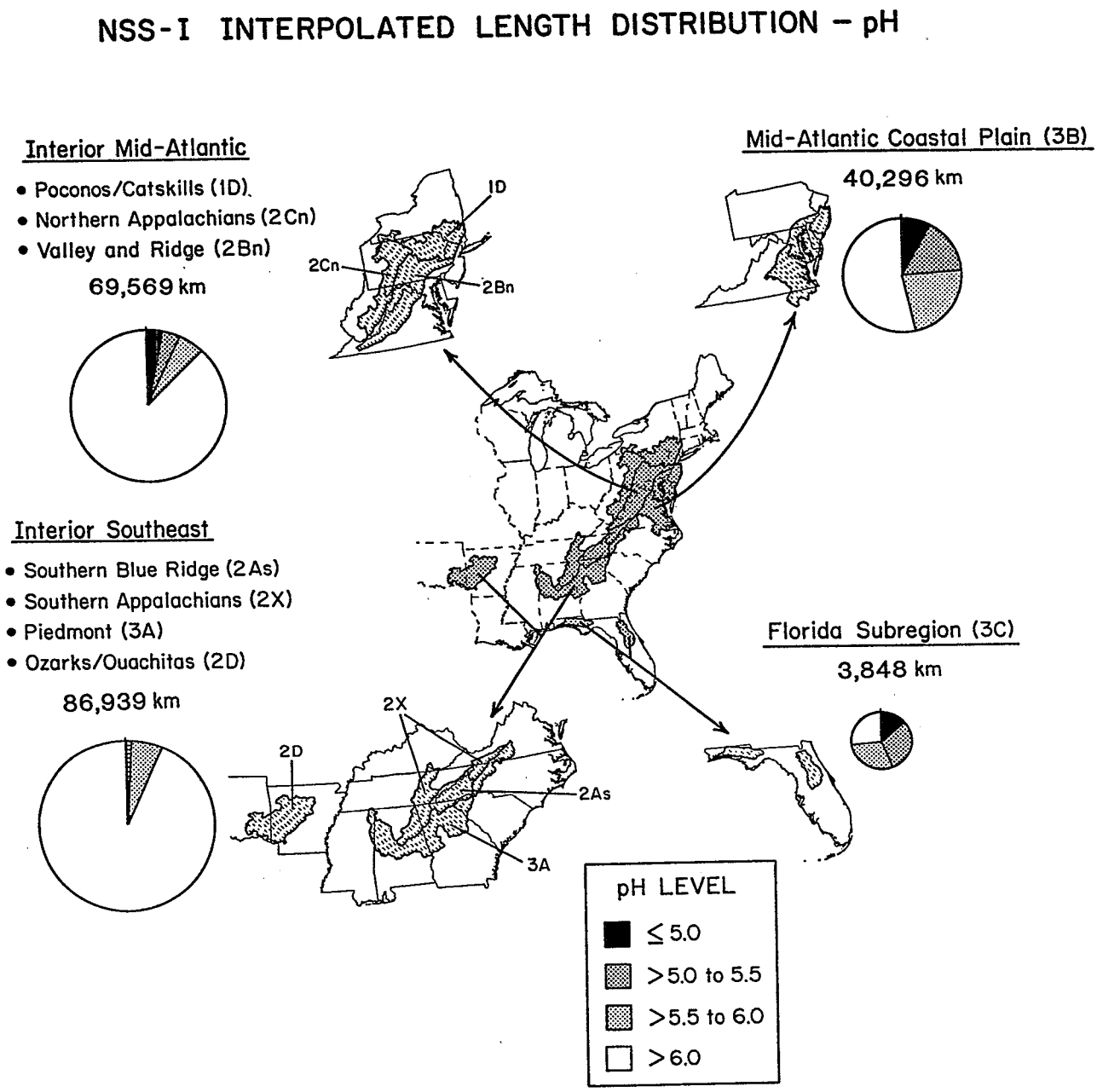

Figure E-3. Population estimates for pH in eastern United States streams. Pie diagram area is proportional to the combined length of target streams in each region.

experience acidic episodes are also often subject to high atmospheric acid deposition rates, and their watersheds may be more susceptible to episodic pH depressions due to their hydrology.

The 200 μeq L^{-1} ANC reference value is of interest because it has been frequently cited in acid deposition literature as a value above which aquatic systems are unlikely to be sensitive to acidification. It should be kept in mind that sensitivity to acid deposition impacts is dependent on other factors besides the ANC of the stream water itself. A stream is an integral part of its watershed; as such, its sensitivity to acid deposition is dependent upon the ability of watershed geology, soils, and vegetation to neutralize incoming acidity.

The variable pH is an inverse measure (negative logarithm) of hydrogen ion concentration. A one-unit decrease in pH represents a ten-fold increase in hydrogen ion concentration. Whereas ANC is a measure of the capacity of a water sample to neutralize acids, pH is a measure of the strength of the acidity.

The pH reference values of 5.0, 5.5, and 6.0 are defined for convenience in comparing results with those of other studies (e.g., EPA's Eastern and Western Lake Surveys) that have reported results referencing these values. The pH reference values bear some relationship to critical values below which populations of different types of fish are not sustained in freshwater ecosystems. Because of the influence of pH on the solubility and chemical form of aluminum, it is difficult to separate the effects of low pH from those of aluminum toxicity. Interpretation of critical pH values are further confounded because of the effect of dissolved organic compounds and calcium in reducing the toxicity of aluminum. However, several researchers have reported that waters with pH chronically below 4.0 are virtually devoid of fish, and waters with pH chronically below 4.5 contain few fish species. Estimates for critical values below which salmonid fish populations (e.g., trout) are not sustained range from pH 4.7 to 5.5. Estimates for smallmouth bass and blueback herring are between 5.0 and 5.7. Except for effects reported on several species of dace, shiners, and minnows, pH levels above 6.0 have not been associated with adverse impacts on fisheries. However, recent research on blueback herring, striped bass, and yellow perch suggests that under certain conditions of high aluminum concentration, pH between 6.0 and 6.5 can lead to increased egg and larval mortality.

Population Distribution Estimates for ANC--

The estimated percentage of the total number of upstream and downstream reach ends (nodes) with spring baseflow ANC less than 0, 50, and 200 μeq L^{-1} are presented in Table E-1. It is evident that acidic (ANC $\leq$ 0) reaches are concentrated in the Interior Mid-Atlantic, the Mid-Atlantic Coastal Plain, and Florida. It is also evident that the target population has generally lower ANC at the upstream reach ends, reflecting a commonly observed pattern of increasing buffering capacity in the downstream direction because of increased time in contact with watershed rock and soils, plus the presence of more landuse impacts and weatherable soils in lowland areas. To simplify discussion of the data, we will focus on the length distributions that combine upstream and downstream chemistry to yield estimates of the combined length of the stream resource within the ANC reference ranges (Table E-2 and Figure E-2). Table E-2 presents the estimated length and percentage of the total target reach length with ANC less than or equal to each of the three reference values. In Figure E-2, the size of each pie diagram is proportional to the total combined length of stream reaches in the target populations within each of the four regions.

Tables E-3, E-4, E-5, and E-6 present detailed population estimates (and statistical confidence bounds) for both ANC and pH in the nine NSS-I subregions and are provided as supplementary reference tables at the end of this Executive Summary. Population estimates for the

Florida subregion are not strictly comparable with those from other subregions, so these are summarized separately from the other subregions in the following discussion.[2]

Acidic (ANC ≤ 0) and very low ANC (0 to 50 μeq L^{-1}) baseflow conditions were observed primarily in the Mid-Atlantic Coastal Plain and the Interior Mid-Atlantic Region (Table E-2, Figure E-2). Acidic reaches (ANC ≤ 0) made up 6%, or 2527 km, of the length of the target stream resource in the Mid-Atlantic Coastal Plain, and were observed mostly in the New Jersey Pine Barrens and on the Coastal Plain west of Chesapeake Bay. Approximately 3%, or 2,324 km, of the target stream length in the Interior Mid-Atlantic Region was acidic during spring baseflow, whereas acidic reaches were rare in the Interior Southeast Region (approximately 0.1% or 117 km). Acidic reaches in these interior subregions were observed largely in forested upland watersheds with drainage areas less than 20 km^2 and were most numerous in the Northern Appalachian subregion of the Interior Mid-Atlantic, where they made up an estimated 7% (1,524 km) of the stream resource.

The estimates of acidic stream reaches in the previous paragraph, and in the figures and tables of this Executive Summary, do not include streams within the size range of the NSS-I target reaches that were acidic and receive acid mine drainage. We estimate 3,500 km in Pennsylvania and West Virginia, and 1,100 km in the Interior Southeastern subregions within this acid mine drainage category. Acidic streams impacted by acid mine drainage comprised approximately 10% of the total number of reaches within the target stream size range in the Northern Appalachian Plateau (subregion 2Cn).

Very low ANC reaches (ANC 0-50 μeq L^{-1}) make up a rather large fraction (17.6%, or 7,109 km) of the target stream resource in the Mid-Atlantic Coastal Plain. In the Interior Mid-Atlantic, 7.3% (5,107 km) of stream reaches were estimated within this very low ANC range. In the Interior Southeast, 4.5% (3,947 km) were within this range, where they were proportionately most common in the Piedmont and Southern Blue Ridge subregions, making up 7% to 8% of the resource. Stream reaches in the moderately low ANC range (50-200 μeq L^{-1}) were abundant in the Interior Southeast, where nearly 38,000 km (43.5%) were within this range. In the Mid-Atlantic Region, 23,804 km (34.2%) of the Interior, and 11,455 km (28.4%) of the Coastal Plain streams were within this low ANC range.

Proportions of the target stream reach population with spring index ANC $\leq$ 200 μeq L^{-1} were similar in the Mid-Atlantic Region and the Interior Southeast Region (Table E-2, Figure E-2). Note that the Interior Southeast Region excludes Florida, whereas the Mid-Atlantic Region combines the Interior Mid-Atlantic and the Mid-Atlantic Coastal Plain. Approximately half the combined reach length in the Mid-Atlantic and Interior Southeast regions had ANC $\leq$ 200 μeq L^{-1}.

The Florida subregion stands out as a geographic area with a relatively high percentage of acidic and very low ANC streams. It is also an area where there are many highly colored streams with high concentrations of dissolved organic carbon (DOC) likely to be contributing to the observed acidity. An estimated 12% (461 km) of streams in the portion of Florida surveyed were acidic and nearly 50% (1,895 km) had ANC between 0 and 50 μeq L^{-1}. Whereas the acidic and very low ANC reaches in the Florida peninsula were typically high in DOC and strongly colored, many of those in the Florida panhandle were clear or slightly colored and had very low ionic strength, with very low sulfate, nitrate, and DOC concentrations.

[2]The Florida sample was drawn from a more restrictive target population focused only on the portion of this state with expected ANC less than 200 μeq L^{-1}, rather than 400 μeq L^{-1} (the criterion for all the other subregions). In addition, the total size of the target population in Florida may be underestimated because many reaches visited were dry or lacked flowing water at the time of sampling.

Population Distribution Estimates for pH--

The estimated number and percentage of upstream and downstream reach ends (nodes) within the four ranges of pH are presented in Table E-1. More detailed estimates, with confidence bounds, are shown in Table E-4. Population distribution estimates for pH mirrored those for ANC, which is not surprising in light of the relationship between ANC and hydrogen ion concentration. As observed for ANC below a reference value of 0 μeq L^{-1}, reaches with spring baseflow index pH less than 5.5 were concentrated largely in the Mid-Atlantic, the Interior Mid-Atlantic, and Florida. Again, the general downstream increase in buffering was reflected in the larger percentages of reaches with low pH at their upstream ends (compared with their downstream ends). To simplify discussion of this upstream and downstream pH data, we focus in this Executive Summary on population estimates that use both upstream and downstream data to yield estimates of the combined length of target reaches within the several pH reference ranges (Table E-2 and Figure E-3). More detailed stream length estimates with statistical confidence bounds are provided for reference in Table E-6. For reasons mentioned in the previous section, Florida estimates are discussed separately from the other subregions.

Reaches with pH of 5.5 or less made up an estimated 24% (9,565 km) of the target stream length in the Mid-Atlantic Coastal Plain (Table E-2). These low pH reaches were observed primarily in the New Jersey Pine Barrens and on the Coastal Plain west of Chesapeake Bay. Potential sources of acidity in streams of this and other regions are discussed in the following sections of this Executive Summary. In the Interior Mid-Atlantic Region, an estimated 4,712 km (6.8%) of target reach length had pH $\leq$ 5.5. These low pH reaches were observed largely in upland forested watersheds with drainage areas less than 30 km^2 and were most common in the Northern Appalachian subregion of the Interior Mid-Atlantic, where they made up an estimted 8.6% (1,870 km) of the combined length of target stream reaches. In contrast, the combined reach length with pH $\leq$ 5.5 in the Interior Southeast was proportionately small, with an estimated 723 km (< 1%) of the target population in this category.

The greatest combined length of target reaches with baseflow pH between 5.5 and 6.0 was estimated in the Mid-Atlantic Coastal Plain (9,142 km or 22.7%). The Interior Mid-Atlantic and the Interior Southeast Regions had similar percentages of their length in this range (5.5% and 5.8%, respectively).

Reaches with spring baseflow index pH greater than 6.0 predominated in the Interior Mid-Atlantic (88% of combined length) and the Interior Southeast (93% of combined length). In contrast, reaches with pH greater than 6.0 made up a little more than half (54%) of the combined length of target streams in the Mid-Atlantic Coastal Plain.

The Florida subregion stands out as an area with a relatively high estimated percentage of its combined target reach length having spring baseflow index pH $\leq$ 5.5 (1708 km, or 44%). Another 1,120 km (29%) were estimated in the pH category between 5.5 and 6.0, leaving only 26.5% of the combined reach length in this subregion with pH greater than 6.0. Note the previous discussion regarding the comparability of Florida results with those in other regions. The potential sources of acidity in streams of Florida and the other areas surveyed by the NSS-I are discussed in later sections of this Executive Summary.

Population Distribution Estimates for Sulfate--

Sulfate is an important chemical constituent for study in stream water because it is often associated with hydrogen ion as sulfuric acid in streams acidified by mine drainage and atmospheric deposition. Stream reaches within NSS-I subregions of the Mid-Atlantic Region had

substantially higher spring baseflow index sulfate concentrations than did those in the Southeast. Subregion median stream water sulfate concentrations ranged from 125 to 238 μeq L^{-1} in the four Mid-Atlantic subregions, whereas those of the five subregions in the southeastern United States ranged from 10 to 71 μeq L^{-1}. The potential sources of sulfate in stream water include wet and dry atmospheric deposition (natural and anthropogenic sources), nonatmospheric anthropogenic sources (e.g., agriculture), and the weathering of naturally occuring sulfur-bearing minerals (which can be accelerated by mining activities). The potential role of sulfate from several sources is discussed in the following paragraphs as it pertains to the observed pH and ANC in stream reaches of the NSS-I target population.

Chemical Relationships

Regional variation in ANC among streams within NSS-I subregions was associated more closely with differences in base cation concentrations than differences in concentration of mineral acid or organic acid anions. This result suggests that watershed geochemical and hydrologic characteristics controlling the supply of mineral weathering products are very important in determining the regional patterns in stream water ANC and therefore buffering of acid inputs.

The only direct way to conclusively demonstrate surface water acidification is through historic water quality data. Because of a lack of such data on a regional scale for the streams of interest in the NSS-I, a second approach for assessing whether streams in the Mid-Atlantic and Southeast have been acidified involves an indirect method of inferring past changes in ANC through an examination of present water chemistry. Previous researchers have used the ANC deficit (nonmarine base cation concentration minus ANC) as a rough measure of surface water acidification resulting from either natural or anthropogenic causes.

It is important to recognize that ANC deficits, in themselves, reflect simply a presence of strong acid anions in water at the time of sampling. ANC deficits can be observed in stream water for a number of reasons: (1) they may reflect a reduction in ANC caused by the addition of a strong acid (like sulfuric acid) to the stream, as might occur with acid deposition onto a poorly buffered watershed; (2) they may reflect an increase in base cation concentration (with no change in ANC) in the stream resulting from cation exchange or the accelerated weathering of watershed soils and rock (this can be due to acidic deposition); (3) they may result from an addition of base cations in neutral salts (e.g., $CaSO_4$), with no change in ANC; or finally (4) they may result from a combination of all these mechanisms. The last combination of factors is the most likely for a heterogeneous assemblage of streams subject to a wide range of influences (e.g., the entire population of NSS-I target streams). However, the interpretation of ANC deficits in a subpopulation of relatively pristine streams draining watersheds underlain by metamorphic rock is not as uncertain. In these pristine streams, ANC deficits were higher in areas that receive larger amounts of acidic deposition. The lack of plausible sources of neutral salts in these streams makes it likely that the observed ANC deficits in such upland, forested streams are due to titration by strong acids or increases in base cation export, and that both mechanisms are probably associated with atmospheric acid deposition.

In order to interpret the observed ANC deficit as a measure of the amount of historic change in ANC, one must first assume that the ANC deficits are due largely to titration by strong acids and that the base cation concentrations in streams have remained nearly constant over time. These assumptions are more likely to be correct in poorly buffered stream waters of low ionic strength. There are indications, however, that base cations may not remain constant

over time in many streams. In addition, several conditions must also be met before the ANC deficit in a given stream could be interpreted as a measure of historic acidification due to atmospheric deposition: (1) an atmospheric source of strong acids can be demonstrated to be of sufficient magnitude to cause the observed ANC deficit, (2) other potential sources of strong acid anions can be quantified or ruled out as unlikely (e.g., sulfide weathering, organic acidity), and (3) concentrations of acids not derived from atmospheric deposition (e.g., organics from watershed sources) have remained relatively constant over time.

All NSS-I subregions had streams with an ANC deficit. The largest ANC deficits were observed in streams of the four Mid-Atlantic subregions (Poconos/Catskills, Northern Appalachians, Valley and Ridge, and Mid-Atlantic Coastal Plain). The observation of smaller ANC deficits in streams of most Southeast subregions, compared with those of the Mid-Atlantic, is generally consistent with the lower atmospheric acid deposition rates and greater sulfate adsorption capacities of soils in the southeastern United States. Sulfate was the dominant strong acid anion in most acidic and low ANC streams and was observed to be in sufficient concentration to account for the observed ANC deficits in the majority of stream reaches in all subregions except Florida and the Mid-Atlantic Coastal Plain.

The distribution of sulfate concentration in streams of the eastern United States that are not affected by large terrestrial sulfate sources corresponds well with sulfate wet deposition rates[3]. A plot of population median stream sulfate concentrations versus rates of sulfate deposition in the nine NSS-I subregions shows a strong positive linear relationship. When data from the NSS-I and the National Lake Survey are combined, a positive near linear relationship is clearly evident among northeastern, mid-Atlantic, western, and upper midwestern surface waters (Figure E-4). It is apparent, however, that a group of southeastern streams and lakes have lower sulfate concentrations than expected, given the sulfate deposition rates in their respective subregions. These observations are consistent with other research showing substantial sulfate retention in watersheds of some parts of the Southeast.

Sources of Acidity in Acidic and Low ANC streams

Potential sources of acidity were examined for the subpopulation of acidic and low ANC ($\leq 200\ \mu eq\ L^{-1}$) streams in the NSS-I target population. Stream reaches affected by acid mine drainage and organic acids were identified by site visits and examination of stream chemical data. After elimination of categories of streams for which sources of acid anions other than acid deposition largely mask the potential effects of acid deposition, a high-interest group of streams remained. Acid deposition is likely to be a major source of acid ions in these streams.

Based on interpolations between upper and lower node chemistry, acidic reaches within the high-interest subpopulation had an estimated combined length of 4,455 km. Most of these reaches (4,272 km) were observed in the Mid-Atlantic subregions, where they comprised 4% of the total length of target stream reaches. Somewhat less than one-third (1,212 km) of these high-interest acidic reaches had chemistry influenced but not dominated by organic anions. Most of these organic-influenced reaches are located in the New Jersey Pine Barrens and in the low-gradient headwaters of reaches in the Glaciated Plateau of Pennsylvania and New York. Estimates based upon the first NSS-I sample visit alone (rather than the average of the two spring visits) were slightly higher than 4,455 km because of a seasonal trend of increasing

[3]Sulfate wet deposition rates taken from Wampler, S.J., and A.R. Olsen. 1987. Spatial estimation of annual wet acid deposition using supplemental precipitation data. Reprinted from the Preprint Volume: Tenth Conference on Probability and Statistics. October 4 and 5, 1987. Edmonton, Alta., Canada. Published by the American Meteorological Society, Boston, Massachusetts.

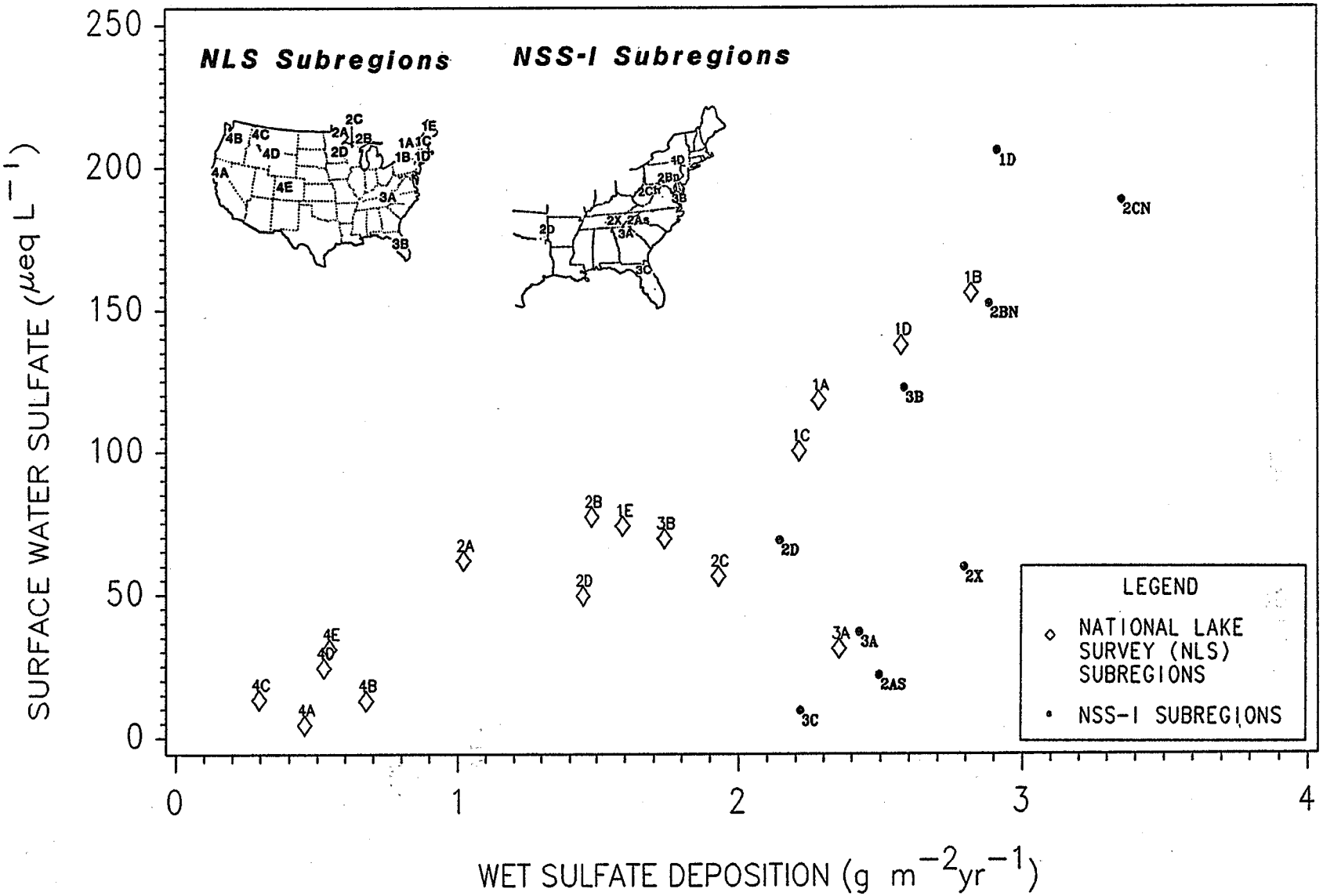

Figure E-4. Relationship between median wet sulfate deposition (1980-1984) and median sulfate concentration in surface waters with $SO_4^{2-} < 400$ μeq L^{-1} in National Lake Survey and NSS-I (upstream reach ends) subregions. Sulfate wet deposition rates taken from Wampler and Olsen (1987).

spring baseflow ANC. Based on the earlier spring sample, a combined length of 7,481 km of acidic stream reaches were within the high-interest subpopulation of streams for which acid deposition impacts cannot be ruled out. Again, most of these reaches were observed in the Mid-Atlantic subregions, where they comprised 6.6% of the total length of the target stream resource. These reaches are located primarily in the forested upland drainages and coastal areas of the Mid-Atlantic Region that experience high rates of atmospheric sulfate deposition. Specifically, most reaches within the high-interest group of acidic streams are located:

- In upland forested drainages of the Allegheny Plateau, in ridges of the Valley and Ridge physiographic province, and in the Glaciated Plateau in northeastern Pennsylvania (included in NSS-I subregions 1D, 2Bn, and 2Cn). An estimated 695 (9.7%) of 7190 reaches in ridges of the Valley and Ridge geographic area and 499 (11%) of 4548 reaches in forested drainages of the Allegheny Plateau were acidic at their upstream nodes.

- In the Pine Barrens of New Jersey (within the Mid-Atlantic Coastal Plain, subregion 3B). Seventy-nine percent of upstream nodes and 93% of downstream nodes were in this high-interest subgroup; approximately one-third of these had chemistry influenced but not dominated by organic anions.

Historic data suggest that streams in the Pine Barrens may have been naturally acidic at least since the early 1900's. There is no reason, however, to believe that most of the upland forested reaches have always been acidic.

Identified within the NSS-I target population was a group of non-acidic stream reaches with very low ANC ($> 0 - \leq 50$ μeq L^{-1}) for which the predominant sulfate source appears to be acid deposition. Based on interpolation between upper and lower node chemistry, an estimated 15,590 km of target reach length is within this group. Approximately two-thirds of these reaches were observed in the Mid-Atlantic subregions, where they made up approximately 9.6% of the combined length of the target population. Calculations of these totals based on the earlier spring sample did not differ from those based on the average from two spring visits. These very low ANC streams are located primarily on upland, forested sites of the Allegheny Plateau, Valley and Ridge Province, Blue Ridge Mountains, and Cumberland Plateau. In addition, a large number of these reaches were found in Coastal Plain areas--Eastern and Western Mid-Atlantic Coastal Plain, New Jersey Pine Barrens, and East and West Gulf Coastal Plain.

Summary and Conclusions Outline

I. Stream Length Population Estimates. (Uncertainties surrounding these estimates are addressed in Tables E-5 and E-6.)

A. Acidic Stream Reaches (ANC ≤ 0 μeq L^{-1} during spring baseflow)

1. 2.7% (5,429 km) of the combined length of streams in the NSS-I target population were acidic.

2. 4.4% (4,851 km) of the combined length of streams in the NSS-I target population in the Mid-Atlantic Region were acidic.

	ANC ≤ 0 μeq L^{-1}	
Mid-Atlantic Subregions	%	Length (km)
Northern Appalachians	7.0	1,524
Poconos/Catskills	3.6	543
Valley and Ridge	0.8	257
Mid-Atlantic Coastal Plain	6.3	2,527

3. 0.6% (578 km) of the combined length of streams in the NSS-I target population in the Southeast Region were acidic.

	ANC ≤ 0 μeq L^{-1}	
Southeast Subregions	%	Length (km)
Florida	12.0	461
Southern Appalachians	0.5	117
Southern Blue Ridge	No acidic reaches observed	
Piedmont	No acidic reaches observed	
Ozarks/Ouachitas	No acidic reaches observed	

B. Stream Reaches with Low Spring Baseflow ANC

1. 11.7% (23,487 km) of the combined length of streams in the NSS-I target population had ANC ≤ 50 μeq L^{-1}, a value commonly used to indicate extreme sensitivity to acidic deposition. 15.5% (17,067 km) of the estimated stream length in the Mid-Atlantic Region and 7.1% (6,420 km) of the estimated stream length in the Southeast Region had ANC ≤ 50 μeq L^{-1}.

	ANC ≤ 50 μeq L^{-1}	
NSS-I Subregions	%	Length (km)
Northern Appalachians	17.1	3,713
Poconos/Catskills	10.6	1,606
Valley and Ridge	6.5	2,111
Mid-Atlantic Coastal Plain	23.9	9,636
Southern Appalachians	3.5	763
Southern Blue Ridge	7.8	706
Piedmont	7.1	2,390
Ozarks/Ouachitas	0.9	205
Florida	61.2	2,356

2. 23.4% (47,060 km) of the combined length of streams in the NSS-I target population had ANC ≤ 100 μeq L^{-1}. 23.9% (26,274 km) of the estimated stream length in the Mid-Atlantic Region and 22.9% (20,786 km) of the estimated stream length in the Southeast Region had ANC ≤ 100 μeq L^{-1}.

NSS-I Subregions	ANC ≤ 100 μeq L^{-1} %	Length (km)
Northern Appalachians	31.9	6,927
Poconos/Catskills	23.8	3,600
Valley and Ridge	14.8	4,852
Mid-Atlantic Coastal Plain	27.0	10,895
Southern Appalachians	12.7	2,778
Southern Blue Ridge	44.1	3,987
Piedmont	21.0	7,044
Ozarks/Ouachitas	19.2	4,307
Florida	69.4	2,670

3. 48.4% (97,125 km) of the combined length of streams in the NSS-I target population had ANC ≤ 200 μeq L^{-1}, a value commonly used to indicate potential sensitivity to acidic deposition. 47.6% (52,327 km) of the estimated stream length in the Mid-Atlantic Region and 49.3% (44,799 km) in the Southeast Region had ANC ≤ 200 μeq L^{-1}. Within the nine NSS-I subregions, the percentage of stream length with ANC ≤ 200 μeq L^{-1} ranged from 28.0% (6,130 km) in the Southern Appalachians to 78.4% (7,084 km) in the Southern Blue Ridge.

4. Regional variation in stream water ANC was closely associated with concentrations of base cations (e.g., sodium, potassium, magnesium, and calcium), indicating that local geology is probably the primary factor controlling the sensitivity of streams to acid inputs.

C. pH Distributions

1. Patterns in stream pH tended to follow the distribution of ANC. An estimated 2.9% (5,900 km) of the combined stream length in the NSS-I had pH ≤ 5.0, 8.3% (16,708 km) had pH ≤ 5.5, and 17.8% (35,797 km) had pH ≤ 6.0.

II. Probable Sources of Acidity

A. Atmospheric Deposition

1. The estimated 5,429 km of acidic NSS-I target stream length corresponds with an estimated 3,476 upstream and 1,323 downstream reach ends (6.1% and 2.3% of the target population, respectively). 63% of the acidic upstream ends and 55% of the acidic downstream ends were classified into a high-interest subpopulation whose major source of acidity is most likely to be acidic deposition. The approximate length of this high-interest subpopulation is 4,455 km. Just over half of these high-interest reaches drained small (< 20 km^2) upland forested watersheds in the Interior Mid-Atlantic (the Poconos/Catskills, Valley and Ridge, and Northern Appalachians subregions), whereas most of the remainder occurred in lowland drainages of the Mid-Atlantic Coastal Plain subregion, primarily in the New Jersey Pine Barrens. However, most of the streams in the Pine Barrens are also influenced by organic acidity and many are likely to have been acidic at least since the early 1900's.

2. An estimated 46% (11,505) of the upstream ends of stream reaches in the Interior Mid-Atlantic Region were located in forested uplands. Of these forested upland reaches, an estimated 11% (1,271) were acidic at their upstream ends and the major source of their acidity is most likely acidic deposition. An estimated 34% (3,857) of the upstream ends of these forested upland stream reaches had ANC $\leq 50\ \mu eq\ L^{-1}$ and the major source of their acid anions is most likely to be atmospheric deposition.

3. Subregional median stream water sulfate concentrations (excluding streams with substantial watershed sulfate sources) were highly correlated with subregional median wet sulfate deposition rates. This finding strongly supports the hypothesis that atmospheric inputs of sulfate are the major source of sulfate in these streams. This correlation was also observed in lake populations in the National Lake Survey.

B. Organic Acidity

1. Organic acidity, which characteristically results from the natural decay of vegetation, is likely to be the major source of acidity in an estimated 79% of the 678 acidic upper reach nodes and more than 99% of the 225 acidic lower reach nodes in the Florida subregion. Similarly, natural organic acids were estimated to be the major source of acidity in 56% of the 1,334 acidic upper nodes and 47% of the 772 acidic lower nodes in the Mid-Atlantic Coastal Plain subregion.

C. Acid Mine drainage

1. Unless specifically noted otherwise, all the estimates in this summary exclude streams affected by acid mine drainage. However, acid mine drainage impacts are common in some NSS-I subregions. In the Northern Appalachians subregion, they make up roughly 10% of the stream population initially sampled in the NSS-I. The NSS-I does not include all sizes of streams or geographic areas affected by acid mine drainage; thus, a comprehensive estimate of acid mine drainage impacts cannot be made. Nevertheless, in streams in the size range sampled by the NSS-I, an estimated 1,377 reaches (4,594 km) in Pennsylvania, West Virginia, and Tennessee were estimated to be acidic due to acid mine drainage.

Table E-3. Population Estimates of the Percentage of Target Stream Lower (L) and Upper (U) Reach Nodes with Spring Index ANC (μeq L^{-1}) in Reference Ranges

		ANC RANGE (μeq L^{-1})											
		≤ 0		> 0 to ≤ 50		> 50 to ≤ 200		> 200		Totals (No. of Reaches)		Sample Size (No. of Reaches)	
SUBREGION		L	U	L	U	L	U	L	U	L	U	L	U
1D	(Poconos/Catskills	*	6	5	16	25	26	70	52	3,235	3,244	(56)	(58)
2Cn	(N. Appalachians)	4	6	20	28	38	32	38	34	8,488	8,663	(61)	(67)
2Bn	(Valley and Ridge)	*	5	*	6	30	27	70	62	13,992	13,038	(47)	(44)
3B	(MA Coastal Plain)	7	12	13	18	21	26	59	44	11,287	11,284	(58)	(57)
2As	(S. Blue Ridge)#	*	*	5	6	74	78	22	16	2,031	2,031	(54)	(54)
3A	(Piedmont)	*	*	8	8	32	40	60	52	7,515	7,515	(47)	(47)
2X	(S. Appalachians)	*	2	7	7	20	20	72	70	5,057	4,936	(40)	(39)
2D	(Ozarks/Ouachitas)	*	*	*	4	66	64	34	32	4,117	4,204	(48)	(49)
3C	(Florida)$	14	39	43	31	24	8	19	22	1,555	1,727	(34)	(31)
Subtotals:													
Interior Mid-Atlantic (1D, 2Cn, 2Bn)		1	5	7	15	32	29	59	51	25,715	24,945	(164)	(169)
Interior Southeast (2As, 3A, 2X, 2D)		*	1	6	7	41	44	54	48	18,720	18,686	(189)	(189)
Mid-Atlantic Region (1D, 2Cn, 2Bn, 3B)		3	7	9	16	29	28	59	49	37,002	36,229	(222)	(226)
Southeast Region (2As, 3A, 2X, 2D, 3C)		1	4	9	9	39	41	51	46	20,275	20,413	(223)	(220)
Total NSS-I	MA + SE	2	6	9	13	33	33	56	48	57,277	56,642	(445)	(446)

*Less than 1%.

#See text: Many S. Blue Ridge upper node spring baseflow index chemistry values were calculated (Appendix B).

$See text: Florida percentages are based on a more restricted sample of low ANC streams. They are not directly comparable to those in the other subregions.

Table E-4. Population Estimates of the Percentage of Target Stream Lower (L) and Upper (U) Reach Nodes with Spring Index pH in Reference Ranges

		pH RANGE											
		≤ 5.0		> 5.0 to ≤ 5.5		> 5.5 to ≤ 6.0		> 6.0		Total No. of Reaches		Sample Size (No. of Reaches)	
SUBREGION		L	U	L	U	L	U	L	U	L	U	L	U
1D	(Poconos/Catskills)	*	5	*	2	3	6	97	87	3,235	3,244	(56)	(58)
2Cn	(N. Appalachians)	3	6	2	7	8	10	86	77	8,488	8,663	(61)	(67)
2Bn	(Valley and Ridge)	*	2	*	3	*	5	>99	89	13,992	13,038	(47)	(44)
3B	(MA Coastal Plain)	7	12	6	12	8	26	78	51	11,287	11,284	(58)	(57)
2As	(S. Blue Ridge)#	*	*	*	*	*	*	>99	>99	2,031	2,031	(54)	(54)
3A	(Piedmont)	*	*	*	*	4	11	96	89	7,515	7,515	(47)	(47)
2X	(S. Appalachians)	*	*	*	2	2	5	98	93	5,057	4,936	(40)	(39)
2D	(Ozarks/Ouachitas)	*	*	*	5	2	5	98	89	4,117	4,204	(48)	(49)
3C	(Florida)$	14	31	9	19	38	22	38	28	1,555	1,727	(34)	(31)
Subtotals:													
Interior Mid-Atlantic (1D, 2Cn, 2Bn)		1	4	1	5	3	7	95	85	25,715	24,945	(164)	(169)
Interior Southeast (2As, 3A, 2X, 2D)		*	*	*	2	3	7	97	91	18,720	18,686	(189)	(189)
Mid-Atlantic Region (1D, 2Cn, 2Bn, 3B)		3	6	3	7	5	13	90	74	37,002	36,229	(222)	(226)
Southeast Region (2As, 3A, 2X, 2D, 3C)		1	3	1	3	5	8	93	86	20,275	20,413	(223)	(220)
Total NSS-I	MA + SE	2	5	2	6	5	11	91	78	57,277	56,642	(445)	(446)

*Less than 1%.

#See text: Many S. Blue Ridge upper node spring baseflow index chemistry values were calculated (Appendix B).

$See text: Florida percentages are based on a more restricted sample of low ANC streams. They are not directly comparable to those in the other subregions.

Table E-5. Population Estimates of the Combined Length (km) and Percentage of NSS-I Target Stream Reaches with Spring Baseflow ANC Less than Reference Values (Standard Errors in Parentheses).#

Subregion	ANC ≤ 0 Length	ANC ≤ 0 %	ANC ≤ 50 Length	ANC ≤ 50 %	ANC ≤ 200 Length	ANC ≤ 200 %	Total Length (km)
Poconos/Catskills	543	3.6	1,606	10.6	5,489	36.2	15,144
	(270)	(1.8)	(500)	(3.3)	(1,100)	(7.3)	(1,912)
N. Appalachians	1,524	7.0	3,713	17.1	12,935	59.5	21,738
	(750)	(3.5)	(920)	(4.2)	(2,200)	(10)	(2,746)
Valley & Ridge	257	0.8	2,111	6.5	12,811	39.2	32,687
	(210)	(0.6)	(990)	(3.0)	(3,400)	(10)	(4,492)
MA Coastal Plain	2,527	6.3	9,636	23.9	21,091	52.3	40,296
	(1,200)	(2.9)	(2,700)	(6.6)	(4,400)	(11)	(5,799)
S. Blue Ridge	*	*	706	7.8	7,084	78.4	9,036
	-	-	(250)	(2.8)	(940)	(10)	(960)
Piedmont	*	*	2,390	7.1	13,554	40.4	33,531
	-	-	(1,300)	(3.9)	(2,900)	(8.5)	(4,402)
S. Appalachians	117	0.5	763	3.5	6,130	28.0	21,892
	(120)	(0.5)	(440)	(2.0)	(1,700)	(8.0)	(2,807)
Ozarks/Ouachitas	*	*	205	0.9	15,092	67.1	22,480
	-	-	(150)	(0.6)	(2,500)	(11)	(2,507)
Florida	461	12.0	2,356	61.2	2,939	76.4	3,848
	(160)	(4.1)	(530)	(14)	(590)	(15)	(678)
SUBTOTALS							
Interior MA	2,324	3.3	7,431	10.7	31,235	44.9	69,569
	(1,000)	(1.4)	(1,700)	(2.4)	(4,300)	(6.2)	(5,601)
Interior SE	117	0.1	4,064	4.7	41,860	48.1	86,939
	(120)	(0.1)	(1,300)	(1.5)	(4,300)	(4.9)	(5,871)
Mid-Atlantic (MA)	4,851	4.4	17,067	15.5	52,327	47.6	109,865
	(1,600)	(1.4)	(3,100)	(2.8)	(6,200)	(5.6)	(8,063)
Southeast (SE)	578	0.6	6,420	7.1	44,799	49.3	90,787
	(210)	(0.2)	(1,500)	(1.7)	(4,400)	(4.8)	(5,910)
Total NSS-I	5,429	2.7	23,487	11.7	97,125	48.4	200,652
	(1,500)	(0.8)	(3,400)	(1.7)	(7,700)	(3.8)	(9,996)

Calculated using linear interpolation between upper and lower reach nodes. Standard errors were approximated by an ad hoc procedure using the variances of separate length estimates based on the upstream and downstream nodes.

* No samples observed below this reference value; estimated percentage is less than 1%.

NOTE: To calculate upper and lower one-sided 95% confidence bounds, multiply the standard error by 1.645 and add or subtract that value from the length estimate. To calculate the two-sided 95% confidence bounds, multiply the standard error by 1.96.

Table E-6. Population Estimates of the Combined Length (km) and Percentage of NSS-I Target Stream Reaches with Spring Baseflow pH Less than Reference Values (Standard Errors in Parentheses).#

Subregion	pH ≤ 5.0 Length	pH ≤ 5.0 %	pH ≤ 5.5 Length	pH ≤ 5.5 %	pH ≤ 6.0 Length	pH ≤ 6.0 %	Total Length (km)
Poconos/Catskills	550	3.6	906	6.0	1,354	8.9	15,144
	(290)	(1.9)	(420)	(2.8)	(520)	(3.4)	(1,912)
N. Appalachians	1,424	6.6	1,870	8.6	3,044	14.0	21,738
	(700)	(3.2)	(710)	(3.2)	(900)	(4.2)	(2,746)
Valley & Ridge	257	0.79	1,937	5.9	4,116	12.6	32,687
	(260)	(0.8)	(1,300)	(4.0)	(1,900)	(5.9)	(4,492)
MA Coastal Plain	3,147	7.8	9,565	23.7	18,707	46.4	40,296
	(1,300)	(3.3)	(3,000)	(7.5)	(4,300)	(11)	(5,799)
S. Blue Ridge	*	*	*	*	*	*	9,036
	-	-	-	-	-	-	(960)
Piedmont	*	*	*	*	2,390	7.1	33,531
	-	-	-	-	(1,200)	(3.7)	(4,402)
S. Appalachians	*	*	313	1.4	920	4.2	21,892
	-	-	(310)	(1.4)	(540)	(2.5)	(2,807)
Ozarks/Ouachitas	*	*	410	1.8	2,437	10.8	22,480
	-	-	(290)	(1.3)	(990)	(4.4)	(2,507)
Florida	522	13.6	1,708	44.4	2,828	73.5	3,848
	(250)	(6.5)	(440)	(12)	(620)	(16)	(678)
SUBTOTALS							
Interior MA	2,231	3.2	4,712	6.8	8,514	12.2	69,569
	(780)	(1.1)	(1,700)	(2.4)	(2,300)	(3.4)	(5,601)
Interior SE	*	*	723	0.83	5,747	6.6	86,939
	-	-	(430)	(0.5)	(1,700)	(1.9)	(5,871)
Mid-Atlantic (MA)	5,378	4.9	14,277	13.0	27,221	24.8	109,865
	(1,500)	(1.4)	(3,400)	(3.1)	(4,800)	(4.4)	(8,063)
Southeast (SE)	522	0.57	2,431	2.7	8,576	9.5	90,787
	(250)	(0.3)	(800)	(0.9)	(1,900)	(2.1)	(5,910)
Total NSS-I	5,900	2.9	16,708	8.3	35,797	17.8	200,652
	(1,600)	(0.8)	(3,400)	(1.7)	(5,200)	(2.6)	(9,996)

Calculated using linear interpolation of $[H^+]$ between upper and lower reach nodes. Standard errors were approximated by an ad hoc procedure using the variances of separate length estimates based on the upstream and downstream nodes.

* No samples observed below this reference value; estimated percentage is less than 1%.

NOTE: To calculate upper and lower one-sided 95% confidence bounds, multiply the standard error by 1.645 and add or subtract that value from the length estimate. To calculate the two-sided 95% confidence bounds, multiply the standard error by 1.96.

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SECTION 1
INTRODUCTION

1.1 OVERVIEW

The role of atmospheric deposition in the acidification of surface waters remains one of the most important and controversial environmental issues of the 1980's. Studies on individual water bodies and on regional lake and stream populations have produced data suggesting that pH and acid neutralizing capacity (ANC) have declined over the past half century in some European and North American surface waters (Beamish and Harvey, 1972; Beamish et al., 1975; Oden, 1976; Wright and Gjessing, 1976; Schofield, 1982; Haines and Akielaszek, 1983; Smith and Alexander, 1983). Declines that have been observed or estimated are most commonly attributed to acidic atmospheric deposition resulting from fossil fuel combustion (Drabløs and Tollan, 1980; National Research Council, 1981, 1983, 1984; U.S. EPA, 1984a; Jeffries et al., 1985; Sullivan et al., 1988b). However, alternative hypotheses for site specific and regional acidification have been discussed and debated in recent literature (Rosenqvist, 1978; Krug and Frink, 1983; Hansen and Hidy, 1982; Havas et al., 1984; Howells, 1984; Cogbill et al., 1984; Lefohn and Brocksen, 1984; Krug et al., 1985; Pierson and Chang, 1986).

A prerequisite that is essential to understanding the environmental effects of acidic deposition in the United States is the availability of quantitative estimates, with known confidence, of the present status and extent of acidic surface waters over broad regional areas. Such estimates cannot be made based on previously conducted independent surveys, monitoring networks, and site-specific research, because these earlier studies lack one or more factors that would allow quantitative regional extrapolation.

Current synoptic-scale studies being performed on monitoring networks cannot be used to characterize surface water quality because they have inadequate statistical sampling designs or regional coverage, inconsistent field or laboratory methods, or insufficient chemical measurements. Also, these studies usually do not have adequate quality assurance data by which potential bias among data collected from different studies can be evaluated. The lack of synoptic data, in turn, thwarts the regional extrapolation of site-specific research results. It is almost impossible to quantitatively extrapolate the results from intensive process-oriented research or long-term monitoring on a small number of watersheds to the larger lake or stream population comprising the resource at risk in a given geographic region. Such regional extrapolation requires a classification of surface waters based on, or linked with, a statistically rigorous description of the physical and chemical characteristics of regional surface waters. Quantitative information is seldom available on whether research sites are broadly typical of the majority of systems in a region, are representative of a relatively small but perhaps important class of surface waters within a subregion, or are in fact unique systems. Research sites are often relatively pristine, probably because of some unique or uncommon characteristic.

1.2 NATIONAL SURFACE WATER SURVEY

In response to the need for knowledge regarding the present extent of acidic or potentially susceptible aquatic resources and their associated biota, the U.S. Environmental Protection Agency and cooperating scientists were asked in 1983 to design a program that would satisfy five major goals:

1. Characterize the chemistry of surface waters (both lakes and streams) in regions of the United States presently believed to be potentially susceptible to change as a result of acid deposition.

2. Examine associations among chemical constituents and define important factors that may affect surface water chemistry.

3. Determine the biological resources within these systems.

4. Evaluate correlations among surface water chemistry and the corresponding biological resources.

5. Quantify any regional trends in surface water chemistry and biological resources.

The program designed to meet these goals was designated the National Surface Water Survey (NSWS). The NSWS became an integral part of the National Acid Precipitation Assessment Program (NAPAP), an interagency research, monitoring, and assessment effort mandated by Congress in 1980. NAPAP provides policy makers with technical information concerning the extent and severity of the effects of acid deposition on human, terrestrial, aquatic, and material resources.

The NSWS design (Figure 1-1) incorporates two parallel components, the National Lake Survey (NLS) and the National Stream Survey (NSS), in order to satisfy the five major research goals. In both components, early project phases contribute to the design and interpretation of subsequent phases. The synoptic surveys of lake and stream chemistry performed in the early phases of the NLS and NSS contribute substantially to the design of subsequent project phases and are essential to the regional extrapolation of their results.

The NSWS design grew out of the recognition that while it is clearly not feasible to perform intensive, process-oriented studies or monitoring programs on all surface waters within the United States, it is equally inappropriate to study a few systems that later may be found to have atypical biological and chemical characteristics. Therefore, each component of the NSWS begins with Phase I, a synoptic survey designed to characterize and quantify the chemistry of lakes and streams throughout the United States, focusing on the areas expected to contain the majority of low alkalinity waters.

The NSWS was designed to overcome the obstacles to assessment discussed in Section 1.1. Lakes and streams were sampled on a regional basis using a statistically rigorous survey design, appropriate standardized field and analytical techniques, a relatively complete set of chemical and physical measurements, and an adequate quality assurance/quality control (QA/QC) program to maximize confidence in the resulting data. The initial survey component (Phase I) provides a snapshot of the present condition of surface waters in regions of the United States most likely to be affected by acid deposition. The Phase I data also serves as a basis for classification of lakes and streams. Such classifications will allow the regional extrapolation, with known confidence, of results from past and future intensive studies on both high-interest aquatic subpopulations and individual lakes and streams.

The impact of acid deposition on biological resources is a major concern, but rather than beginning a study of the problem with a biotic survey of all surface waters in a region, regardless of water quality, it is more effecient to first characterize surface waters in terms of the physico-chemical factors that are expected to impact biota. The present study design, based on the Phase I chemical classification, can be used not only to quantify the present status of

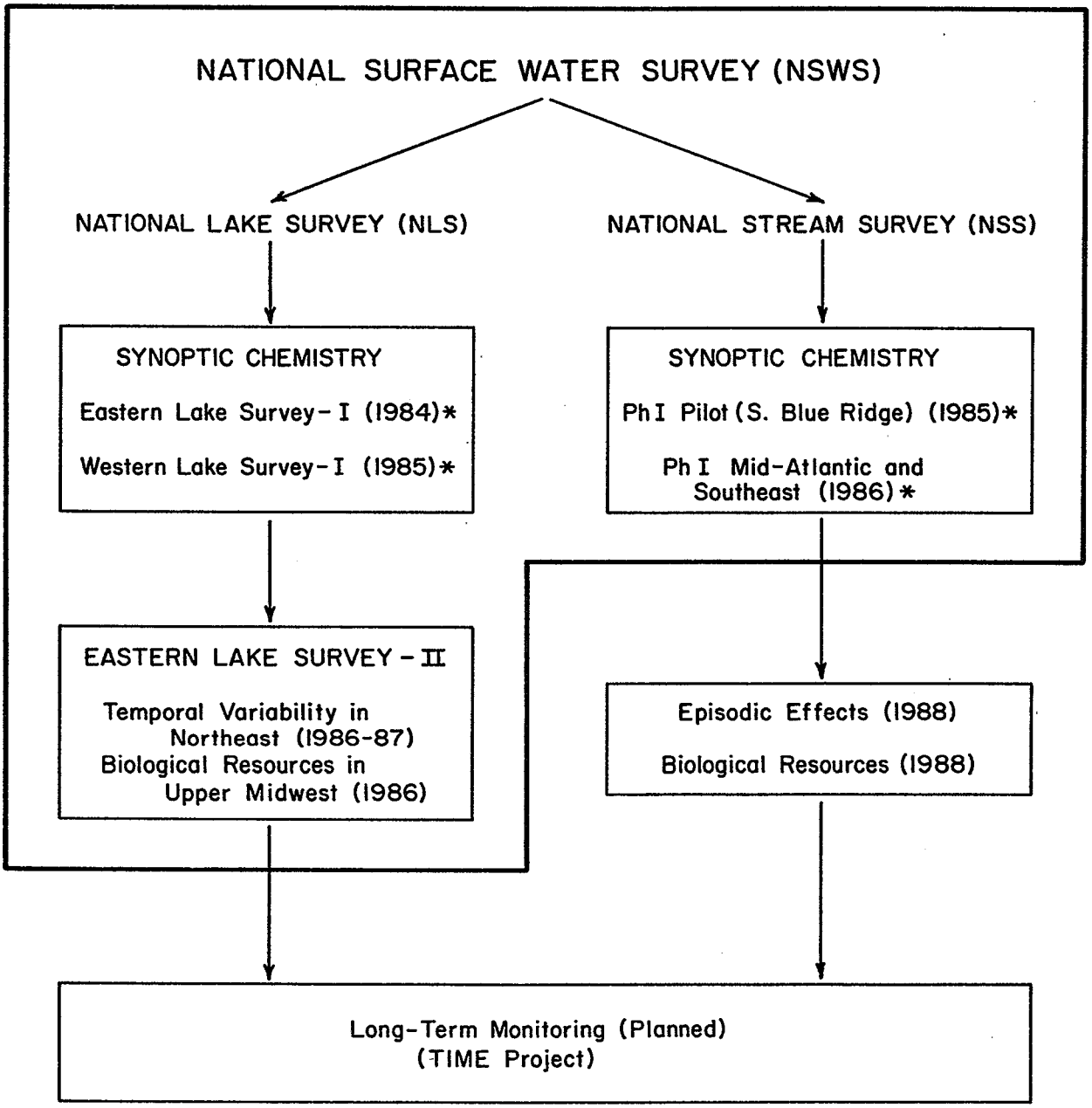

Figure 1-1. Organization of the National Surface Water Survey, showing the two major components, National Lake Survey and National Stream Survey, and their relationship to later phases of study. Dates in parentheses are year of field data collection. Final reports are completed for those marked with an asterisk.

aquatic resources, but also to examine correlative relationships within relatively homogeneous lake and stream types. It also allows the selection of geochemically representative sites for more studies of intensive biological characteristics, temporal variability in water chemistry, and long-term changes.

In the second phase of the NLS, the Eastern Lake Survey - Phase II (ELS-II), and in the Episodic Response Project (ERP), short-term (seasonal, weekly, or episodic) variability in water chemistry is quantified within and among representative lakes and streams in each geographical region. The definition of representativeness is based on Phase I water chemistry and associated hydrology, aquatic organisms, regional acid deposition inputs, land use, physiography, and other basin characteristics. Some regionally representative sites will later become the foundation for a long-term monitoring program, the Temporal Integrated Monitoring of Ecosystems (TIME), presently being designed (Thornton et al., 1987a) to detect and quantify future chemical and biological changes in potentially susceptible lakes and streams in critical subregions. Many lakes and streams that have been the focus of intensive or long-term studies in the past are included in the Phase I lake and stream surveys as special interest sites. Such sites found to be representative of important classes of aquatic systems in their respective regions could serve as nuclei for long-term monitoring efforts.

Phase I of the NLS has been completed. A total of 1,798 lakes in the eastern United States were sampled in the fall of 1984 (Linthurst et al., 1986), and 752 lakes were sampled in selected areas of the western United States in the fall of 1985 (Landers et al., 1987). Phase II field work measuring seasonal variability in lakes took place in 1986 and 1987. The ERP will begin field work in 1988, concentrating on short-term chemical variation in streams and the effects of these changes on fish populations. The NSS has been implemented in two regions, the Mid-Atlantic and a large area of the Southeast. The status of the NSS is discussed further in Section 1.3.

1.3 NATIONAL STREAM SURVEY

1.3.1 Phase I Goals and Objectives

Planning for Phase I of the National Stream Survey (NSS-I) began in mid-1984 and resulted in a Draft Research Plan (U.S. EPA, 1984b). NSS-I was designed to chemically and physically characterize a target population of streams existing within any relatively homogeneous physiographic region, based on a probability sample of those streams. It has the joint major goals of describing and classifying streams in the target population. The specific primary objectives of NSS-I are:

1. To determine the percentage, extent (number, length, and drainage area), location, and chemical characteristics of streams in the United States that are presently acidic, or that have low ANC and thus might become acidic in the future.

2. To identify streams representative of important classes in each region that might be selected for more intensive study or long-term monitoring.

The NSS-I was designed to achieve these objectives within known confidence limits. It was also designed to allow these objectives to be met for any chemical or physical variable measured. For example, the NSS-I design allows an estimation of the percentage of the stream population within a given region having sulfate, nitrate, aluminum, or calcium concentrations

above or below any criterion value of interest. Should some other characteristic of target streams, such as frequency or duration of biologically deleterious episodes, or sensitivity to chronic acidification, be acceptably defined in the future, based on one or more of the variables measured on sample streams, the NSS-I design will also permit the regional extrapolation of such information. The sampling design lends itself to many comparative evaluations. For example, other questions that could be investigated by means of the design include:

1. Do stream ANC and pH decrease as elevation increases?
2. What is the relationship between stream ANC (or pH) and watershed area?
3. Are acidic streams found primarily in small watersheds?
4. Are most acidic streams found in geographic areas with high atmospheric acid deposition?
5. Are sulfate and base cation concentrations in streams of different regions of the United States correlated primarily with regional deposition chemistry or with watershed soils and geology?
6. How may NSS-I chemical data be used to refine existing alkalinity maps?
7. What associations exist among water chemistry, land use, vegetation type, and geographic data?
8. To what extent can sources of acidity be inferred from chemical, physical, and geographical data collected by the NSS?

Except for question number 6, dealing with the refinement of alkalinity maps, all these questions are addressed in this report, at least at a broad regional level. More detailed analyses addressing many of these questions are underway and will be reported in the scientific literature.

1.3.2 National Stream Survey Components

The highest priority for NSS field activities was placed on low alkalinity subregions that have high atmospheric acid deposition rates, but do not contain abundant lakes. Unlike subregions covered by the Eastern and Western Lake Surveys (Figure 1-2), no synoptic data (existing lake or stream data) were available for these subregions from which rough inferences about regional stream chemistry could be made. Such low alkalinity subregions included the New Jersey Pine Barrens and Chesapeake lowlands, the northern portion of the Valley and Ridge Province, and the Northern Appalachians in the Mid-Atlantic United States.

The Poconos/Catskills in the southern part of the glaciated Northeast also were given high priority because data in this subregion (like data from the Southern Blue Ridge) could be compared with ELS data (Linthurst et al., 1986) for the same land area, allowing us to evaluate the feasibility of making regional predictions of stream chemistry on the basis of ELS results.

In the southeastern subregions shown in Figure 1-2 (Northern and Central Blue Ridge, Southern Appalachians, Southern Valley and Ridge, the Piedmont, and the Ozarks/Ouachitas), where atmospheric deposition rates are lower and where soils are expected to have higher sulfate adsorption capacities, a less intensive screening survey was undertaken in the spring of 1986. This Southeast Screening survey also included portions of Florida, in order to test the NSS-I design and logistic protocols in lowland stream networks.

Concurrent with the Mid-Atlantic and Southeast Screening components of the NSS-I, an episodes pilot study was undertaken in the Mid-Atlantic Region to provide a preliminary assessment of the frequency, duration, and causes of short-term episodic changes in chemistry during storm events.

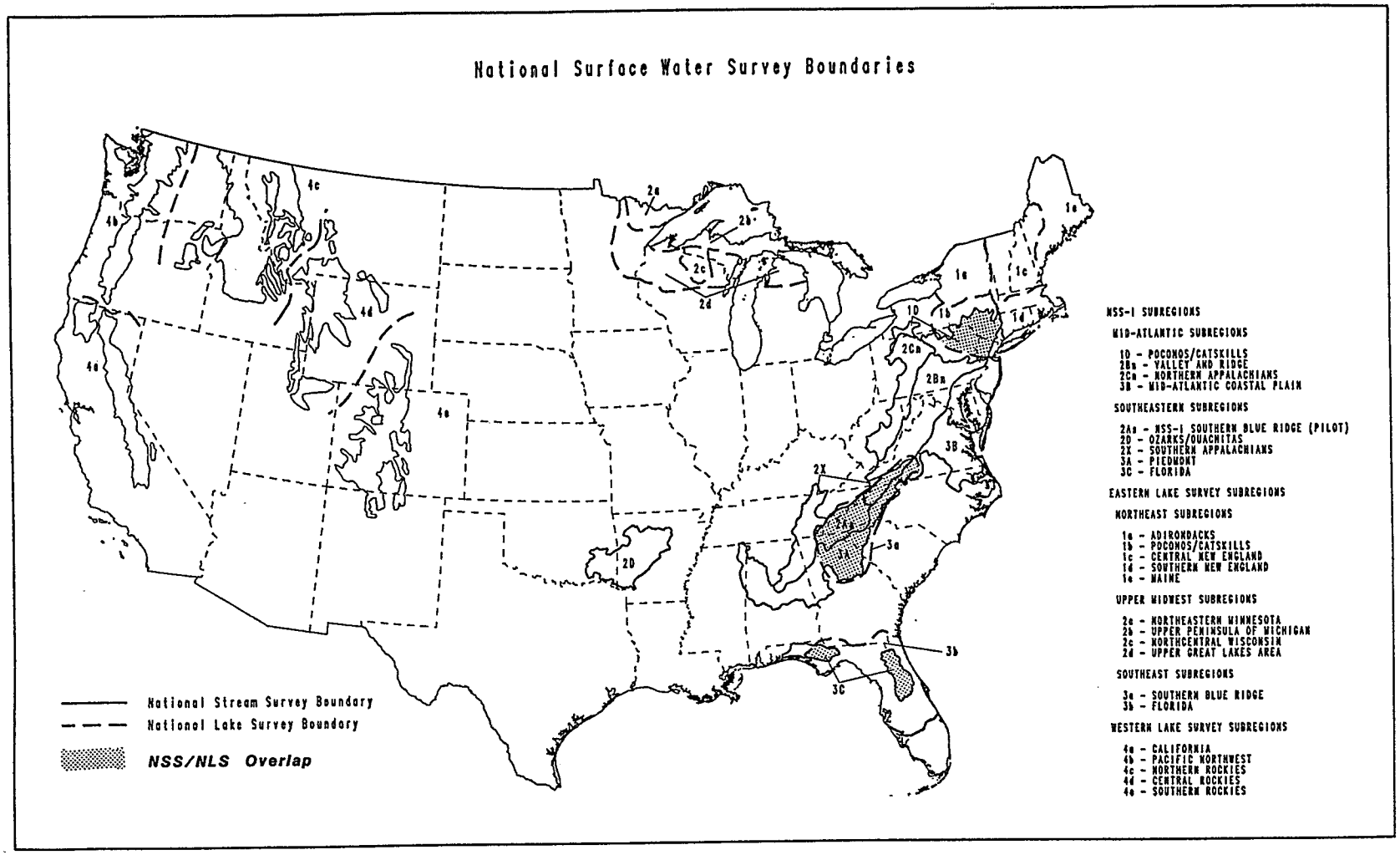

Figure 1-2. Regions and subregions of the United States used to define target populations of the National Surface Water Survey.

1.3.2.1 NSS-I Pilot Survey--

At an initial NSS-I design workshop held in Washington, D.C., in December 1984, peer reviewers recommended that the full-scale survey be preceded by a pilot study, the findings of which might optimize the design of a full-scale effort. The NSS-I Pilot Survey was conducted in the Southern Blue Ridge province during the spring and summer of 1985, and is described in detail by Messer et al. (1986), Drouse et al. (1987), and Knapp et al. (1987). A probability sample of 54 stream reaches was drawn from a target population of blue-line streams on 1:250,000-scale topographic maps, draining catchments less than 155 km^2 (60 mi^2) and satisfying specific site inclusion criteria. Downstream ends of these reaches were visited three times during the spring season and once during the summer. Upstream ends of the reaches were visited during the spring (incomplete sample) and during the summer. The objectives of the pilot survey were as follows:

1. Test the ability of the NSS-I sampling design to meet Phase I objectives, based on analysis of data collected during the pilot survey.

2. Evaluate the Phase I logistics plan (including safety aspects and uncertainties concerning legal and physical site access) and alternative methods of collection, handling, and chemical analysis of samples.

3. Develop and test a data analysis plan for Phase I, using actual data collected in the pilot survey.

The NSS-I Pilot Survey demonstrated that a regional-scale synoptic survey of streams is logistically feasible and that it will produce population estimates, with known confidence, for important variables such as pH and ANC. These population estimates appear to be robust and are not particularly sensitive to small chemical changes that take place during the spring sampling season (Messer et al., 1986, 1988). In addition, Messer et al. (1986) concluded that spring temporal variability does not preclude chemical classification of target systems in the Southern Blue Ridge, providing that data collected during storm episodes are not used in such analyses.

The draft research plan (U.S. EPA, 1985), implementation, and data analysis of the full-scale Phase I stream survey incorporated a number of changes as a result of pilot survey experience. The more important changes, peer reviewed in January 1986, included:

1. Making minor alterations in the stream reach inclusion criteria and the method of selecting sample reaches to better address the assessment objectives of the survey and to increase sampling efficiency.

2. Reducing sampling to two spring visits prior to leaf-out, to satisfy the classification objective, or to one visit, to satisfy the objective of population estimation.

3. Sampling reaches at both their upstream and downstream ends on each visit to characterize spatial variability within reaches.

4. Increasing sample holding time protocols to 24 hours to allow central placement of mobile analytical laboratories, thereby greatly increasing the logistical efficiency of the survey.

5. Changing a number of field measurement techniques to improve accuracy and reliability.

6. Altering QA/QC and data management techniques to increase efficiency.

7. Developing new data analysis techniques to aid interpretation in an assessment context.

1.3.2.2 Mid-Atlantic Phase I Survey--

The focus of the full-scale NSS-I field activities in 1986 was on the Mid-Atlantic region and the survey was designed to fully meet the NSWS primary and secondary objectives outlined in subsection 1.3.1. In the Mid-Atlantic component of the NSS-I, more than 1,000 water chemistry samples were collected from approximately 270 stream reaches in an area bounded by the Pocono/Catskill Mountains to the north, the North Carolina-Virginia state line to the south, the approximate western boundaries of Pennsylvania and West Virginia to the west, and the Atlantic Ocean to the east (Figure 1-2). This region was subdivided into four physiographic subregions on the basis of climate, geology, soils, land use and vegetation. The Mid-Atlantic region is known from previous water quality data (Omernik and Powers, 1983; Omernik and Kinney, 1985; Lynch and Dise, 1985; Witt and Barker, 1986; Murdoch, 1986) to contain waters of low alkalinity. The region generally has high acid deposition rates (NADP, 1987) and many upland areas are known to be overlain with thin soils with a relatively low capacity to neutralize acidity. Field sampling was more intensive in the Mid-Atlantic region than in the Southeast. Each reach was sampled twice during the spring baseflow period, March 15 to May 15, at each of the upstream and downstream reach ends.

1.3.2.3 Southeast Screening--

Previously existing stream water quality databases are not adequate for making quantitative regional chemical distribution estimates in the southeastern United States. The Southeast Screening component of the NSS-I was originally designed to provide the minimal synoptic chemical data required to decide whether Phase I stream sampling efforts should be extended beyond those high priority areas targeted in the Mid-Atlantic. National Lake Survey results (Linthurst et al., 1986; Landers et al., 1987) are useful in targeting potential areas in the Northeast, Midwest, and West that were not sampled in the NSS-I but where substantial numbers of acidic and low ANC streams may exist. However, virtually no data were available for the southeastern states other than the historical data depicted on regional alkalinity maps (Omernik and Kinney, 1985; Omernik and Griffith, 1986a,b) and synoptic surveys in relatively small geographic areas such as the Southern Blue Ridge (Messer et al., 1986; Winger et al., 1987).

The sampling/statistical design of the Southeast Screening component allows regional characterization (e.g., population distribution estimates with known confidence of acidic and low ANC streams), as did the Mid-Atlantic Phase I Survey component. However, each stream in the Southeast Screening was sampled only once at each reach end, thereby providing less stable chemical index values with no estimate of temporal variance during the spring sampling period. As in the Mid-Atlantic, stream water quality sampling was avoided during extreme hydrologic events (episodes). The single spring base flow sample was not originally expected to provide enough information for the robust classification of sample streams that would identify regionally representative sites or important classes of streams for more intensive study of episodes, watershed manipulation, or long-term temporal changes. However, results from the NSS-I Pilot Survey

(Messer et al., 1986, 1988) indicated that chemical classifications of Southern Blue Ridge streams based on single spring base flow samples from each stream were virtually the same as those based on the average of three such samples, suggesting that classifications based on Southeast Screening data are probably robust. Without additional data, however, the stability of these classifications cannot be quantitatively evaluated.

The Southeast Screening includes subregions of the United States expected, on the basis of alkalinity maps (Omernik and Powers, 1983), to contain low alkalinity surface waters of widely different geochemical types experiencing a broad range of acid deposition rates. The region includes the Southern Piedmont, the Ozarks/Ouachitas, the Florida panhandle and peninsula, and parts of the Southern Appalachians that were not sampled as part of the NSS-I Mid-Atlantic Survey or the NSS-I Pilot Survey in the Southern Blue Ridge. The Southern Appalachians and the Ozarks/Ouachitas represent two types of upland watersheds separated by hundreds of miles that experience different deposition rates. The Piedmont is characterized by lower elevation, predominantly clearwater streams. Florida contains both colored and clearwater lakes and streams at low elevations. The target areas studied in the Southeast Screening also provide an indication of the types and occurrence of low ANC waters to be found in large areas of the South Atlantic and Gulf coastal plains. The field effort in the Florida subregion provides a test of the utility of the NSS-I design and logistical protocols in lowland stream networks. Approximately 400 samples were collected from 200 stream reaches in the Southeast Screening area between March 15 and May 15, 1986, one sample from each upstream and downstream end of the sample reaches.

1.3.2.4 Mid-Atlantic Episodes Pilot--

The primary objective of the Episodic Response Project (ERP) is to predict the magnitude, frequency, duration, and causes of episodic events in streams and lakes (Thornton et al., 1987b). These events cause marked shifts in pH and associated chemistry from baseflow conditions. In areas dominated by snowpack, such episodes result from snowmelt and are often exacerbated by warm days or rainfall. In warmer regions, episodes are usually associated with rainfall. The Mid-Atlantic Episodes Pilot, a precursor to the ERP, was undertaken in parallel with the NSS-I Mid-Atlantic field effort during the spring of 1986. This pilot effort was aimed at providing a preliminary assessment of the frequency, duration, and causes of such episodes in the Mid-Atlantic. It was also aimed at testing a regional synoptic design for episodes sampling. Messer and Eshleman (1987) summarized the results of the Mid-Atlantic Episodes Pilot and concluded that a synoptic survey of episodes was not cost effective. Rather, a model-based study would be needed to satisfy data needs concerning episodic effects. The results of the Episodes Pilot were used, however, to aid in the design of a cost-effective, regional study of episodes, the ERP, to be implemented in 1988 (Thornton et al., 1987b). The results of the Mid-Atlantic Episodes Pilot are summarized by Messer and Eshleman (1987) and will not be discussed further in this NSS-I data report.

1.3.3 The NSS-I Data Report

This report documents the design and methods of the NSS-I Mid-Atlantic and Southeast Screening surveys, reports the results of these studies, and discusses current interpretations.

Section 2, Survey Design, defines the target stream population of interest and describes how representative samples were drawn from it in time and space. It then outlines the procedure by which regional population estimates of stream chemistry were made.

Section 3, Methods, describes procedures for field sample collection, handling, and chemical analysis. It also describes the QA/QC protocols, including data management procedures such as verification, validation, and the construction of the database used for analysis.

Section 4, Data Quality Assessment, discusses aspects of data completeness, chemical detectability, analytical accuracy, and sampling/analytical precision in light of the results of blank, duplicate, and audit sample analyses.

Section 5, Target Population--Physical Characteristics, describes the physical characteristics of the stream resource sampled. The section presents total resource estimates for the NSS-I subregions, along with distributions of such characteristics as drainage area, Strahler order, and elevation. Section 5 also describes the general categories of streams included in the sampled population, such as those affected by acid mine drainage. By removing several types of streams from the general categories, a more restricted target population of interest for assessing acid deposition effects is delineated. This is the population for which population distribution estimates are made in Section 6.

Sections 6 through 9 report and discuss the major results of the NSS-I, including those previously published for the NSS-I Pilot Survey in the Southern Blue Ridge (Messer et al., 1986). Section 6 summarizes the regional distribution estimates of stream chemistry, which are the primary outputs of the NSS-I. Section 7 discusses the uncertainties regarding these estimates in terms of temporal variability in baseflow chemistry. Section 8 presents a geochemical interpretation of the relationships observed among measured chemical constituents in stream water. Section 9 describes the chemical characteristics and geographic distribution of a selected group of target streams of highest assessment interest--those that are acidic or that have low ANC. The discussion covers the potential sources of acidity in these streams. Those for which substantial acidification by atmospheric deposition is very unlikely are systematically eliminated from consideration. Section 9 then examines the chemistry of the remaining streams (those for which atmospheric deposition remains a possible cause of acidification).

Section 10 examines evidence for acidification of NSS-I sample streams and summarizes our current regional understanding of the potential for acid deposition impacts on streams in the Mid-Atlantic and Southeastern United States.

Finally, Section 11 summarizes the important findings of the NSS-I in the Mid-Atlantic and Southeast, Section 12 lists the references, and Section 13 provides a glossary of abbreviations and symbols, and defines terms used throughout the report.

Volume II, the data compendium, is a companion document to this report. It contains data listings and additional statistical analyses of the NSS-I physical and chemical data.

SECTION 2
SURVEY DESIGN

2.1 OVERVIEW

Phase I of the National Stream Survey (NSS-I) employed a randomized, systematic technique for selecting a probability sample of stream reaches (Overton, 1986, 1987; Messer et al., 1986) within areas of the United States expected, on the basis of previous chemical data (Omernik and Powers, 1983; Omernik and Kinney, 1985), to contain waters of low acid neutralizing capacity (ANC). Field crews then visited these stream sampling locations, made field physical and chemical measurements, and collected water samples for later analysis (Section 3). Identification of the target population for the NSS-I involved two separate activities: (1) identification and prioritization of geographical regions expected to contain significant numbers of low pH or low ANC streams, and (2) identification of the types of streams within these regions that were of interest from the standpoint of assessing the present extent of effects due to acid deposition.

The highest priority for NSS-I field activities was placed on low alkalinity subregions that have high atmospheric acid deposition rates, but that do not contain abundant lake resources. Subregions of high interest that do contain such lake resources (the Northeast, Upper Midwest, and West) were sampled by the Eastern and Western Lake Surveys (ELS and WLS) (Linthurst et al., 1986; Landers et al., 1987).

Within the NSS-I subregions, target stream reaches were identified as those that have drainage areas less than 60 square miles (155 km^2) at their lower ends, but that are large enough to be represented as blue lines on 1:250,000-scale U.S. Geological Survey (USGS) topographic maps. The development and justification for this definition is discussed in Section 2.3. The targeted size range was accepted by reviewers as a reasonable compromise that would include streams large enough to be recreationally and economically important for fish habitat, yet still small enough to be susceptible to change as a result of acidic deposition.

The NSS-I relies, as do other components of Phase I of the National Surface Water Survey (NSWS), on samples taken from a number of water bodies during an appropriate season to provide an index of the chemical characteristics of the water bodies in the region. The reasons for choosing a spring index sampling period for the NSS-I are discussed and justified in Section 2.5. The choice involved a trade-off between minimizing within-season and episodic chemical variability and collecting samples during the season most likely to exhibit conditions potentially limiting for aquatic organisms. As a result of NSS-I Pilot Survey experience (Messer et al., 1986), the average of two spring samples taken between snowmelt and leaf-out was deemed sufficient for establishing a chemical index for streams in the Mid-Atlantic subregions. In the Southeast, where it is less probable that substantial amounts of present surface water acidification (not necessarily watershed acidification) have been caused by acidic deposition, and where the Survey was aimed at broad-scale regional screening for potential effects, one spring sample was taken at each sampling location. To quantify and incorporate the variability between upstream and downstream ends of reaches, chemical and physical variables were measured at both ends.

The chemical variables measured included (1) those related to biological effects--pH, extractable aluminum, and competing ligands such as fluoride and dissolved organic carbon (DOC), (2) others related to potential sensitivity and related geochemistry--ANC, base cations, sulfate and other acid anions, and silica, and (3) others indicative of pollution or other relevant factors--phosphorus, iron, ammonium, and turbidity. Samples were stabilized within 24 hours of collection and rigorous quality assurance (QA) and quality control (QC) protocols were followed during sample handling, chemical analysis, and data reporting (Section 3). The data were stored

in several readily accessible data bases, again following rigorous QA/QC protocols, prior to analysis and interpretation.

An important strength of the NSS-I design, and that of the NSWS in general, is that it employs a regionally well-distributed probability sample of streams. This statistically rigorous sampling frame allows quantitative regional extrapolations to be made from survey data or from any additional information about NSS-I sample streams obtained at a later date. Furthermore, regional extrapolations can be made using data from other streams that fit within specific classes based on NSS-I sample data. The combination of the NSS-I sampling frame with this stream classification allows an accurate appraisal of the regional significance of past studies and the focusing of future detailed, process-oriented research efforts or long-term monitoring on streams that represent important stream types or ones that are regionally characteristic.

2.2 PROJECT DESIGN CRITERIA

The design criteria of the NSS-I were intended to overcome some of the historical problems that occurred in past data sets as noted in Section 1. Not all of the design criteria in a project like the NSS-I (aimed at description and classification) can be so narrowly and quantitatively defined that data not in conformance with the criteria are useless. Instead, some of the design criteria represent ideal targets. However, even qualitative specification of the design criteria in the planning process resulted in significant improvements to project designs and protocols. The following design criteria were established:

1. The target population will explicitly and accurately represent the set of streams of interest in this investigation (those constituting the most important resource at risk from acid deposition).

2. The NSS-I sample population will be a probability sample from the target population.

3. The suite of variables measured will be complete enough to provide information on (1) the suitability of streams for key fish species and (2) the geochemical parameters that can be used to classify the streams and formulate hypotheses about past and future acidification. Phase I data may be supplemented from other data sources during later phases to meet some of these objectives.

4. The data must be of high quality, with low and quantifiable analytical error, and with known precision, representative of the state-of-the-art attainable in high volume contract analytical laboratories. Data quality objectives (DQOs) for chemical data are discussed in Section 4 and Appendix A.

5. Sample sizes will be large enough to provide precise population estimates and robust stream classifications, to the extent that natural classes exist in the target populations.

For certain aspects of the project design criteria, evaluation of how well the criteria were met is necessarily subjective. For example, the streams of interest to this investigation were explicitly represented and the probability sample was extracted from these streams, but there is room for questioning the degree to which the streams that were sampled constitute the most important resource at risk from acid deposition. The degree to which design criteria 3 (vari-

ables measured) and 5 (sample size) were met is based on the precision and utility of results. The project goals for analytical detection, bias, precision, and data completeness, specified through DQOs, are discussed in Section 4 and in Cougan et al. (1988), along with the degree to which these were met and the implications of the results for data interpretation. Aspects of temporal and spatial variance not quantified by the spatial sampling design or QA program are evaluated in Section 7.

2.3 DEFINING THE RESOURCE AT RISK

2.3.1 Regions of Interest

Regions of interest for the NSS-I were defined as all areas of the conterminous United States whose surface water alkalinity was expected to be less than 400 μeq L^{-1}, and which also are subject to higher-than-background levels of atmospheric acid deposition. These criteria should encompass those areas with surface waters most likely to exhibit chemical and biological effects resulting from acid deposition. Although the NSS-I is potentially a nationwide effort, we know that many regions of the United States are not likely to contain a significant number of low ANC or low pH waters. These areas were initially delineated by Omernik and Powers (1983) for the whole nation, and more recently, at greater resolution, for individual regions (Omernik and Kinney, 1985; Omernik and Griffith, 1985, 1986a,b). Figure 2-1 shows the areas of the United States where ANC was expected to be < 400 μeq L^{-1}. Nonsensitive areas include vast portions of the Great Plains, as well as low-elevation areas in central and coastal states where soils or bedrock geology provide ample buffering capacity for neutralizing acid inputs from either natural or anthropogenic sources. These areas were excluded from consideration to allow resources to be directed at areas in which low surface water alkalinity is more likely to be found. In the conterminous United States, streams with low alkalinity are found in the following areas:

1. Continental glaciated regions of the Northeast
2. Continental glaciated regions of the Upper Midwest
3. High elevation glaciated (alpine) portions of the mountainous west
4. Appalachians and Ozark Plateau region
5. Mid-Atlantic Coastal Plain, including the New Jersey Pine Barrens
6. Southern Piedmont, Southeast Coastal Plain, and Gulf Coastal Plain

For the NSS-I, two regions, the Mid-Atlantic and Southeast (Figure 2-2), were judged to contain most of the land area not included in the National Lake Survey in which clearwater (low in organic acids) streams of low alkalinity were likely to be found in the conterminous United States. The boundaries of these areas were based on a national map of surface water alkalinity (Omernik and Powers, 1983), individual regional maps of surface water alkalinity (Omernik and Kinney, 1985; Omernik and Griffith, 1986a,b), land surface form (Hammond, 1970), and physical divisions (Fenneman, 1946). The criteria used to draw geographical boundaries of the regions differed somewhat between the NSS-I and Phase I of the National Lake Survey (NLS), because of the different focus of the two surveys, the different logistical and statistical design constraints, and the different factors understood to control surface water quality in each area. The differences in the region numbering systems between the NLS and the NSS-I are arbitrary, but have become sufficiently ingrained in the NSWS literature and data bases to make change inadvisable.

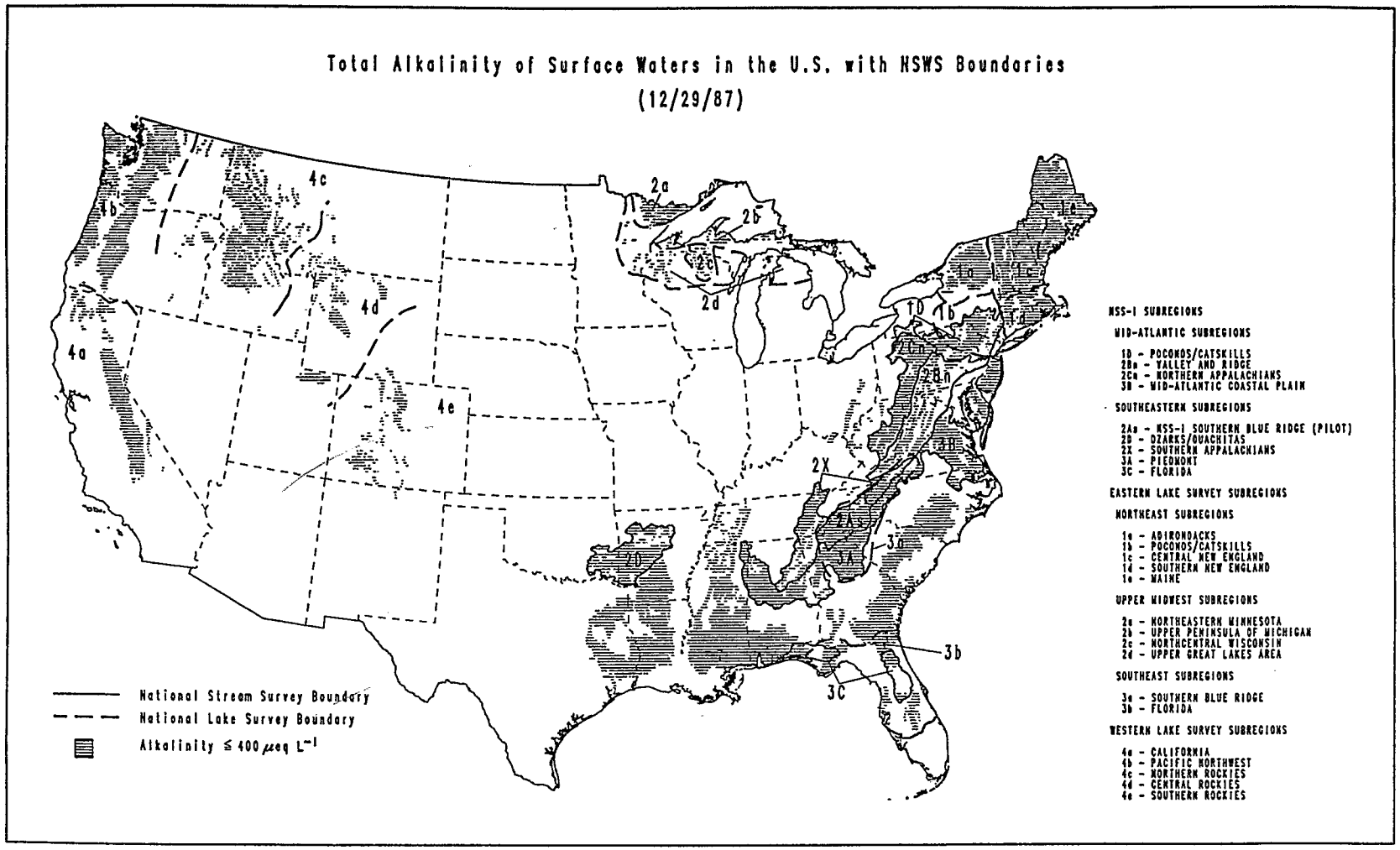

Figure 2-1. Regions of the United States expected, on the basis of historical data, to contain surface waters with alkalinity < 400 μeq L^{-1}, shown with National Surface Water Survey boundaries.

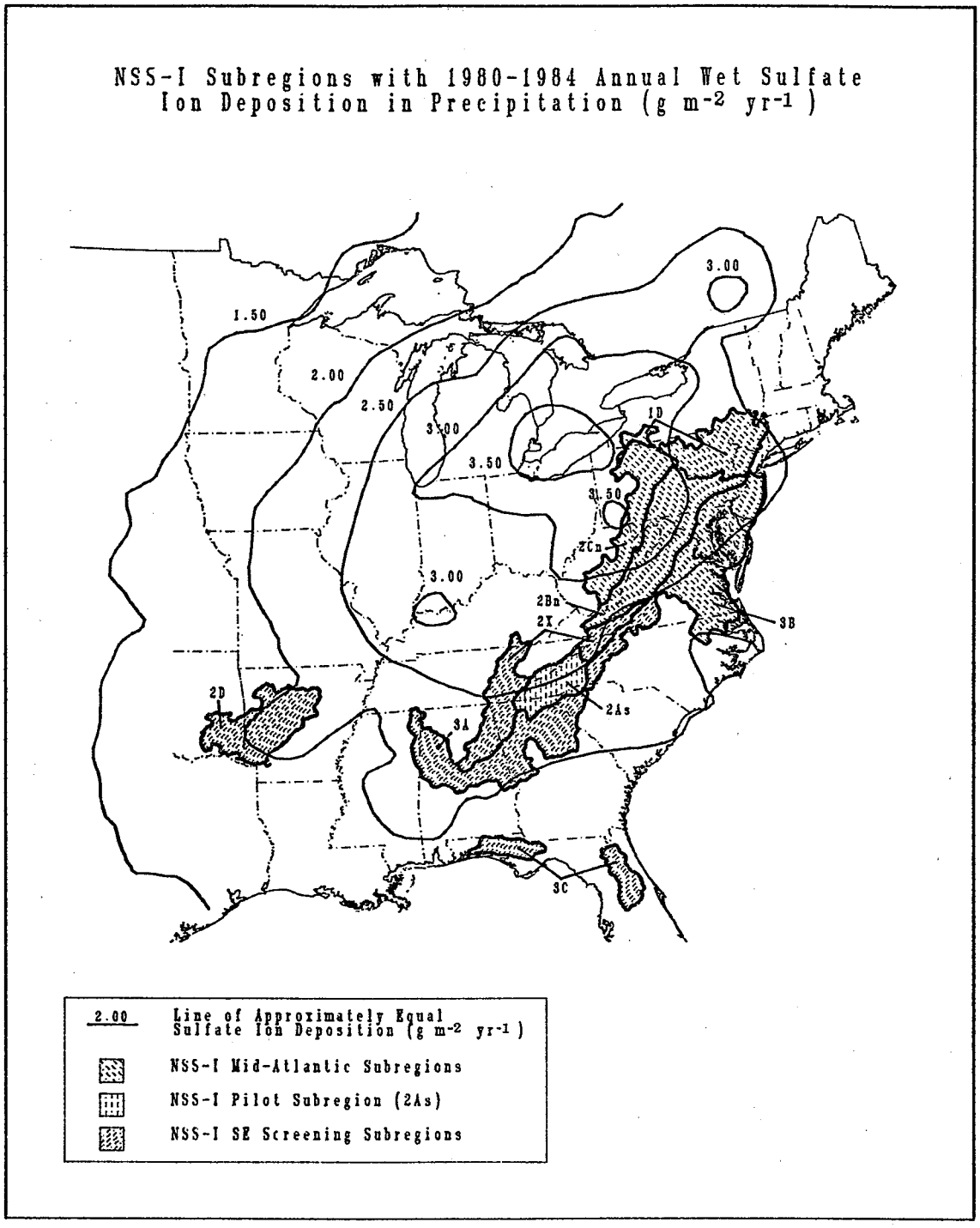

Figure 2-2. NSS-I Mid-Atlantic and Southeast subregions, with atmospheric wet sulfate deposition rates. Wet sulfate deposition isopleths were taken from Wampler and Olsen (1987).

To ensure that representative samples were drawn from each distinct portion of a region, the regions were divided into subregions (Figure 2-2 and inside front cover). Subregions were defined by assessing the spatial associations between pre-existing water chemistry data and terrestrial characteristics important to the understanding of surface water sensitivity to acidification. These characteristics included land surface form, land use patterns, and potential natural vegetation. It was intended that by delineating subregions as sampling strata for the NSS-I, inter-regional sampling variance could be reduced. Characteristics of the subregions sampled (subsection 2.3.2) are summarized in Table 2-1.

It was desirable to focus physical sampling on areas most likely to have potentially sensitive streams. Not all areas delineated within the subregions shown in Figure 2-1 are likely to be sensitive. The areas sampled within each subregion were delineated on the basis of the 400 μeq L^{-1} isopleth on the regional alkalinity maps. At the NSS-I sampling plan workshop, however, researchers decided that where internal valleys or basins and external boundary intrusions with alkalinity > 400 μeq L^{-1} were expected to occur, it would be preferable to include the valleys and basins and smooth the boundaries (Figure 2-1). Conditions within the corresponding subregions could thus be described without relying on unproven assumptions to interpret the historical data and construct the alkalinity map. Expanding the system boundaries could reduce the estimated percentage of streams below any particular ANC value, if the maps are correct, but the procedure should increase the estimate of the total number of stream miles in the area in the same ANC category. In Florida, the subregion boundaries were drawn on the basis of the 200 μeq L^{-1} isopleth on the alkalinity maps. This approach was undertaken in Florida because the NSS-I field activities in this subregion were viewed as a way of providing supplemental information on streams in an area already surveyed by the ELS, while at the same time testing the feasibility of the NSS-I sampling design for application to other low elevation, low relief areas of the Southeastern and Gulf coastal plains.

2.3.2 Regional Prioritization

Choice of the regions and subregions for study in this first regional implementation of the NSS-I was somewhat subjective. The overall plan was to provide some level of synoptic information (Phase I or Screening) for as broad an area of the eastern United States as possible before providing increased precision in any one region. For initial assessment purposes, it was more valuable to know whether acidic waters exist in areas previously not known or expected to contain them than to supplement the NLS estimates of lake chemistry by conducting a Phase I stream survey in the same areas.

Four subregions were identified for the Phase I survey in the mid-Atlantic states (Table 2-1, Figure 2-1, and inside front cover):

1. The Poconos and Catskills (1D)
2. The Mid-Atlantic Coastal Plain (3B), including the New Jersey Pine Barrens and the Chesapeake Bay area
3. The northern portion of the Valley and Ridge Province (2Bn)
4. The Northern Appalachians (2Cn)

Table 2-1. Characteristics of the NSS-I Subregions

SUBREGION 1D - POCONOS/CATSKILLS

Geographic Extent

- Covers the Pocono Mountains, the Catskill Mountains, the glaciated highlands of Southern New York and Northeastern Pennsylvania, and the Valley and Ridge Province of Northeastern Pennsylvania and Southeastern New York.

Terrestrial Characteristics

- Tablelands with considerable relief, open high hills, and low mountains.
- Elevations 500 to 3,000 feet.
- Vegetation cover is northern hardwoods and Appalachian oak forests.
- Land use is generally woodland and forest with some cropland pasture.

Precipitation/Hydrological Characteristics

- Annual precipitation 40-48 inches, with most rainfall occurring during May-August.
- Annual surface water runoff 20-30 inches.
- Approximate annual evapotranspiration 28-32 inches.
- Low stream flow, August-September; high flow, March.

Aquatic Characteristics

- Clearwater streams.
- Low alkalinity streams generally drain watersheds < 50 mi^2, usually above 1,500 feet elevation.
- Alkalinity values are generally low in spring.

SUBREGION 2As - SOUTHERN BLUE RIDGE

Geographic Extent

- Includes the Southern Blue Ridge Mountains and the French Broad River Valley of North Carolina and Tennessee.

Terrestrial Characteristics

- Uniformly dissected low mountains.
- Elevations 1,800 to 5,200 feet.
- Vegetation cover is Appalachian oak forest with pockets of northern hardwoods.
- Land use is forest and woodland, mostly ungrazed, mixed with cropland and pasture.

Precipitation/Hydrological Characteristics

- Annual precipitation 45-80 inches, with most rainfall occurring during January-April.
- Annual surface water runoff 15-40 inches.

- Approximate annual evapotranspiration 32-40 inches.
- Low stream flow, September-October; high flow February-March.

Aquatic Characteristics
- Clearwater streams.
- Low alkalinity streams generally drain watersheds < 200 mi^2; lowest alkalinity streams generally drain watersheds < 25 mi^2, usually above 2,500 feet elevation.
- Alkalinity values are generally low in spring.

SUBREGION 2Bn - VALLEY AND RIDGE

Geographic Extent
- Centered over the Valley and Ridge Province of Pennsylvania, Maryland, West Virginia, and Virginia. Includes western section of the Piedmont in Virginia and Maryland.

Terrestrial Characteristics
- Open hills, plains with low mountains, and open low mountains.
- Elevations 600 to 3,700 feet.
- Vegetation cover is Appalachian oak and oak-hickory-pine forests.
- Land use is forest and woodland, mostly ungrazed on the ridges, with cropland and pasture in the valleys.

Precipitation/Hydrological Characteristics
- Annual precipitation 40-50 inches, with most rainfall occurring during July-August.
- Annual surface water runoff 20-30 inches.
- Approximate annual evapotranspiration 32-40 inches.
- Low stream flow, September-October; high flow February-March.

Aquatic Characteristics
- Clearwater streams.
- Lowest alkalinity streams generally drain watersheds < 20 mi^2, usually above 2,000 feet.
- Alkalinity values are generally low in spring.
- Subregion characterized by trellised drainage patterns.

SUBREGION 2Cn - NORTHERN APPALACHIANS

Geographic Extent
- Covers the northern Appalachian Plateau of Western New York, Pennsylvania, Western Maryland, and West Virginia. Includes western sections of the Valley and Ridge Province in West Virginia and Maryland.

Table 2-1. Characteristics of the NSS-I Subregions (Continued)

Terrestrial Characteristics

- Open high hills, high hills, and low mountains.
- Elevations 600 to 3,000 feet.
- Vegetation cover is Appalachian oak and mixed mesophytic forests.
- Land use of low alkalinity streams is generally forest and woodland, mostly ungrazed, with some cropland and pasture.

Precipitation/Hydrological Characteristics

- Annual precipitation 40-55 inches, with most rainfall occurring during May-July.
- Annual surface water runoff 20-30 inches.
- Approximate annual evapotranspiration 28-36 inches.
- Low stream flow, September-October; high flow, March.

Aquatic characteristics

- Mostly clearwater streams with some colored water streams.
- Low alkalinity streams generally drain watersheds < 100 mi^2; lowest alkalinity streams generally drain watersheds < 10 mi^2.
- Alkalinity values are generally low in spring.

SUBREGION 2D - OZARKS/OUACHITAS

Geographic Extent

- Includes the Boston Mountains, the Ouachita Mountains, and the Arkansas River Valley in Arkansas and Eastern Oklahoma, as well as northern portions of the Gulf Coastal Plain.

Terrestrial Characteristics

- High hills and open low mountains.
- Elevations 500 to 2,500 feet.
- Vegetation cover is oak-hickory-pine and oak-hickory forests.
- Land use of low alkalinity streams is generally forest and grazed woodland.

Precipitation/Hydrological Characteristics

- Annual precipitation 48-56 inches, with most rainfall occurring during April-June.
- Annual surface water runoff 10-20 inches.
- Approximate annual evapotranspiration 42-50 inches.
- Low stream flow, August; high flow, April.

Aquatic Characteristics
- Clearwater streams.
- Low alkalinity streams generally drain watersheds < 200 mi^2.
- Alkalinity values are generally low in spring.

SUBREGION 2X - SOUTHERN APPALACHIANS

Geographic Extent
- Covers southern portions of the Appalachian Plateau and the Valley and Ridge Province in Tennessee, Georgia, and Alabama. Central protions of the Blue Ridge Mountains in North Carolina and Virginia are also included.

Terrestrial/Hydrological/Aquatic Characteristics
- This subregion includes characteristics of subregions 2As, 2Bn, and 2Cn.

SUBREGION 3A - PIEDMONT

Geographic Extent
- Covers the western margin of the Piedmont in Virginia, North Carolina, South Carolina, and Georgia. Includes northern portions of Gulf Coastal Plain in Alabama and Mississippi.

Terrestrial Characteristics
- Tablelands, plains with high hills, and open high hills.
- Elevations 300 to 1,500 feet.
- Vegetation cover is predominantly oak-hickory-pine forest.
- Land use is cropland with pasture, woodland, and grazed forest.

Precipitation/Hydrological Characteristics
- Annual precipitation 40-55 inches, with most rainfall occurring during January-April.
- Annual surface water runoff 15-20 inches.
- Approximate annual evapotranspiration 34-42 inches.
- Low stream flow, October; high flow March.

Aquatic Characteristics
- Clearwater streams.
- Low alkalinity streams generally drain watersheds < 300 mi^2; some streams draining watersheds as large as 1,000 mi^2 may be relatively low.
- Alkalinity values are generally low in spring.

Table 2-1. Characteristics of the NSS-I Subregions (Continued)

SUBREGION 3B - MID-ATLANTIC COASTAL PLAIN

Geographic Extent

- A geographically diverse subregion that includes the following:
  - The Piedmont of Southern Pennsylvania, Maryland, and Virginia.
  - The Pine Barrens of Southern New Jersey.
  - The Coastal Plain covering Delaware, Southern New Jersey and the eastern sections of Maryland, Virginia, and Northern North Carolina.

Terrestrial Characteristics

- Flat plains and irregular plains.
- Elevations 0 to 300 feet.
- Vegetation cover is oak-hickory-pine and northeastern oak-pine forests.
- Land use is cropland with pasture, woodland, and grazed forest and pockets of forest and woodland (mostly ungrazed).
- Soils are very sandy and nutrient poor.

Precipitation/Hydrological Characteristics

- Annual precipitation 40 inches, with most rainfall occurring July-August.
- Annual surface water runoff 15-20 inches.
- Approximate annual evapotranspiration 34-38 inches.
- Low stream flow, September-October; high flow, February-March.

Aquatic Characteristics

- Mostly colored streams with some clearwater streams.
- Low alkalinity streams generally drain watersheds < 500 mi^2; lowest alkalinity streams generally drain watersheds within the Pine Barrens < 50 mi^2.
- Alkalinity values are generally low from late winter to early summer.

SUBREGION 3C - FLORIDA

Geographic Extent

- Covers the Florida panhandle and the northcentral portion of the Florida peninsula.

Terrestrial Characteristics

- Flat marine plain with sand hills, swamps, sinks, and lakes.
- Elevations 0 to 100 feet.
- Vegetative cover is mostly southern mixed forest with pockets of sand pine scrub and wetlands.
- Soils are sandy and nutrient poor; subregion contains areas of karst topography.

Table 2-1. Characteristics of the NSS-I Subregions (Continued)

Precipitation/Hydrological Characteristics

- Annual precipitation 56 inches, with most rainfall occurring during July-August (panhandle); most rainfall occurring during June-September (peninsula).
- Annual surface water runoff 10-30 inches.
- Approximate annual evapotranspiration 46 inches.
- Low stream flow, May (panhandle); high flow, August.
- Low stream flow, November (peninsula); high flow, March (peninsula).

Aquatic Characteristics

- Subregion contains mostly colored and some clearwater streams.
- Low alkalinity streams that are clear generally drain the sand hills and have watersheds < 50 mi^2; colored water, low alkalinity streams generally drain watersheds < 200 mi^2; however, due to the lack of relief and drainage patterns, topographic watersheds are poorly defined.
- Alkalinity values are generally lowest in winter and spring.
- Streams are generally slow moving and often have imperceptible flow in swamps.

Four additional subregions were targeted for the Southeast Screening Survey (Table 2-1, Figure 2-2, and inside front cover):

1. The Piedmont (3A)
2. The Ozarks and Ouachitas (2D)
3. Florida (3C)
4. The Southern Appalachians (2X), which includes the southern portions of the Appalachians (2Cs) and the Valley and Ridge Province (2Bs) not sampled as part of the NSS-I Mid-Atlantic Survey, and a northern portion of the Blue Ridge Mountains (2An) not sampled as part of the NSS-I Pilot Survey. These areas have been combined into the heterogeneous subregion labeled 2X.

In many of the areas cited above, there is no synoptic lake chemistry data from the NLS, and the general state of the surface water resource from the standpoint of the NSWS objectives was unknown. The regions chosen for the Mid-Atlantic Phase I Survey are particularly notable for their high acid deposition rates (Figure 2-2) relative to other regions of the country. The concern over declines in salmonid fisheries in mountainous areas of the eastern United States (Schofield, 1982; Magnuson et al., 1984), and over the decline of the blue herring, American chad, striped bass, yellow perch, and other warmwater fisheries in the Chesapeake Bay (Hall et al., 1985, 1987; Hall, 1987; Klauda and Palmer, 1987; Bowman, 1988 [pers. comm.]), any or all of which may be related to acid deposition, also contributed to the prioritization decision. Only the Poconos/Catskills subregion (1D) in the northeastern part of the Mid-Atlantic was sampled during the ELS-I. A comparison of lake versus stream chemistry in that subregion, together with data collected during the ELS Phase II Episodes Pilot, may be useful in determining the criteria for prioritizing future NSS field work. The four Mid-Atlantic subregions are contiguous and extend their coverage over a large area, facilitating the logistical and sampling designs.

The screening areas in the southeastern United States were included because they exemplify areas expected to contain low ANC surface waters of widely different geochemical types. The Southern Appalachians and the Ozark Plateau represent two types of upland watersheds that are separated by hundreds of miles and that have different acid deposition rates (Figure 2-2). The Piedmont is characterized by lower elevations, but still predominantly clearwater streams. Based on the ELS-I results, Florida was known to contain both colored and clearwater acidic lakes, and the target areas studied should provide a good example of the types and occurrence of colored or clearwater low ANC waters typical of the broad expanses of the Coastal Plain that were not surveyed in the 1986 field implementation of the NSS-I. The Florida subregion also tests the utility of NSS-I logistical and design protocols in lowland stream networks. The implementation of NSS-I activities in 1985 (Pilot Survey) and 1986 (full-scale survey) did not include areas of the Northeast, Upper Midwest, and West. Whereas these regions are expected to contain acidic streams or low ANC streams potentially sensitive to acidic deposition, they also contain numerous lakes that were sampled as part of the ELS-I in 1984 (Linthurst et al., 1986) and the WLS in 1985 (Landers et al., 1987). In addition, NSS-I field activities to date have not included synoptic stream chemistry sampling in parts of the South Atlantic and Gulf coastal plains expected to contain predominantly low ANC surface waters (Figure 2-1).

2.3.3 Identifying the Stream Resource of Interest

A sampling design depends on the identification of a target population, that is, a collection of entities about which we want to make estimates, and ultimately management decisions. Only when such a population of interest is explicitly defined can representative samples be drawn from it in order to make statistical inferences about the properties of that population. In the case of the NSS-I, the first design criterion indicates that the population studied should best represent the resource at risk. As a first approximation, this population was assumed to be located in areas of historically low ANC surface waters that receive acid deposition. Furthermore, the primary resource of interest within the regions studied is presumed to be water quality for sport fisheries, and the size of streams of interest should reflect the portion of the stream continuum that provides the majority of fish habitat for critical life stages. This first regional implementation of the NSS-I was limited largely to areas not sampled by the NLS. Consequently, NSS-I field activities in 1985 and 1986 were undertaken in potentially sensitive regions in which streams, as opposed to lakes, are the predominant surface water resource. Full implementation of the NSS-I in lowland coastal regions with lower rates of acidic deposition in the Southeast has not yet been accomplished.

Identification of the target population of streams (design criteria 1) required consideration of the characteristics of large versus small streams with respect to the aquatic resource potentially at risk from acid deposition. Provided that differences among fish species are ignored, larger streams provide considerably more fish habitat per unit stream length than do very small streams, and thus are relatively more important from a fishery resource standpoint. However, in most regions of the United States, very large streams or rivers generally do not experience low pH conditions, because natural and anthropogenic buffering sources (e.g., agricultural liming or discharge of treated wastewater) tend to buffer any atmospherically derived acidity, once a river has descended into populated valley bottoms.

At the other end of the size spectrum, low-order, high-elevation streams within a given basin are expected to exhibit lower pH and ANC than their downstream counterparts and are therefore more likely to serve as early warning indicators of acid deposition impacts. These smaller streams, however, offer quantitatively less fish habitat, and for that reason may not best represent the biological resource at risk. While the impacts of acidification on spawning and detritus processing in very small headwater and intermittent streams should not be discounted, it would be very difficult, given the present state of the science, to relate headwater acidification to fish productivity further downstream. Given this uncertainty, together with the frequently observed pattern of maximum productivity and species diversity of fish and invertebrates in mid-order reaches (Platts, 1979; Vannote et al., 1980; Minshall et al., 1983), the small to medium-size stream category appeared to be the best target for Phase I sampling from a biological resource standpoint.

Rivers and streams at opposite ends of the size spectrum also present special logistic and sampling design difficulties. Larger rivers require substantially different physical sampling (measurement) techniques and equipment than those used on smaller streams. The geographical point sampling frame that was used for the statistical sampling design (Section 2.4) also works less effectively on reach populations containing watersheds of drastically different sizes (Overton, 1987). On the other hand, populations of very small streams are poorly represented on maps and often very difficult to access physically, and their flow may dry up entirely in some years or seasons.

These general criteria define a conceptual population of interest that is not easily defined in quantitative, explicit terms that facilitate rigorous statistical sampling. Ideally, there may be

a single size range of streams that satisfies these abstract criteria. In practice, however, even if habitat characteristics in streams of interest could be quantitatively defined, it would be difficult to arrive at an explicit definition of this population so that it might be targeted for sampling. There are two aspects to the problem of explicitly and quantitatively defining the conceptual population of interest. The first deals with actual stream locations and characteristics, and the second with the correspondence between these "on-the-ground" characteristics and abstract representations of them. A simple solution to the first aspect of the problem is confounded by the regional, temporal, species, and life stage differences in fish habitat requirements (not to mention different ways of defining stream size), which make a precise definition of the size of streams in such a population impossible. Once we satisfactorily define the size of streams of interest, we must then contend with the bias and imprecision associated with our abstract representation of the assemblage of streams on maps, lists, and remote imagery.

Given all these considerations, the most expedient approach for the NSS-I was to explicitly define a target population in terms of blue-line representation of streams on 1:250,000-scale topographic maps, modified by certain site inclusion criteria. The resulting target population was our best attempt to define this conceptual population of interest. Its precise definition (subsection 2.4.1) was influenced by the expertise of local fishery biologists in a number of regions and was tempered with our understanding of watershed response to acid deposition. The decision was also constrained by logistical considerations that influenced the number of sites that could be sampled. The physical characteristics of target streams reaches are examined in Section 5 along with an evaluation of whether that target population is a reasonable representation of the population of interest.

2.3.4 Alternative Methods for Identifying the Target Population

During the planning stages, several different approaches were evaluated before the final decision was made to use a sampling frame based on 1:250,000-scale map representations of streams. Subsection 2.3.3 identifies the conceptual population of interest (the resource at risk) as all reaches that are not grossly polluted, that drain watersheds of intermediate size, and that occur within certain relatively homogeneous physiographic areas expected to contain surface water with ANC predominantly $< 400\ \mu eq\ L^{-1}$. Several alternative approaches were evaluated for identifying or listing sample sites from which a probability sample of streams could be selected for field visitation. These included computerized data files originally constructed for other purposes, remote imagery collected by satellite or aircraft, and blue-line representations of streams on several scales of USGS topographic maps.

The use of existing computerized lists of streams was rejected, because they tend to describe large streams and rivers. For example, the U.S. EPA REACH data file (Olsen et al., 1981) comprises only those reaches large enough to appear on 1:500,000-scale topographic maps. At this scale, the stream resources of interest (subsection 2.3.3) are not adequately represented. A large number of these smaller streams that could be potentially sensitive to acidic deposition but that are still large enough to offer abundant fish habitat are not included (SFI, 1984). Generally, streams that appear on medium- (1:250,000) and large-scale (1:24,000) maps are too small to be of interest to water supply managers and therefore have not historically been represented in computerized water resources data bases. Remote imagery was rejected as being too costly and time-consuming for constructing a frame of thousands of reaches. As a result, the most expedient approach for the NSS-I was to define a target population in terms of blue-line representations of streams on topographic maps.

Of the two applicable map scales (1:250,000 and 1:24,000), the former was chosen because it was judged to best represent the conceptual population of interest for the NSS-I. An earlier survey (TIE, 1981) indicated that historical fishery and aquatic resources values are more closely associated with blue-line streams on medium-scale (1:250,000) maps. Although the relationship varies from map to map, 1:250,000-scale maps generally exclude the smaller streams (streams with drainage areas < 0.5 km^2 at their first confluence) that appear on the corresponding 1:24,000-scale maps for the eastern United States.

Although streams and stream reaches to be sampled in the survey are identified on 1:250,000-scale maps, measurements of physical characteristics, including length of stream reach, total watershed area, and direct watershed area, as well as latitude and longitude for sample sites were calculated from 1:24,000-scale topographic maps. Field sampling crews were provided with 1:24,000-scale maps to aid them in locating the sampling sites.

2.4 STATISTICAL SAMPLING DESIGN

The statistical sampling design for the NSS-I was developed by Overton (1986, 1987; Overton and Stehman, 1987). In statistical terminology, the stream survey is a double sample, with a third sampling level on (within) a sample reach. The term stage refers to the two levels of the double sample (Stage I and Stage II) and also to the sampling within a reach (Stage III). The major stratification structure is provided by subregions. Secondary stratification is provided by expected ANC class (greater than 50 μeq L^{-1} and less than 50 μeq L^{-1}) as represented on maps of expected alkalinity prepared by Omernik and Kinney (1985) and Omernik and Powers (1983).

2.4.1 The Stage I Sample

The target population for the NSS-I has been defined as that set of blue line segments appearing on 1:250,000-scale USGS topographic maps, within the designated regions of interest, and conforming to a specified set of criteria designed to eliminate those reaches not in the designated resource of interest. The maps on which the population is defined are archived as a part of the permanent record. It is important to recognize that it would be possible to enumerate this set of reaches for any region to produce a list containing each reach in the population of that region. Such a list would provide a list frame that could be the basis of a sampling design. The explicit nature of the population is established by the possibility of generating this list frame; the population that is being described is precisely this set of reaches.

A reach is a blue-line segment on the identifying maps. A blue-line segment is identified at each end either by the end of a blue line or by the confluence of two blue lines. The upper or lower node of a reach can also be defined by artificial or natural structures that interfere with stream patterns, like reservoirs or lakes. A target reach must have at least half its length within the subregion and must not be excluded by one or more of the site rules (discussed in detail in subsection 2.4.2). A reach is excluded from the target population if it has an attribute identifying it as noninterest; for example, a reach may drain a total watershed area greater than 155 km^2 (60 mi^2) or it may drain a watershed that is predominantly urban.

The site rule criteria are applied at the time sample reaches are identified from maps. Other criteria identifying nontarget reaches are not available from maps, and are applied to sample reaches at the time of field visitation. Any condition that excludes a reach from consideration in the resource at risk, and that will be apparent from visiting the reach, can be applied at that time. For example, reaches may be considered nontarget because of gross pollu-

tion, as by mine drainage, oil field drainage, or tidal influence. This process reduces the field sample below the number selected for the Stage II sample, but does not affect the validity of that sample. The subpopulation of the modified set of target reaches is then characterized from the subsample.

The conceptual frame contains all reaches considered to be target reaches by virtue of inspection of the map materials, and this entire set is the *frame population.* The stream survey generated a sample of this population without generating the list, by the simple device of an area/point frame and a rule of association between a sample on this frame and the population of reaches. Specifically, a square dot-grid transparent overlay was constructed, with a scale that projected 64 mi^2 of the 1:250,000-scale maps per point on the overlay. Thus, the distance between the dots on the overlay projects to 8 mi on the maps. To select a sample, the overlay is randomly placed on the map, with the result that the points are randomly, but not independently, placed on the study area.

The Stage I sample of reaches is then obtained by applying a rule of association between a point identified on the map and the network of blue-line streams. From a point, a line is traced perpendicular to map contours, down the fall line, until either a blue line is encountered, or some other structure that is not a stream is encountered. If a blue line is encountered, then the stream segment from the nearest upstream confluence, or beginning of the blue line, to the nearest downstream confluence, is the selected reach. This reach is examined to determine if it qualifies as a target reach, according to the site rules. All of the target reaches, so selected by the dot-grid overlay, constitute the Stage I sample of target reaches. Each sample point within the study area leads to: (1) no reach, (2) a nontarget reach, or (3) a target reach. The effective sample size associated with this selected sample is given by the number of grid-dots that fall within the boundary of the study area. Figure 2-3 illustrates the selection of reaches by the point frame. Point 98 in the figure selects a nonheadwater reach, whereas point 99 selects a headwater reach. The topographic direct drainage area of sample reach downstream nodes is designated as a_1. The size of a_1 is an important variable measured on maps in the NSS-I, because the probability of selecting any given reach is proportional to this area. Area a_2 in Figure 2-3 represents the area draining into the upstream node of the nonheadwater reach.

The sample selected by the grid-point frame is a probability sample of the population. Every member of the population has the potential of being selected. The probability (π_i) that any member is selected (included in the sample) is given by a known function of a measurable property of that member. Specifically, $\pi_i = a_{1i}/64$, where a_1 is defined in the next paragraph, and 64 is the area (square miles) per grid dot. Reach order is determined from the 1:250,000-scale maps, being the number of headwater reaches in the full watershed of the target reach.

The next step requires transfer of the selected reach to 1:24,000-scale maps for identification of the direct watershed and measurement of the physical attributes. Reach length, l, in miles, and area of direct watershed, a_1, in sq mi, were obtained by planimeter (on 1:24,000-scale maps) on the full Stage I sample. In particular, it is important that a_1 be determined very precisely, because the weights used in estimation will be inversely related to the a_1's, and errors in measurement of a_1 cause biases in the estimates. Additionally, the area draining into the upstream node of the selected target reach is determined from planimetering. The direct drainage area contributing to the upstream node of headwater reaches is included in area a_1; watershed areas for reaches of order 2 or greater, determined from the 1:250,000-scale maps, are designated as a_2 and measured on the finer scale maps (1:24,000).

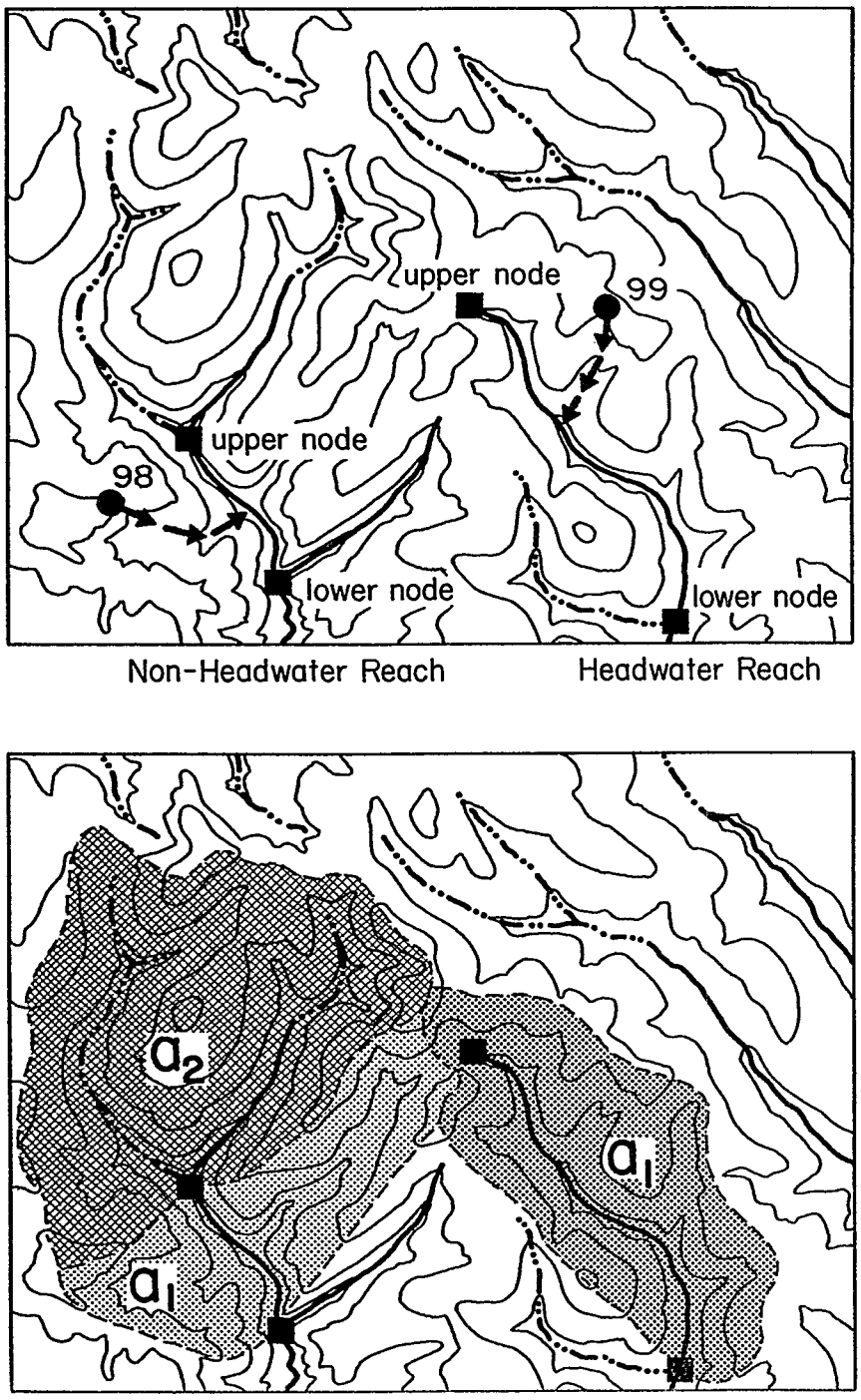

Figure 2-3. Representation of the point frame sampling procedure for selecting NSS-I Stage I reaches. Area a_1 represents the direct drainage area to the lower node of nonheadwater reaches, or the total drainage area to the lower node of headwater reaches. Area a_2 is the total drainage area to the upper node of nonheadwater reaches.

The *frame population* is thus explicitly defined, but not explicitly identified. It is represented by a Stage I probability sample. It is reasonable to consider the *frame population* as the *initial target population*, but it must be remembered that additional sample reaches are eliminated from target status at the field sampling stage. Thus the *target population* is a subset of the *frame population*. Selection of the Stage II sample visited in the field is treated in a later section.

2.4.2 Site Inclusion Criteria (Site Rules)

The reaches identified by the grid points are categorized into various target or nontarget categories according to the criteria discussed in the following paragraphs. The target population thus defined is identical to that which might have been defined by a list frame. Unlike the exhaustive population defined by a list frame, however, the point frame (with inclusion criteria) defines a probability sample of that population. The inclusion criteria that were used for drawing the first stage sample of NSS-I sites are shown in Table 2-2. Specific decision protocols provided by the site inclusion criteria were used by the project geographers to identify the resource at risk, as addressed in general by Project Design Criterion 1 (Section 2.2).

Each grid dot may lead to a nontarget reach, a target reach, or no reach at all. Table 2-3 is a breakdown of the disposition of all Stage I grid points in the NSS-I subregions; the table also includes the Stage II sample numbers discussed in subection 2.4.5. A grid dot identifies no reach if the topographic fall line identifies a reach wholly outside the study area boundary, or if the dot identifies something other than a reach (e.g., a lake, reservoir, swamp, or closed basin). Nontarget reaches are excluded because some characteristic puts them in a noninterest category. Reaches with highly urbanized drainages, for example, were excluded by the NSS-I.

Reaches contacting the NSS-I subregion boundaries may penetrate far enough into suspected high ANC regions outside the study area to be unlikely to have low alkalinity over much of their length. Boundary reaches were excluded if more than 50% of their length was outside the study area.

2.4.3 The Stage I Data

The first stage data base includes a listing for each grid point, including:

1. Site identification code (e.g., 3B041016L). An eight digit code containing three fields that indicate the NSS-I subregion code (3B), the 1:250,000-scale map ID (041), special interest site designation (0 = Routine site, 9 = Special Interest Site), the grid-dot identification (16), and the node identification (L = Lower, U = Upper).
2. Stream name. This is recorded from 1:250,000-scale or 1:24,000-scale maps.
3. Site inclusion criteria applicable to the grid point (Section 2.4.2). For target reaches, certain additional information is obtained as described in 4 to 7 below.
4. County and state in which the reach is located.
5. State in which the associated watershed is located.
6. Administrative jurisdiction, if sites lie within national or state parks or on military reservations.
7. Miscellaneous comments.

Table 2-2. NSS-I Site Inclusion Criteria

I. NON-TARGET GRID DOTS. Grid dots that do not identify a stream reach.

- NO1. **Reach Out.** The topographic fall line leading from the grid dot leads out of the study area before intersecting a reach.
- NO2. **Reservoir.** The grid dot falls in a reservoir, or the topographic fall line leads to a reservoir shoreline.
- NO3. **Lake.** The grid dot falls in a lake, or the topographic fall line leads to a lake shoreline.
- NO4. **Closed Basin.** The topographic fall line leading from a grid dot leads into a closed basin that does not contain a reach.
- NO5. **Swamp.** The grid dot falls in an area with insufficient topographic relief to identify a reach.

II. NON-INTEREST REACHES. Grid dots identify a reach that is not in the target population.

- N1. **Boundary Reach.** The reach identified by a grid dot crosses an external study area boundary, such that > 50% of its length lies outside the study area.
- N13. **River Reach.** The total drainage area above the downstream node of a nonheadwater reach is > 60 mi^2.
- N14. **Metro Reach.** The grid dot falls in a metro area, or the dot identifies a reach with > 20% of its total drainage area occurring within a metro area, as indicated on either a 1:250,000- or 1:24,000-scale topographic map.

III. TARGET REACHES. Grid dots identify a target reach.

- N2. **Target Reach (general).** The indicated reach has a total drainage area ≤ 60 mi^2 and ≥ 50% of its length within the study area boundary.
- N21. **Wetland Reach.** The indicated reach has a topographically definable watershed, but contains cross channels that may interconnect it with adjacent watersheds under some hydrologic regimes.
- N23. **Large Headwater Reach.** The indicated reach has a direct drainage area > 60 mi^2 but is a headwater reach.
- N28. **Tailwater Reach.** The indicated reach drains a lake or reservoir, but the total drainage area is ≤ 60 mi^2.

Table 2-3. NSS-I Stage I Sample Grid Point Disposition

	SUBREGION*								
	1D	2BN	2CN	2D	2X	3A	3B	3C	2As
Total Sites (Number of Grid Points)	302	501	305	360	333	607	564	165	168
Sites Excluded:									
NO1 Reach Out of Study Area	4	-	2	2	2	4	77	3	2
NO2 Reservoir	5	3	9	4	9	19	4	2	8
NO3 Lake	20	7	2	15	10	18	10	50	3
NO4 Closed Basin	-	4	1	-	-	1	-	-	-
NO5 Swamp	-	-	-	-	1	-	17	1	-
N1 Boundary Reach	5	-	1	8	5	11	11	3	2
N13 River Reach	69	98	65	65	62	128	73	22	17
N14 Metro Reach	6	6	-	-	1	3	24	-	-
Subtotal (Exclusions):	109	118	80	94	91	184	216	81	32
Target Reaches:									
N2 Target Reach (general)	188	380	219	245	240	413	316	81	134
N21 Wetland Reach	-	-	-	8	-	-	32	3	-
N23 Large Headwater Reach	1	1	-	-	-	-	-	-	-
N28 Tailwater Reach	4	2	6	13	3	10	-	-	2
Subtotal (Target Reaches)	193	383	225	266	243	423	348	84	136
Stage II Sample Size	61	53	74	50	50	50	62	50	54
Effective Sample Size (Stage II)#	91	70	100	68	66	72	100	94	84

* 1D = Poconos/Catskills
2Bn = Valley and Ridge
2Cn = Northern Appalachians
2D = Ozarks/Ouachitas
2X = Southern Appalachians
3A = Piedmont
3B = Mid-Atlantic Coastal Plain
3C = Florida
2As = Southern Blue Ridge

Effective sample size (ESS) is the number of grid points examined to obtain the Stage II sample reaches to be visited in the field. ESS is stratum specific. Exact values for each ANC stratum and its application in variance calculations are discussed and detailed in Sale (1988).

The information listed in the seven items on page 29 was critical in the reconnaissance procedures described in Section 3. In addition, data were recorded for certain quantitative geographic variables, including:

8. The area of direct drainage, a_1. This is the portion of the watershed that drains directly into the chosen reach (Figure 2-3), and also the area within which a grid point will select the same reach. This variable is very important, as it is a measure of the probability of selecting the reach, and is used in making all population estimates. It was measured as accurately as possible on the 1:24,000-scale maps.

9. Reach order, R. The number of reach regions (headwaters) in the watershed above and including the selected reach, as identified on the 1:250,000-scale maps. This reach ordering system is basically that of Shreve (1966), and has certain topological advantages over the more familiar Strahler or Horton ordering systems.

10. For reaches of order higher than 1, the area, a_2, of the upstream watershed. The variable a_2 is the area of the entire watershed that produces the streamflow that enters the selected reach at the upstream node, determined from surface topography on 1:24,000-scale maps. (This value is zero for first order reaches).

11. Reach length, l, is the length of the selected reach. Locations of the reach ends were determined on 1:250,000-scale maps, but measurement of l was made on 1:24,000-scale maps.

12. Headwater drainage area, a_3, being the area draining into upper node of each headwater stream (identical to a_2 for reaches with $R > 1$).

2.4.4 Stage I Estimates

The sampling design described in the preceding subsections produced a sample of target reaches from each of the nine subregions, with sample sizes ranging from 84 to 423 (Table 2-3). These samples were subsampled (subsection 2.4.5) to yield the Stage II samples that provided the water chemistry data. The full set of Stage I samples were used to estimate the physical attributes of the initial target populations in the nine subregions. However, because field derived information was subsequently used to eliminate some sites, designating them as not representative of the refined target population, the physical characteristics reported in Section 5 are calculated from the Stage II sample.

Details of estimation, and the statistical foundation of the methods, are provided elsewhere (Overton, 1986, 1987; Blick et al., 1987; Overton and Stehman, 1987; Stehman and Overton, 1987a, 1987b). The general form of estimator is provided by the Horvitz-Thompson Theorem:

$$\hat{T}_y = \sum_S y/\pi = \sum_S wy$$

where:

$\hat{T}_y$	is the estimate of the total of any attribute, y, over the population.
y	is any reach attribute of interest, known over the sample, S.
Σ S	indicates summation over the appropriate sample of target reaches, whether the full sample, a subsample, or mixed subregion sample.
a_1	is the area of direct watershed of a reach.
$\pi = a_1/64$	is the inclusion probability of a reach, where 64 is the map area per grid-dot.
$w = 1/\pi$	is the weight assigned to a reach in making population estimates.

By assigning different definitions to y, and by summing over different sets of sample units, S, the various population attributes can be estimated from this one equation. Specifically, in the NSS-I, several attributes are identified as parameters of the resource at risk:

1. Total number of target reaches ($\hat{N}$), $y = 1$: $\hat{N} = \Sigma w$.
2. Total Area of Direct Watershed ($\hat{A}$), $y = a_1$: $\hat{A} = \Sigma w a_1$
3. Total Length of Target Reach ($\hat{L}$), $y = l$: $\hat{L} = \Sigma w l$
4. Total Discharge Index ($\hat{D}$), $y = (a_1 + a_2) = d$: $\hat{D} = \Sigma w d$
5. Total Stream Surface Area ($\hat{S}$), $y = s$: $\hat{S} = \Sigma w s$

Other attributes are best estimated by ratios of these estimates, as for example Stream Density,

$$\text{Stream Density} = \hat{L}/\hat{A} .$$

Additionally, a number of subpopulations are apparent. Several examples will serve to identify the nature of subpopulation definition:

1. The subpopulation is defined as the set of all headwater reaches; the sample is the set of headwater reaches in the Phase I sample.
2. The subpopulation is defined as the set of reaches having total watershed area $(a_1 + a_2) \leq 5.0$; the sample is the set of reaches in the sample having this property.

Similarly, combinations of subregion populations are assessed by combining the samples from those subregions, and in general it is only necessary for the sample subset to be defined in exactly the same way as the estimated population. The possibilities are virtually unlimited.

Stage I variance estimates, leading to estimated standard errors (SE) of the estimated attributes, are obtained by the Horvitz-Thompson variance estimator, with second order inclusion probability specified for this design (Overton, 1986; Stehman and Overton, 1987a). Several of the studies cited earlier addressed the basis for and validity of this variance estimator in the context of the stream survey. The formula for estimated variance, incorporating the features explicit for the established treatment, is:

$$\hat{V}(\hat{T}y) = \sum_{S} y^2 w(w-1) + \sum_{i \in S} \sum_{\substack{j \in S \\ j \neq i}} y_i y_j v_{ij}$$

where n is the effective sample size, and $v_{ij} = [(w_i + w_j)/2 - w_i w_j]/(n - 1)$, if i and j are from the same stratum; if i and j are from different strata, then $v_{ij} = 0$.

This same formula will be used for Stage II estimates. The only change is that the effective sample size will be defined differently.

2.4.5 The Stage II Sample

The Stage I sample generated a sample point for each 64 square miles of each subregion. A substantial fraction of these sample points resulted in sample target reaches. There were too many to visit in the field for assessment of water chemistry, so the sample size had to be reduced for the field sampling stage of the survey. A subsample size of 50 to 74 target reaches was selected from each subregion in a manner that provided good spatial distribution (Overton, 1986, 1987). The subsample was a probability sample of the Stage I sample, resulting in a double sample allowing general estimation methodology to be used. Figure 2-4 maps the locations of Stage II sample sites in the Mid-Atlantic subregions; those in the Southeast and the Pilot survey subregions are shown in Figure 2-5. Spatial sampling density was considerably greater in the Pilot Survey subregion, because that survey was used to provide information concerning the desirable density for the full-scale Phase I Survey (Messer et al., 1986, 1988).

Within several of the subregions, there are areas where ANC was expected to be very low ($< 50\ \mu eq\ L^{-1}$) on the basis of historical alkalinity data. It was desirable for all Stage I sample reaches in these areas to be field sampled, so they were all included and identified in a separate stratum. Then subsampling occurred only in the stratum of higher ANC. The low ANC stratum sites are separately identified in Figure 2-4, as are special interest sites that were not part of the probability sampling frame (Section 2.6).

In the stratum of higher ANC, the Stage II sampling design provided for variable probability selection that neutralized, so far as possible, the variable probability selection that occurred at Stage I. Specifically, the Stage I inclusion probabilities were proportional to direct watershed size (a_1). Then the Stage II sample was selected from the Stage I sample with inclusion probabilities inversely proportional to a_1. A slight complication arose, since some of the Stage I sample reaches had such small a_1's that they came into the Stage II sample with certainty (i.e., with conditional inclusion probability = 1). The resultant Stage II sample for field visitation in a particular subregion had the following structure:

1. Stratum 1 (most reaches) inclusion probability = $n^*/\hat{N}^*$
2. Stratum 1 (a few reaches) inclusion probability = $a_1/64$
3. Stratum 2 inclusion probability = $a_1/64$,

where n^* is the number of Stage II sample reaches in that subset of Stratum 1 and $\hat{N}^*$ is the Stage I estimate of number of reaches in that subset of Stratum 1. Only the first of these three categories represents a subsample of the Stage I sample; the last two contain all the Stage I sample reaches in these categories.

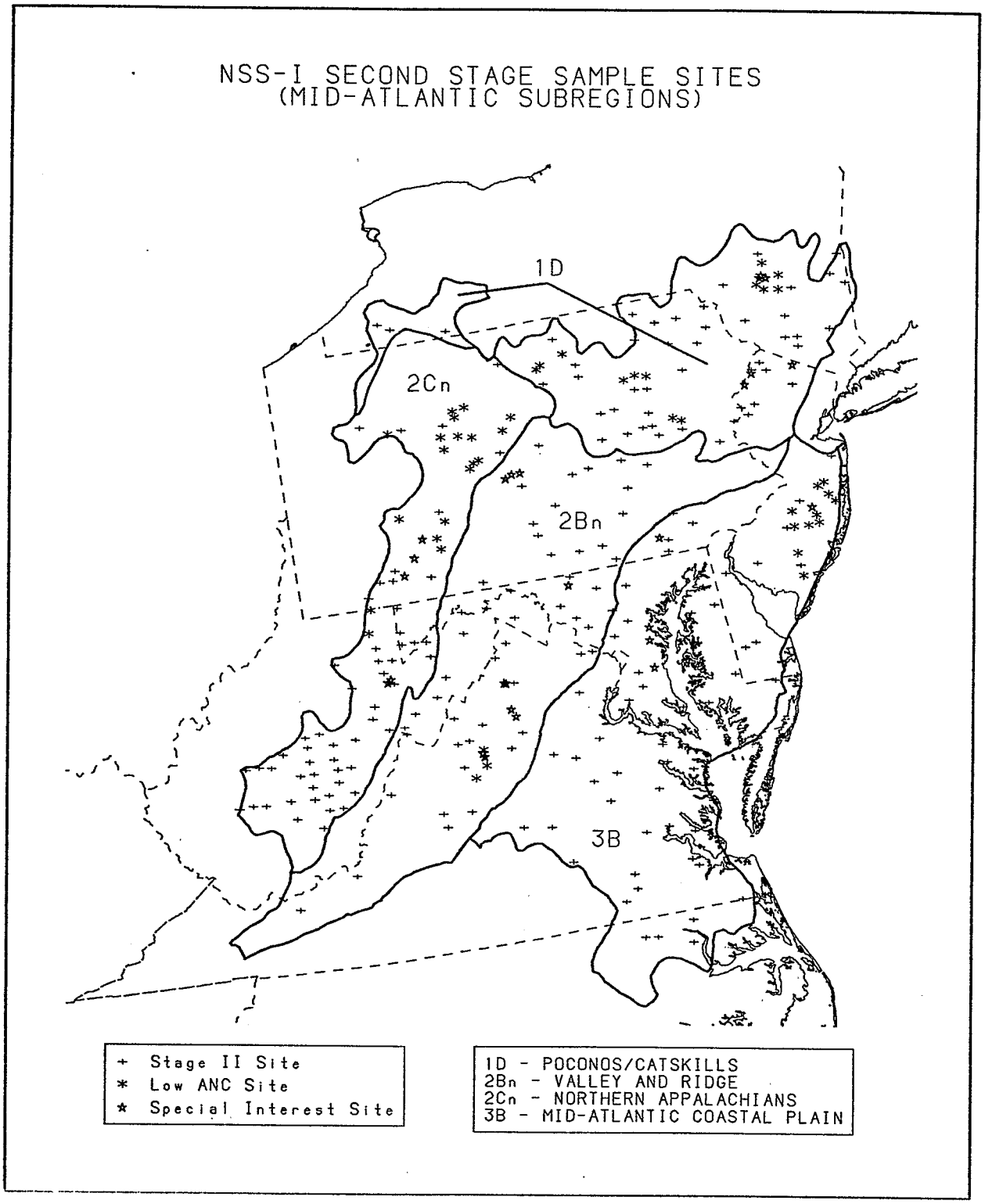

Figure 2-4. **NSS-I Stage II sample reaches and special interest sites in the Mid-Atlantic subregions.**

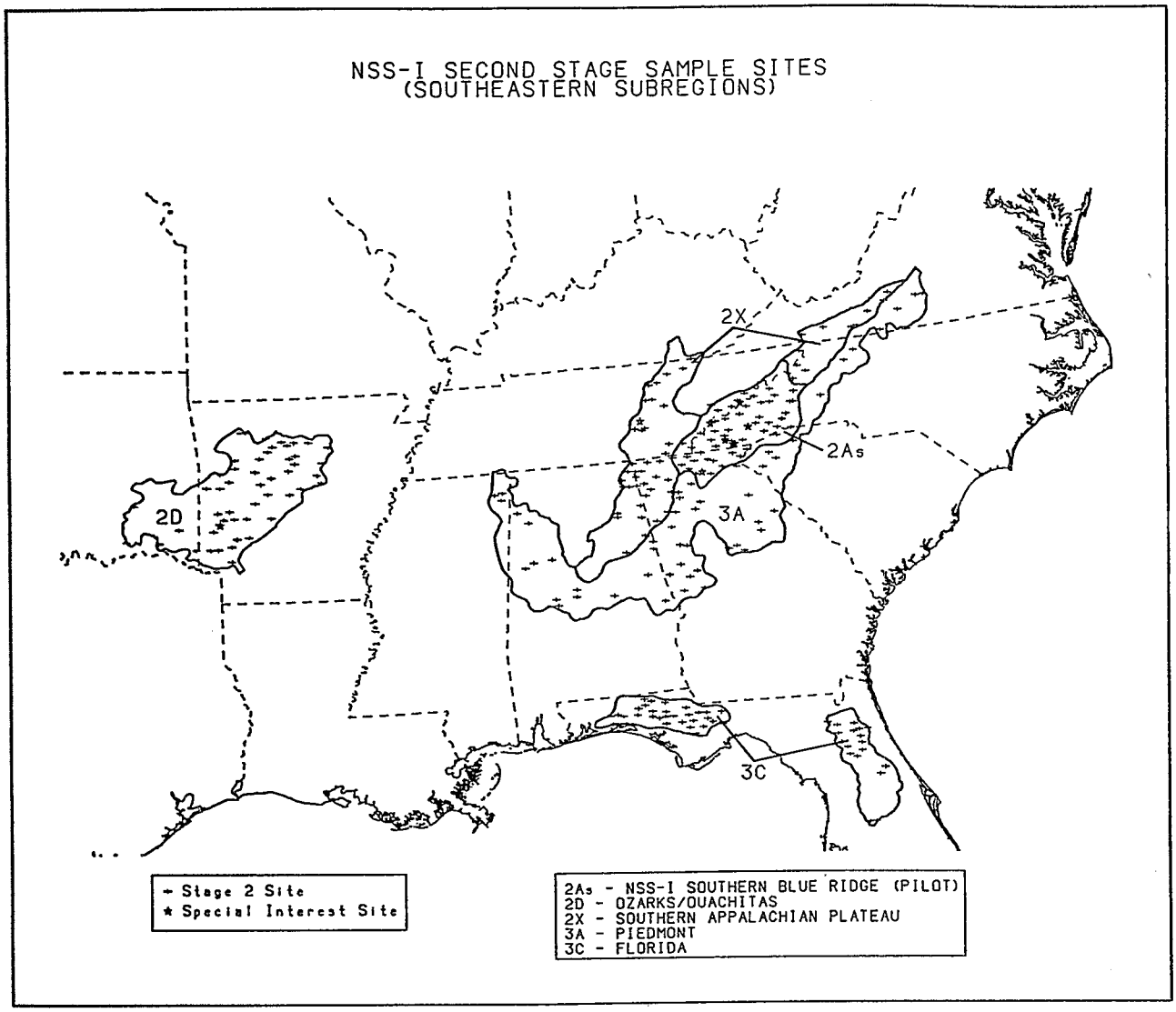

Figure 2-5. NSS-I Stage II sample reaches and special interest sites in the Southeast subregions.

The weights used in estimation and analysis are inverses of the inclusion probabilities, and uniform within subregions in the first of the three categories. The second part of Stratum 1 and Stratum 2 still have variable weights, but these are minor parts of the samples, and create minor complexity in estimation and analysis.

In order to obtain good spatial distribution of the Stage II sample illustrated in Figures 2-4 and 2-5, a modification of the standard variable probability systematic sample was used. Specifically, spatially compact clusters of Stage I points were identified on the maps, and a list was constructed with these clusters blocked in the list. This ensured that some sample elements were taken from each cluster. An additional element to the design was randomization of the points within the clusters, so that zero pairwise inclusion probabilities were eliminated from the second stage selection.

2.4.6 Stage II Estimates

Estimation of population attributes and standard errors from the Stage II sample followed the same pattern as that applied to the Stage I sample. The physical attributes of the initial target population were best estimated from the full Stage I sample. However, the identity of the target population was refined further based on information obtained from field visitation, so the attributes of this most refined target population had to be estimated from the Stage II sample. To estimate the physical attributes of the population, the values of the chemical variables were ignored, unless those values were invoked in defining the target population. These estimates were used as denominators of the distributions described in the next paragraph.

The primary outputs of the Stage II analyses are descriptions of the various distributions of the chemical variables. Distributions of chemistry within any subset of the target population were analyzed in the same way. That is, an estimate was made of the number of reaches in the subpopulation having a value of the chemical equal to or less than a particular value:

$$\hat{N}(x) = \sum_{X \leq x} w.$$

This is also applied to the other attributes estimated,

$\hat{A}(x) = \sum_{X \leq x} wa_1$, estimating total area of direct watershed of reaches having $X \leq x$,

$\hat{L}(x) = \sum_{X \leq x} wl$, estimating total length of target reaches having $X \leq x$,

$\hat{D}(x) = \sum_{X \leq x} w(a_1 + a_2)$, estimating total discharge index of target reaches having $X \leq x$.

Distributions are generated by computing the above estimates for each value of x in the sample, and then scaling these estimates by the estimated population total. Associated confidence bounds are generated by estimating the Standard Errors (SE) of each of these quantities for all values of x, from which are determined the confidence bounds on the quantities estimated; these are similarly scaled by dividing by the estimated total quantities. For example:

$$F(x) = \hat{N}(x)/\hat{N}, \qquad F_u(x) = \hat{N}_u(x)/\hat{N}, \qquad \hat{N}_u(x) = \hat{N}(x) + 1.645[SE(\hat{N}(x))]$$

and $SE(\hat{N}(x))] = \sqrt{\hat{V}(\hat{N}(x))}$

where $\hat{V}(\hat{N}(x))$ is calculated in exactly the manner of $\hat{V}(\hat{N})$, with summation further restricted by $X \leq x$.

Such distributions can be generated for any quantity generated by the general estimators. For example, the distribution, F(x), described above and illustrated in Figure 2-6 is the frequency distribution, interpreted as the proportion of numbers of target reaches in the particular subpopulation having the attribute, $X \leq x$. To read this figure, pick a value, x, of the attribute X, along the horizontal axis (ANC in this example) and read the y-axis value of the two curves, F(x) and $F_u(x)$ at this value. Then F(x) is the estimated proportion of reaches in the population with a value of the attribute equal to or less than X. $F_u(x)$ is the upper confidence bound on this proportion, to be read as: one is 95% confident that the true proportion is less than this bound. Some distributions plot the declining function, 1 - F(x). For these, read the distribution as the estimated proportion of reaches having a value of the attribute equal to or greater than X. Confidence bounds are as before: an upper confidence bound on the true proportion.

A lower one-sided confidence bound on F(x) can be generated, if needed, by measuring the distance between the two curves, and projecting the identical distance below F(x). This curve is not presented because it could be confused with two-sided confidence bounds, which are of different width. The bound provided is the one usually considered appropriate for expressing the status of the resource.

By generating distribution functions for the other characteristics, such as direct watershed area, length, or total drainage area, other types of distributions can be obtained. G(x) is the proportion of direct watershed area associated with reaches having attribute, $X \leq x$. H(x) is the proportion of reach miles (or km) having reach attribute, $X \leq x$. D(x) is the proportion of reach total drainage area (a crude index of discharge) having reach attribute, $X \leq x$. In all cases, these distributions and the represented confidence bounds are dimensionless, and a shift from miles to kilometers or square miles to the metric equivalent has no effect on F(x) or $F_u(x)$. Any other distribution, such as stream surface area, or reach density, can be analyzed in exactly the same way, requiring only an appropriate reach attribute that sums to the population attribute.

Other population statistics of interest can be generated from the distributions. Each distribution has identified quantiles, the *median* and the four *quintiles*, $Q_1, Q_2 ..., Q_4$. The median of F is the value of x such that $F(x) = 1/2$. Q_i of F is the value of x such that $F(x) = i/5$. These statistics are defined for all distributions.

Additionally, from the frequency distribution, F(x), the mean and standard deviation of the variable x on the population is estimated.

$$Mean(x) = \Sigma wx/\Sigma w,$$

$$SD(x) = \sqrt{\Sigma wx^2/\Sigma w - [\Sigma wx/\Sigma w]^2}.$$

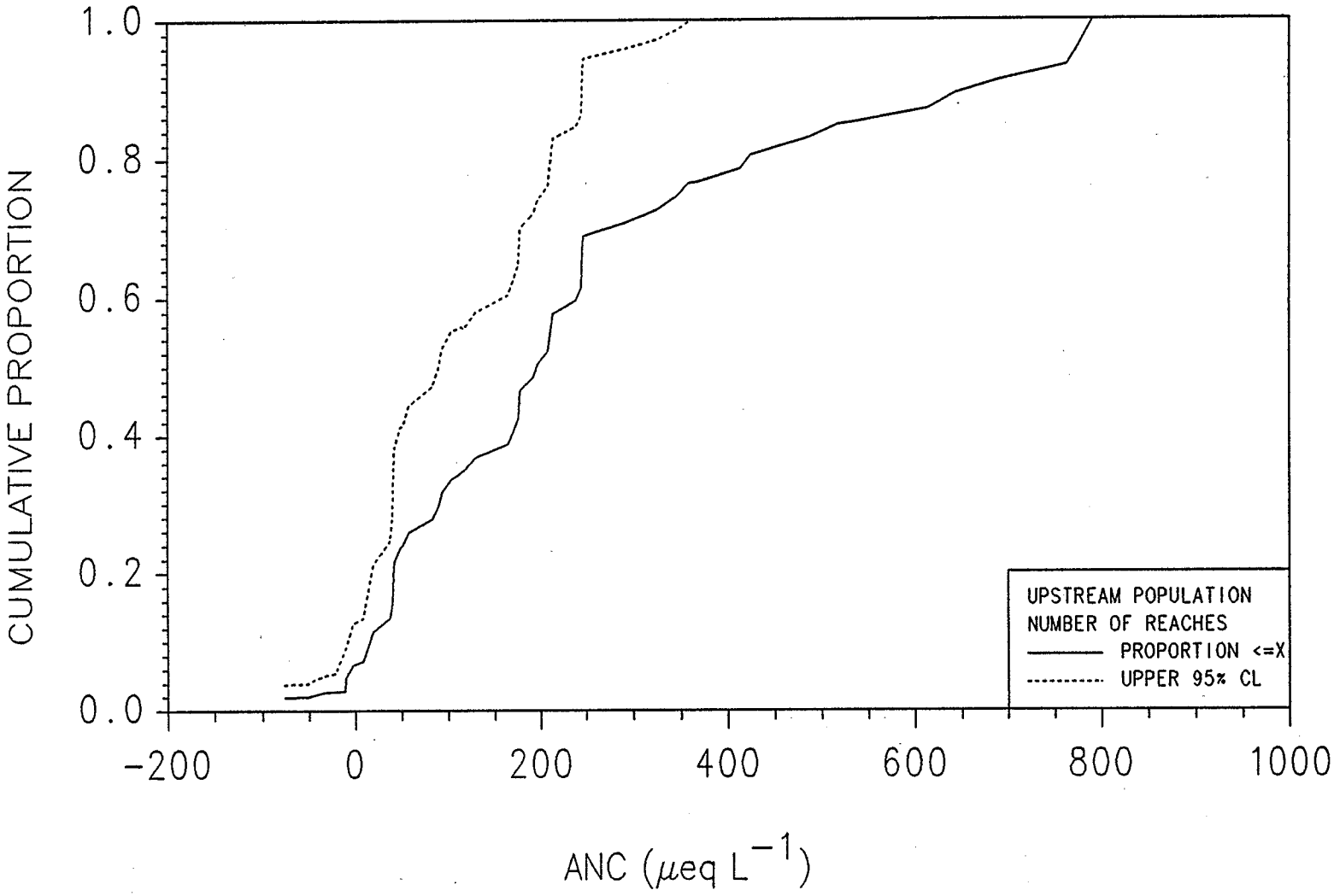

Figure 2-6. Example of the type of cumulative distribution function plot used in the NSS-I.

2.5 INDEX SAMPLING

The collection of water samples and associated observations on reaches in the Stage II subsample constitutes Stage III of the statistical design of the NSS-I. Sampling at this third stage was not conducted as a probability sample, but rather in a way that would best characterize or index the properties of a sample reach. Like the ELS-I components of the NSWS, the NSS-I relied on samples taken during an appropriate season from a representative sample of water bodies to provide an index of the chemical characteristics of the target population (Messer et al., 1986). In the Eastern and Western Lake Surveys (Linthurst et al., 1986; Landers et al., 1987), a single mid-lake sample taken during well-mixed conditions at fall turnover provided a reasonably good spatial representation of the nonlittoral lake water volume. Furthermore, this fall index sample for lakes can be related to water quality during other seasons of the year when chemical conditions may be more critical for biota (Driscoll and Newton, 1985; Newell, 1987). In lakes, relatively long hydraulic residence times (low flushing rates) tend to integrate the inputs of water and dissolved materials from the lake watershed, which reduces that portion of the chemical variability caused by changes in input rates. Streams generally exhibit greater within- and among-season variability than do lakes. Since streams have little temporal integrative capacity within their channels, it is necessary to draw an index sample during a period of the year that is expected to exhibit chemical characteristics most closely linked to acidic deposition or to its most deleterious effects. Sampling the relatively stable chemistry of late summer baseflows dominated by groundwater, for example, would provide a poor index of potentially limiting conditions during winter and spring periods when the stream water is poorly buffered against pH changes. The choice of the spring index sampling period for streams was based on a literature search followed by a series of meetings with hydrologists, biochemists, and fishery experts in Pennsylvania, Virginia, North Carolina, Florida, and Arkansas to discuss ongoing projects involving stream chemistry and fisheries in the proposed NSS-I study areas (U.S. EPA, 1984b). The choice involved a trade-off between minimizing within-season and episodic chemical variability and maximizing the probability of sampling during chemical conditions potentially limiting for aquatic organisms.

A number of sources of stream chemistry data from several geographic areas support the choice of a spring index sampling period for observing prolonged periods of low pH and ANC. Ford et al. (1986), for example, summarized the results of four recent (1984-1985) studies of seasonal and short-term variability in six second- and third-order streams in the Catskill Mountains of New York (Murdoch, 1986), the Laurel Hills of Pennsylvania (Witt and Barker, 1986), the Southern Blue Ridge Province of North Carolina and Tennessee (Olem, 1986), and the Ouachita Mountains of Arkansas (Nix et al., 1986). Minimum flow-weighted pH values and concentrations of base cations and ANC occurred during the spring at almost all sites. Those sites with minimum values during the winter had spring values nearly as low.

For a spring index sampling period to be biologically relevant, however, sensitive life-stages of aquatic biota must also be present during the sampling period. Studies have indicated that all life stages of fish are not equally sensitive to acidity and chemical constituents that accompany low pH conditions in surface waters. Some of these studies involved observations of acidic lakes and streams in which viable eggs were found together with older age classes of fish that appeared to be spawning successfully, but in which young age classes were absent (e.g., Beamish et al., 1975; Muniz and Leivestadt, 1980; Kelso and Gunn, 1982; Gunn and Keller, 1984; Sharpe et al., 1984). Such a population structure suggests more pronounced effects of acidity on larval fish than on egg hatching or adult survival. These field observations are in agreement with laboratory bioassays that also indicate greater sensitivity of fry to low pH conditions,

relative to other fish life stages (Schofield, 1976; Haines, 1981). Fry of the most important sport fish are present in the NSS-I study area during the March 15 - May 15 period. Fry of some trout (Salmo spp.) populations may also be present at other times of the year.

In summary, spring appears to be the most appropriate index sampling period for streams, because ANC is typically low, and life stages of aquatic biota that are sensitive to low pH are likely to be present at this time. The low ANC during the season minimizes buffering against episodic pH changes accompanying high runoff. Although pH and ANC depressions can also occur during other seasons, they may be more pronounced during the spring because short hydraulic residence times in the soil during the spring minimize acid neutralization. Also, acid-sensitive, swim-up fry of key fish species are typically present in streams during the spring in many parts of the United States. The index sampling period for the NSS-I thus was chosen as the time period following snowmelt but prior to leafout (mid-March to mid-May, depending on the subregion). Results of the NSS-I Pilot Survey in the Southern Blue Ridge showed very little difference in separate population distributions of pH, ANC, and major cations and anions based on three successive spring baseflow samples during this sampling window (Messer et al., 1986, 1988). The occurrence of large episodic chemical changes over the course of hours or days during storm runoff, however, makes the use of spring samples for indexing water chemistry difficult, unless sampling during such events is avoided (Messer et al., 1986). To avoid alterations in index chemistry caused by atypical stormflow samples, the NSS-I avoided sampling within 24 hours following significant rain events (> 0.2 inches).

Unlike lakes, for which a single mid-lake sample taken during well-mixed conditions at fall turnover can provide a reasonably good spatial representation of the nonlittoral lakewater volume, a sample taken at a single point on a stream reach would not adequately describe chemistry for the whole length of the reach (Messer et al., 1986). Streams were expected to exhibit substantial trends in chemistry over their length at any given time during the spring index period. To incorporate this variability and to establish a basis for quantifying relationships between upstream and downstream chemistry on sample reaches, samples from both ends of the reaches were collected in the NSS-I.

2.6 SPECIAL INTEREST SITES

In addition to the reaches selected in the probability sample, the NSS-I sampled 36 special interest reaches. These reaches were selected as sites similar in drainage area to those in the NSS-I target population, but where intensive process-oriented studies or long-term monitoring projects are underway. The special interest sites included sites selected for long-term study in the Long-Term Monitoring (LTM) Project, part of NAPAP Task Group E, at which storm events were also monitored. The special interest reaches (listed in Table 2-4) were sampled in the same manner as those included in the probability sample. However, data from these sites cannot be analyzed as part of that probability sample. Classification of special interest sites (Section 9 and future work) will become increasingly useful for placing the intensive study results from those sites into a regional perspective.

Table 2-4. Special Interest Sites

Reach ID	Stream Name	State	Cooperator	Org.	Elevation (Ft)	Watershed Area (mi^2)
1D030910	Biscuit Brook	NY	Pete Murdoch	USGS	2090	3.59
1D030911	High Falls Creek	NY	Pete Murdoch	USGS	1910	2.75
1D030912	E. Branch Neversink	NY	Pete Murdoch	USGS	2140	9.04
1D030924	Van Campens Brook	NJ	Bill Stansley	Bur. of	660	4.66
1D030925	Green Brook	NJ	Bill Stansley	Freshwater	960	0.65
1D030926	Tillman Brook	NJ	Bill Stansley	Fisheries	710	1.47
2A07891	Cosby Creek	TN-NC	Harvey Olem	TVA	2457	11.5
2A07892	Twenty-mile Creek	NC	Harvey Olem	TVA	1426	8.1
2A07893	Jarrett Creek	NC	Harvey Olem	TVA	3052	5.5
2A07894	Shope Fork/Gauge 8	NC	Jack Waide	USFS	2259	3.6
2A07895	Moses Creek	NC	Harvey Olem	TVA	2298	9.1
2A07896	Pinnacle Branch	NC	Jack Waide	USFS	3091	0.4
2A08891	Chester Creek	GA	Harvey Olem	TVA	2515	2.8
2B036903	Detweiler Run	PA	Jim Lynch	Penn State	995	3.29
2B036904	Leading Ridge #1	PA	Jim Lynch	Penn State	870	0.45
2B036905	Laurel Run	PA	Jim Lynch	Penn State	990	10.74
2B042922	Hunting Creek	MD	Owen Bricker	USGS	1045	3.87
2B047916	White Oak Run	VA	Jim Galloway	U. of Va.	1480	1.93
2B047917	Deep Run	VA	Jim Galloway	U. of Va.	1360	1.32
2B047918	N. Fork Dry Run	VA	Jim Galloway	U. of Va.	1600	0.94
2B047919	Mill Run	VA	Owen Bricker	USGS	1175	1.15
2B047920	Old Rag Run	VA	Owen Bricker	USGS	1440	1.09
2B047929	Mill Run Trib	VA	Owen Bricker	USGS	1180	1.18
2C035913	N. Fork Bens Creek	PA	Jim Barker	USGS	1539	3.11
2C035915	N. Br. Quemahoning	PA	Jim Barker	USGS	1940	2.63
2C041901	Fernow Control	WV	David Helvey	USFS	2440	0.14
2C041902	Elk Lick Run	WV	David Helvey	USFS	1680	5.84
2C041914	Cole Run	PA	Jim Barker	USGS	1915	1.32
2C077923	Camp Branch	TN	Mike Kelly	TVA	1705	0.37
2D083927	N. Fork Saline	AR	Joe Nix	Ouachita	1210	0.84
2D083928	E. Fork Saline	AR	Joe Nix	Baptist U.	1080	2.58
3B042907	Magothy River	MD	Tony Janicki	MD DNR	10	5.40
3B042908	Bacon Ridge	MD	Tony Janicki	MD DNR	10	6.97
3B042921	Pequea Creek	PA	Owen Bricker	USGS	600	0.22
3B043909	McDonalds Branch	NJ	Debbie Lord	USGS	115	2.10
3B048906	Lyons Creek	MD	Ron Klauda	MD DNR	17	14.54

SECTION 3
METHODS

3.1 OVERVIEW

This section discusses the methods employed in the National Stream Survey - Phase I (NSS-I) for sample collection, handling, and analysis. It also describes the quality assurance and quality control (QA/QC) protocols that were implemented, including the procedures for data management (verification, validation, and construction of the final data bases used for analysis).

Much of the NSS-I methodology was shared with the Eastern and Western Lake Survey components of the National Lake Survey (NLS). The QA/QC sample collection design and the data management protocol for the NSS-I were similar to the procedures implemented in the NLS. The protocols used by the sample processing laboratories during the NLS also applied to the NSS-I. The NLS procedures for sample collection and in situ measurements, however, were not applicable to the NSS-I. All NSS-I field techniques were developed or refined during the NSS-I Pilot Survey, conducted in the Southern Blue Ridge in 1985 (Messer et al., 1986; Knapp et al., 1987).

An Episodes Pilot Survey was conducted concurrently with NSS-I sampling in order to determine the feasibility of sampling acidic episodes in streams in the Mid-Atlantic sampling area. This study evaluated the use of a probability-based sampling design to assess the extent, duration, and frequency of acidic episodes on a regional scale. The Episodes Pilot Survey also attempted to test proposed physical and chemical sampling protocols. The design, methods, and results of the Episodes Pilot Survey are summarized by Messer et al., 1986.

The NSS-I data acquisition process began with the collection of water samples and descriptive site information about the stream sample points. The 35 chemical and physical characteristics of stream water that were selected for in situ or laboratory measurement for the NSS-I effort are listed in Table 3-1. A brief description of each parameter is given in the NSS-I analytical methods manual (Hillman et al., 1987). Once collected, water samples were transported via express courier to a central processing laboratory where they were preserved and split into aliquots within 24 hours after sample collection. In addition to preparing the samples for shipment to the contract analytical laboratory, the processing laboratory measured pH, dissolved inorganic carbon (DIC), color, turbidity, conductance, and certain aluminum species. At the analytical laboratory, 24 chemical variables were measured (Table 3-1). Data from the analytical laboratory were entered into a data base, which then underwent a series of stringent QA checks.

In addition to the chemical data, geographic data were compiled for all NSS-I sample streams. This information represents an important component of the data base, as the weighting factors used in making population estimates are related to the direct drainage of each NSS-I stream (subsection 2.4.1). The geographic data compiled for each stream, the U.S. Geological Survey (USGS) map scale used to calculate the data, and the NSS-I data base variables are listed in Table 3-2.

3.2 FIELD SAMPLING PLAN

The NSS-I logistics plan specified that field samples were to be collected during a spring index sampling period between snowmelt and leafout (mid-March to mid-May) at 533 streams (1,037 sampling points) in a geographic area totaling more than 200,000 mi^2. Based on hydrology and phenology, this plan was designed to provide sampling consistency among areas and to

Table 3-1. Chemical and Physical Variables Measured in NSS-I and Methods Employed

Parameters	Instrument or analytical methods	Reference laboratory methods*
FIELD SITE		
pH, in situ	Portable meter (Beckman pHI-21); glass combination electrode (Orion Ross Model 8104)	Hagley et al. (1988)
Specific conductance and temperature, in situ	Portable conductivity meter with probe (YSI 33 S-C-T)	Hagley et al. (1988)
Dissolved oxygen in situ	Portable dissolved oxygen meter (YSI Model 54A); pressure-compensating oxygen-temperature probe (YSI 5739)	Hagley et al. (1988)
Current velocity	Electromagnetic current meter (Marsh-McBirney, Model 201-D)	Hagley et al. (1988)
PROCESSING LABORATORY		
Aluminum		
Total monomeric	Colorimetry (pyrocatechol violet, automated flow injection analyzer)	Hillman et al. (1987)
Nonexchangeable monomeric	Colorimetry as with total monomeric (after passing through strong cation-exchange column)	Hillman et al. (1987)
Specific conductance	YSI conductivity meter (Model 32); YSI probe (YSI 3417)	EPA 120.1
pH, closed system	pH meter (Orion Model 611); glass combination electrode (Orion Model 8104)	EPA 150.1

* EPA methods are taken from U.S. EPA (1983); USGS methods are from Skougstad et al. (1979).

Table 3-1. Chemical and Physical Variables Measured in NSS-I and Methods Employed (Continued)

Parameters	Instrument or analytical methods	Reference laboratory methods*
Dissolved inorganic carbon, closed system	Infrared spectrophotometry (Dohrmann DC-80 carbon analyzer)	EPA 415.2 (modified)
True color	Comparator (Hach Model CO-1)	EPA 110.2 (modified)
Turbidity	Nephelometer (Monitek Model 21)	EPA 180.1
CONTRACT ANALYTICAL LABORATORY		
Acid neutralizing capacity (ANC)	Acidimetric tritration, modified Gran analysis	Hillman et al. (1987); Kramer (1984)
Aluminum		
Extractable	Atomic absorption spectroscopy (furnace) on methyl-isobutyl-ketone extract	Hillman et al. (1987); EPA 202.2
Total	Atomic absorption spectroscopy (furnace)	EPA 202.2
Ammonium	Colorimetry (phenate, automated)	EPA 350.1
Base neutralizing capacity (BNC)	Alkalimetric titration, modified Gran analysis	Hillman et al. (1987); Kramer (1984)
Calcium	Atomic absorption spectroscopy (flame)	EPA 215.1
Chloride	Ion chromatography	ASTM (1984); O'Dell et al. (1984)

* EPA methods are taken from U.S. EPA (1983); USGS methods are from Skougstad et al. (1979).

Table 3-1. Chemical and Physical Variables Measured in NSS-I and Methods Employed (Continued)

Parameters	Instrument or analytical methods	Reference laboratory methods*
Dissolved inorganic carbon (DIC)		
Initial	Infrared spectrophotometry	EPA 415.2 (modified)
Air equilibrated	Infrared spectrophotometry, after bubbling with 300 ppm CO_2 air for 20 minutes	EPA 415.2 (modified)
Dissolved organic carbon (DOC)	Infrared spectrophotometry, after acidification and sparging to remove DIC	EPA 415.2
Fluoride, total dissolved	Ion-specific electrode	EPA 340.2 (modified)
Iron	Atomic absorption spectroscopy (flame)	EPA 236.1
Magnesium	Atomic absorption spectroscopy (flame)	EPA 242.1
Manganese	Atomic absorption spectroscopy (flame)	EPA 243.1
Nitrate	Ion chromatography	ASTM (1984); O'Dell et al. (1984)
pH		
Air equilibrated	pH electrode and meter, after bubbling with 300 ppm CO_2 air for 20 minutes	EPA 150.1
Initial ANC	pH electrode and meter, at start of ANC titration	EPA 150.1
Initial BNC	pH electrode and meter, at start of BNC titration	EPA 150.1

* EPA methods are taken from U.S. EPA (1983); USGS methods are from Skougstad et al. (1979).

Table 3-1. Chemical and Physical Variables Measured in NSS-I and Methods Employed (Continued)

Parameters	Instrument or analytical methods	Reference laboratory methods*
Phosphorus, total dissolved	Colorimetry (phosphomolybdate automated), after acid-persulfate digestion	USGS I-4600-78 (modified)
Potassium	Atomic absorption spectroscopy (flame)	EPA 258.1
Silica	Colorimetry (silicomolybdate, automated)	USGS 1-2700-78
Sodium	Atomic absorption spectroscopy	EPA 273.1
Specific conductance	Conductivity cell and meter	EPA 120.1
Sulfate	Ion chromatography	ASTM (1984); O'Dell et al. (1984)

* EPA methods are taken from U.S. EPA (1983); USGS methods are from Skougstad et al. (1979).

Table 3-2. Geographic Variables Measured in NSS-I

Geographic Attribute	USGS Map Scale	NSS-I Data Base Variable Name
Watershed area above the site (km^2)	1:24,000	A_WS
Direct drainage area (mi^2)	1:24,000	A1
Watershed area above lower site (km^2)	1:24,000	A4
Site elevation (m)	1:24,000	ELEV
Stream gradient (%)	1:24,000	GRADE
Site latitude (decimal form)	1:24,000	LAT_STD
Site longitude (decimal form)	1:24,000	LON_STD
Reach length between upper and lower sample sites (km)	1:24,000	L2
Number of headwater reaches	1:250,000	RCH_HW
Reach length between stream confluences (km)	1:250,000	RCH_LN
Shreve order	1:24,000	SHREV75
ANC stratum (1 or 2)	(section 2.4)	STRATUM
Strahler order	1:24,000	STRA75
Reach identification code	--	RCH_ID
Stream identification code	--	STRM_ID
State (2-character code)	1:250,000	STATE1
Stream name	1:24,000	STRMNAM
Subregion identification code		SUB_ID

minimize the influence of external factors affecting stream chemistry during the season of maximal plant growth. Florida was an exception to the phenological scheduling because leaf-out was essentially completed by the time the survey began.

Sampling followed a pattern of early to late leafout (in general, early to late seasonal warming). In order to visit streams during the index period, the sampling crews moved through the Mid-Atlantic areas in such a way that they collected the second set of samples from a given stream at least two weeks after the first visit, but before leafout.

Sampling crews visited streams between March 17 and May 15, 1986, accessing stream sampling sites by foot and by means of two- or four-wheel drive vehicles. Water samples were collected from the center of each stream at mid-depth by means of a peristaltic pump, which pumped water through Tygon tubing held in position by a sampling boom. The NSS-I field sampling activities are shown in Figure 3-1.

Thirty-nine sites served as temporary base stations for field operations, based on proximity to NSS-I stream sites. Two-member sampling teams collected samples from one or two streams each day at both upstream and downstream locations.

In order to avoid the bias that could be caused by diel fluctuations in chemistry resulting from stream biota, sampling crews did not visit downstream and upstream nodes (sample locations) at the same time each day. Half of the streams were selected randomly for sampling at the upstream location first; the other half was sampled at the lower location first. In order to determine sampling order, crews treated multiple visits to one stream as independent visits to separate streams.

Although nontarget reaches were originally screened out by means of mapped information, (subsection 2.3.1), on-site data was used to further refine the target population. The following criteria were established to assist in identifying noninterest reaches:

1. Intermittent: reaches that were at least 90% dry or stagnant.

2. High conductance: reaches having an in situ specific conductivity > 500 $\mu S\ cm^{-1}$ (e.g., reaches contaminated by oil well brine, industrial pollution).

3. Low pH: reaches having a field pH value of 3.3 or less (e.g., reaches impacted by acid mine drainage).

4. Tidal influence: coastal reaches with water chemistry influenced by tides (e.g., specific conductivity greater than 250 $\mu S\ cm^{-1}$).

5. Reservoir: reach inundated by water project.

6. Episode (other than spring baseflow conditions): reach chemistry influenced by a precipitation event at the time of sampling (e.g., high turbidity and high flow). The identification of precipitation episodes is discussed in subsection 3.8.3.1.

7. No channel, dry: no sample could be collected because of a lack of water (dry) or explicit stream channel (swamp).

8. Other: reach inaccessible because access permission had not been given or because of a permanent feature of the watershed (e.g., active military area).

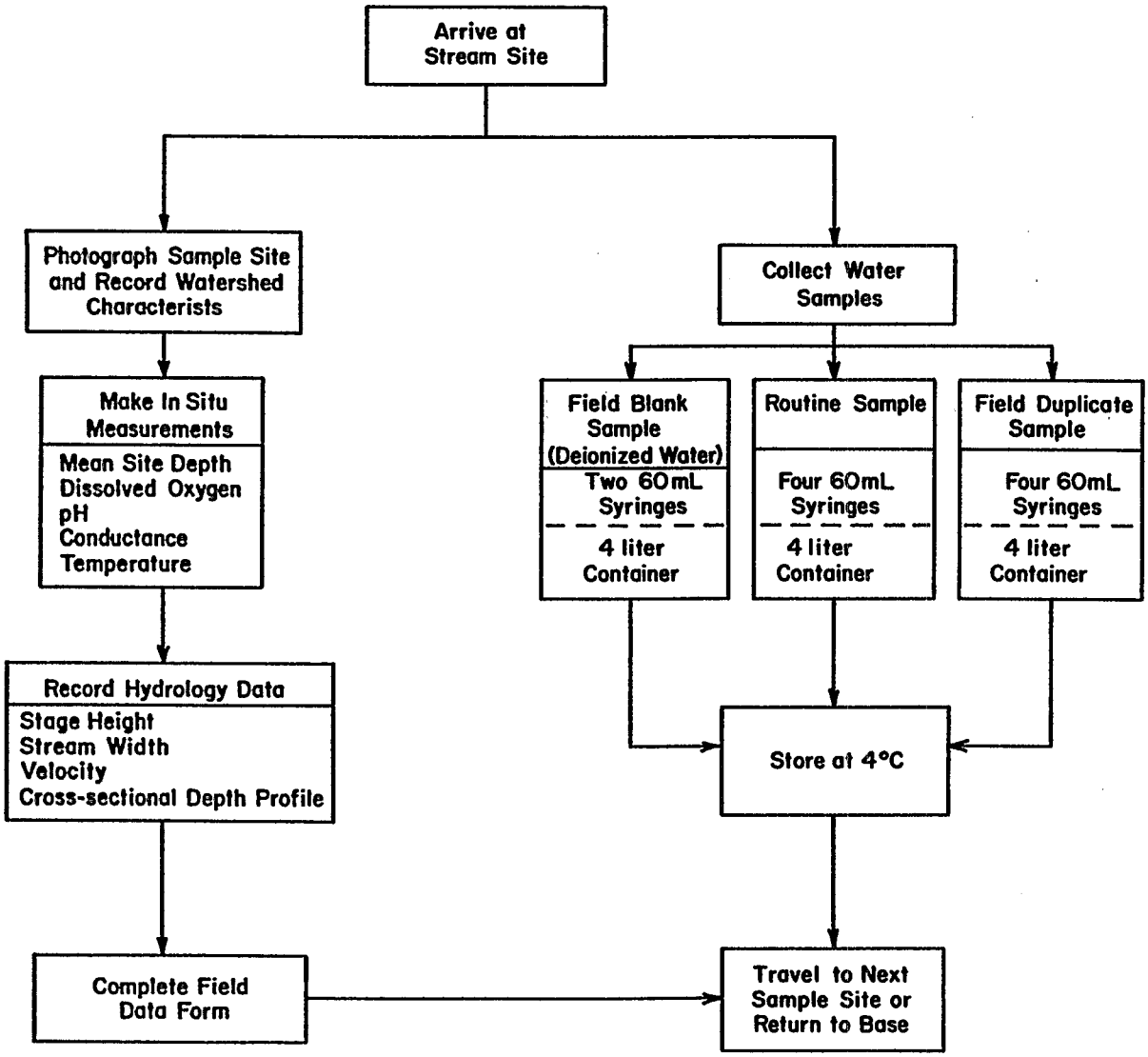

Figure 3-1. Field sampling activities, NSS-I (summarized from Hagley et al., 1988).

3.3 FIELD METHODS

3.3.1 Site Characteristics

On the first visit to a stream sampling location (node), photographs were taken of the site. Watershed disturbances, land use, bank vegetative cover, and stream substrate were recorded. At downstream nodes, sampling crews collected hydrologic data, including stream channel and flow measurements. In Mid-Atlantic subregions, these included stream stage, discharge, width, and depth. On the first visit to each downstream site, nonrecording staff gauges were installed and read. Mean depth and width were estimated. On the second visit, discharge was measured using the velocity-area integration method. Flow velocities (0.6 depth from surface) were measured at 8 to 15 intervals across the stream with an electromagnetic current velocity meter; the calibration was checked each morning and again on site before each set of measurements. At the downstream sites of the Southeast Screening areas, flow was estimated by timing the movement of a floating object through a measured length of stream. Width and mean depth were estimated.

3.3.2 Sample Collection

Water samples were collected using the techniques developed for the NSS-I Pilot Survey. Routine samples were collected from each stream by pumping water through 1/4-inch Tygon tubing held in the center of the stream at mid-depth with a 6-foot sampling boom. Water samples were pumped into a 4-liter polyethylene Cubitainer using portable, battery-driven peristaltic pumps. In addition, four gas-tight 60-mL polypropylene syringe samples were collected without exposing the samples to the atmosphere in order to minimize changes in the water sample prior to analysis. These syringes were used for the analysis of pH, dissolved inorganic carbon (DIC), and total monomeric and nonexchangeable aluminum performed in the processing laboratory. Detailed discussions of these techniques appear in Knapp et al., 1987, and Hagley et al., 1988.

Two types of QC samples were collected. Each day two teams collected a field blank sample at the first site visited using reagent grade water from the processing laboratory. This water was carried to the sample site and pumped through Tygon tubing into clean sample containers using techniques identical to those used to collect routine samples. In addition, two teams each day collected a field duplicate. A second set of sample containers (Cubitainer and syringes) was filled with stream water immediately after the routine sample was collected, using identical techniques.

3.3.3 In Situ Measurements

Streamside and in-situ chemistry measurements included pH, conductivity, dissolved oxygen, and temperature. Measurement and calibration techniques are described in detail in Hagley et al. (1988). All field pH determinations were made using portable meters with combination electrodes and temperature compensators. Field pH meters were calibrated each morning using commercially available high ionic strength buffer solutions (pH 4 and 7). A quality control check solution (QCCS) was used to check the calibration of the meter before leaving for the field and again before and after in-situ measurements. Measurements of pH were made in beakers of stream water, collected with the peristaltic pump. Replicate readings were taken on new sample aliquots until two successive readings agreed within 0.03 pH units. The final pH and temperature were the values reported.

Conductivity was measured in situ using a portable meter with the probe immersed in the stream at mid-depth. Three different concentration solutions were used to check the factory calibration of the meters before each day's sampling activities. The meter calibration was rechecked before and after each stream reading.

Dissolved oxygen concentration in a stream was measured using a dissolved oxygen meter combined with a pressure compensating oxygen-temperature probe. The instrument was air calibrated each morning, at each stream site, and at the base site at the conclusion of sampling. The calibration was checked using air-saturated water after morning and evening calibrations. In-situ measurements were taken by immersing the probe at mid-depth in the streamflow.

3.4 SAMPLE HANDLING

Water samples were transported from the sample site in coolers containing chemical refrigerant packs that maintained a temperature of approximately 4°C until they arrived at the processing laboratory. Samples were shipped by overnight courier to ensure their arrival at the processing laboratory in Las Vegas, Nevada, on the morning after collection. Upon arrival at the processing laboratory, samples were organized into a batch for processing. A sample batch consisted of a group of routine stream samples and related QA samples. In almost all cases, processing laboratory analyses were completed and samples were preserved and split into aliquots within 24-36 hours after sampling.

Within each batch, each sample was assigned a unique identification number to distinguish it from all other samples in the survey. After the batch of samples was preserved and split into aliquots, it was shipped by overnight courier to a contracted analytical laboratory for chemical analysis.

3.5 PROCESSING LABORATORY TECHNIQUES

The processing laboratory provided a controlled environment for processing and preserving water samples and performing certain chemical measurements that needed to be completed as soon as possible after sample collection. Figure 3-2 illustrates the processing laboratory activities. Chemical parameters that tend to become unstable over time (i.e., pH, DIC, and the aluminum species) were measured in the processing laboratory.

Each 4-liter Cubitainer stream sample was split into seven aliquots and prepared for shipping to analytical laboratories for additional analyses. Subsamples were also taken from each Cubitainer for measuring turbidity, conductance, and true color.

Field crews capped the syringe samples with air-tight valves to prevent air equilibration from occurring before analysis. The syringe samples were used to measure pH, DIC, and total and nonexchangeable monomeric aluminum species and to prepare the total extractable aluminum aliquot. Processing laboratory measurements of these variables were essential for providing quality data within holding time requirements. Processing laboratory analytical methods are described in Hillman et al. (1987).

Figure 3-2 depicts the seven aliquots prepared from each Cubitainer. The aliquots were stabilized by filtration (0.45 μm filter), acid preservation, or refrigeration, or some combination of these procedures. Filtration removed suspended material in order to reduce biological activity and to eliminate surfaces that could adsorb or release dissolved chemical species. Acid was added to some aliquots to prevent loss of dissolved analytes through precipitation, chemical reaction, or biological reaction. All aliquots were stored and shipped at 4°C to reduce biological activity and, for total extractable aluminum aliquots, to reduce volatilization of solvent.

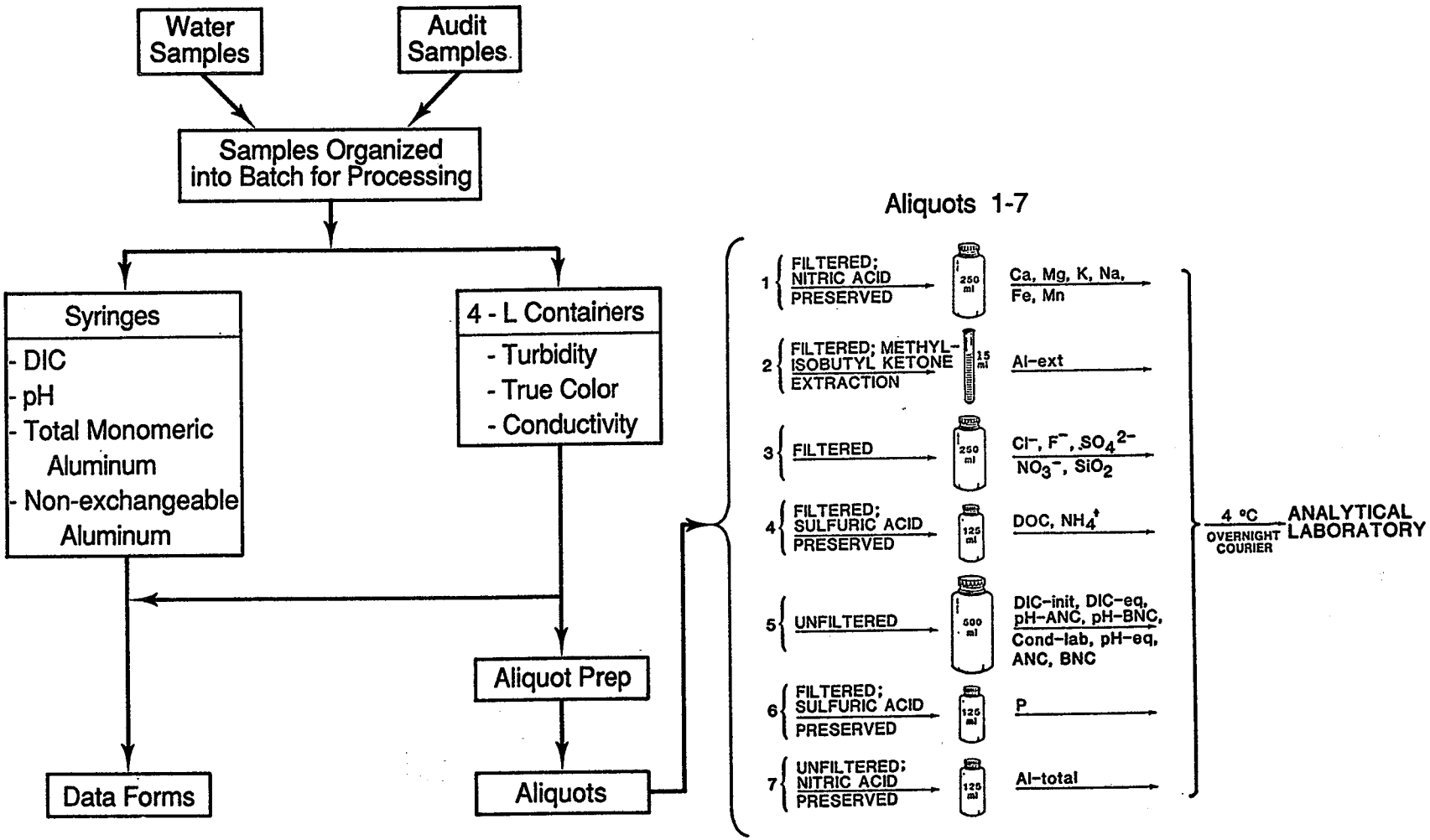

Figure 3-2. Processing laboratory activities, NSS-I.

Table 3-1 lists the instruments and analytical methods used in the processing laboratory. The processing laboratory also prepared and shipped reagents and supplies to field base sites. Arent et al. (1988) give a detailed discussion of processing laboratory protocols for the NSS-I.

3.6 ANALYTICAL LABORATORY SUPPORT

Analytical contract laboratories were solicited by bid and selected through the analysis of performance evaluation samples and on-site inspections (Cougan et al., 1988). Two analytical laboratories were used to analyze NSS-I water samples. Table 3-1 lists the analytical instruments and methods used by the analytical laboratories. A brief description of each analytical method is given in the NSS-I analytical methods manual (Hillman et al., 1987). The maximum allowable holding time for each analyte before analysis is given in Table 3-3.

3.7 QUALITY ASSURANCE AND QUALITY CONTROL PROTOCOLS

An important design criterion of the NSS-I is that the data collected must be of known quality. An extensive data QA program was established to meet this requirement. The QA program has two separate but integrated components that include both operational and data management activities. In the operations component, the QA procedures ensured that all samples were collected and analyzed in a consistent manner. QC samples were collected to provide data from which the accuracy and precision of the reported values could be estimated with a known degree of confidence. The data management component established a program that stored and tracked the data, identified and corrected entry, reporting, and analytical errors, and kept a record of such changes. These procedures produced documented files of data of known quality that were accessible to project scientists and extramural users.

3.7.1. Quality Assurance Plan

The NSS-I QA plan (Drouse et al., 1986) defines the activities required to ensure that procedures are performed consistently and that the quality of the data generated can be determined. QA and QC activities identified in the plan include (1) training field sampling and processing laboratory crews, (2) maintaining communication with management, sampling, and analytical personnel, (3) conducting on-site field and laboratory inspections, and (4) collecting and analyzing QA and QC data in order to quantify data quality. Quality assurance protocols (Drouse et al., 1986) were developed for collecting, preparing, preserving, shipping, and analyzing samples, as well as for reporting, verifying, and validating analytical results. Both the processing laboratory and the analytical laboratories analyzed QC samples within each batch.

3.7.2 Quality Assurance and Quality Control - Data Collection and Analysis

The NSS-I QA program used several types of QC samples (Table 3-4 and Figure 3-3) to ensure that sampling and analytical methods were performed according to specifications. The results from QC sample analyses were used to evaluate the performance of field sampling methods, field procedures, and laboratory analyses. The interpretations of QC data were also used to evaluate overall data quality for the survey. Analyses of the QC samples allowed field samplers and laboratory personnel (in both the processing and analytical laboratories) to identify and immediately correct specific problems such as poor instrument performance or reagent contamination before and during routine sample analyses.

Table 3-3. Maximum Holding Times Specified for NSS-I Samples

Variable	Holding Time
NO_3^{-}[&]; extractable aluminum	7 days
ANC; BNC; specific conductance; DIC; DOC; pH[#]	14 days
P; NH_4^+; Cl^-; SO_4^{2-}; F^-; SiO_2	28 days
Ca; Fe; K; Mg; Mn; Na; total aluminum	28 days[$]

& Although the EPA (U.S. EPA, 1983) recommends that nitrate in unpreserved samples (unacidified) be determined within 48 hours of collection, evidence exists (Peden, 1981; APHA, 1985) that nitrate is stable for 2 to 4 weeks if the sample is stored in the dark at 4°C.

Although the EPA (U.S. EPA, 1983) recommends that pH be measured immediately after sample collection, evidence exists (McQuaker et al., 1983) that it is stable for as long as 15 days if the sample is stored at 4°C and sealed from the atmosphere. The pH was also measured in a sealed sample at the processing laboratory within 24-36 hours of sample collection.

$ Although the EPA (U.S. EPA, 1983) recommends a 6-month holding time for these metals, this study required that all the metals be determined within 28 days, which ensured that significant changes would not occur and that data would be obtained in a timely manner.

Table 3-4. NSS-I QC Samples

Sample type	Description	Function	Frequency of use
Field blank	Reagent-grade deionized water* subjected to sample collection, processing, and analysis	Estimate system decision and detection limits; identify sample contamination	One per batch
Processing Laboratory blank	Reagent-grade deionized water* subjected to sample processing and analysis	Estimate background due to sample processing and analysis	In lieu of field blank when logistical constraints prevented its collection
Field duplicate	Duplicate stream sample	Estimate field and system variability	One per batch
Field Performance Audit	Synthetic or natural lake sample; processed at processing laboratory	Estimate analytical precision of processing and analytilaboratory measurements; estimate accuracy and interlaboratory bias	As scheduled
Laboratory Performance Audit	Synthetic or natural lake sample; processed at analytical laboratory	Estimate analytical precision of analytical laboratory measurements; estimate accuracy and interlaboratory bias	As scheduled
Calibration blank	Reagent-grade deionized water*	Identify signal drift	One per batch

*ASTM (1984)

Table 3-4. NSS-I QC Samples (Continued)

Sample type	Description	Function	Frequency of use
Reagent blank	Reagent-grade deionized water* plus reagents for total Al, SiO_2 analyses	Identify contaminants present in reagents	One per batch
Quality control check solution (QCCS)	Standard solution from source other than calibration standard	Determine accuracy and consistency of instrument calibration	Before the first measurement and as specified
Detection limit QCCS	Standard solution at 2 to 3 times the required detection limit	Determine accuracy and precision at lower end of linear dynamic range of measurement method	One per batch
Processing laboratory duplicate	Split of stream sample	Determine precision of processing laboratory measurements	One per batch
Analytical laboratory duplicate	Split of sample aliquot	Determine precision of analytical laboratory measurements	One per batch

*ASTM (1984).

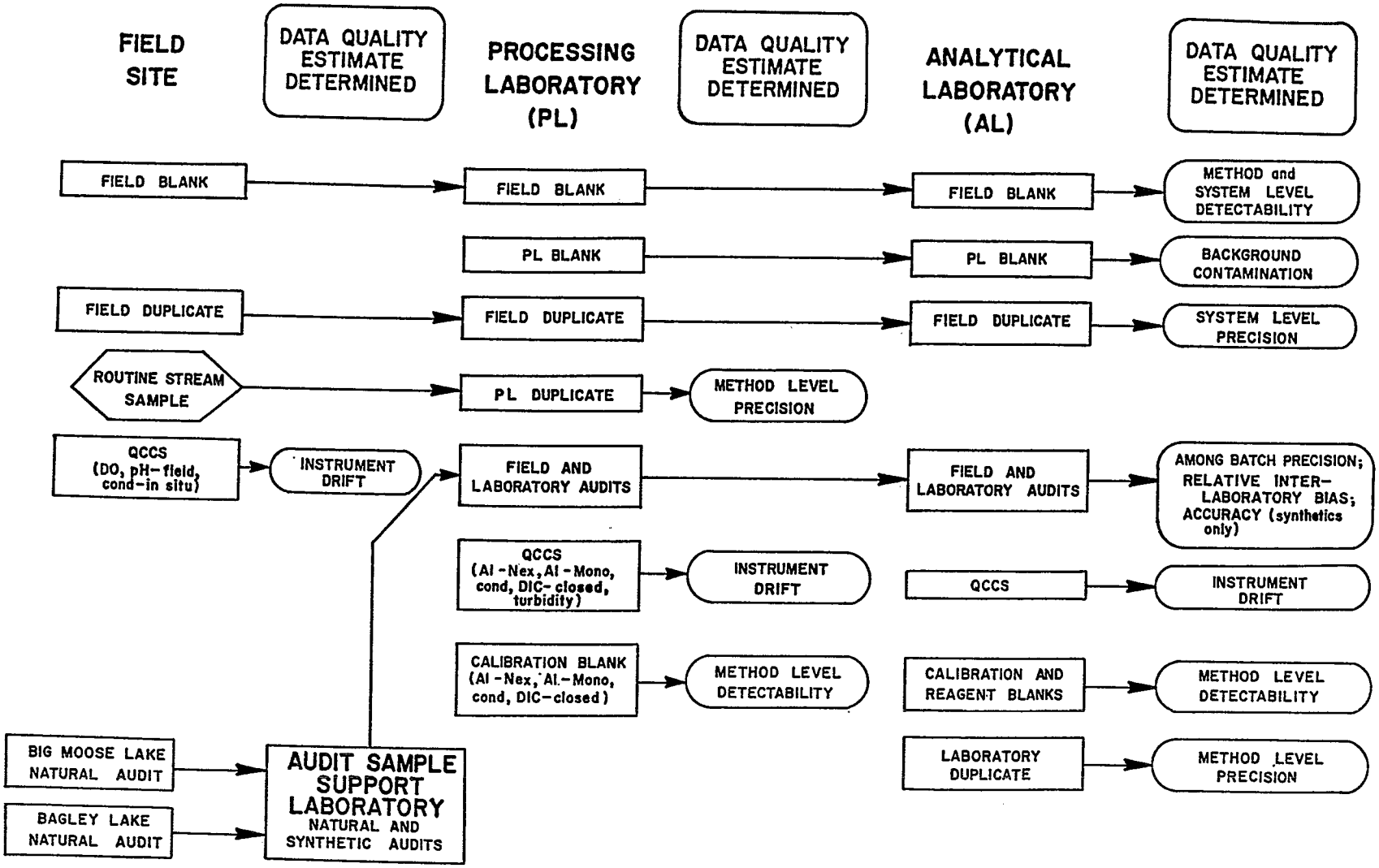

Figure 3-3. QC sample flow for the NSS-I.

Additional QC samples, introduced into batches of stream samples at the stream site or at the processing laboratory, were analyzed at the processing and analytical laboratories. These samples were used to judge the overall performance of NSS-I sampling and analytical activities and to establish data quality. Analytical laboratories were not told the origin, identity, or chemical composition of audit samples. Thus, the audit samples were analyzed as if they were routine stream samples.

3.7.3 Training and Site Audits

Field personnel participated in a training program that covered NSS-I objectives, stream sample collection and measurement techniques, orienteering, outdoor skills, and safety. Processing laboratory personnel training covered all technical aspects of laboratory operations, including analytical methods, instrument calibration, sample handling, QA, and safety procedures. On-site evaluations were conducted to ensure that sampling and analysis activities were being performed according to the QA plan and the statement of work. The field base sites, the processing laboratory, and one contract analytical laboratory were evaluated during the NSS-I. Budget constraints precluded an on-site evaluation of the other contract laboratory (Cougan et al., 1988). Quality control sample data were reviewed and used in conjunction with on-site inspections to identify the need for changes in sampling or analytical protocols.

3.8 DATA BASE MANAGEMENT

NSS-I data management and analysis were patterned after procedures developed for the NLS (Kanciruk et al., 1986) and are described in detail in Sale (1988). All NSS-I data sets were maintained at Oak Ridge National Laboratory (ORNL) on tandem IBM 3033 mainframe computers, using the Statistical Analysis System (SAS) software package (SAS Institute, Inc., 1985). When the data sets were complete, they were transferred to the National Computer Center (NCC) at Research Triangle Park, North Carolina, via magnetic tape, where they could be accessed by NSS scientists at the Las Vegas and Corvallis laboratories.

Ultimately, the success of the NSS-I will be based on the ability of the data to produce robust population estimates regarding the target population of streams as defined in this report. The NSS-I data base used in making population estimates has been subjected to four levels of stringent QA evaluation to ensure that the data collected during NSS-I is representative of the physical and chemical characteristics of the streams at the time of sampling. These checks were also useful in identifying reaches that are unusual with respect to others in the target population and that may represent polluted sites, or episode samples.

An important tool in the development of the NSS-I data base is the use of data qualifiers to mark an individual value or even an entire stream as having a particular feature that may be useful in data interpretation. Two types of data qualifiers, flags and tags, are used to document notes made about particular data records or values in the NSS-I data base. Tags identify specific notes made in the field, at the processing laboratory, or at the analytical laboratory. Flags identify observations or notes made during the QA process (verification and validation) involved in creating the enhanced data base. These qualifiers provide a method for identifying nonrepresentative and questionable data with appropriate flags and tags.

The completion of each level of QA produced a new working data set of increased refinement. These working data bases are defined as: raw (Data Set 1), verified (Data Set 2), validated (Data Set 3), and enhanced (Data Set 4). The final product of this refinement process,

the enhanced data set (Data Set 4), incorporates data substitution and replacement of missing values. This is the data set that is used for calculating NSS-I population estimates. Figure 3-4 summarizes the development of these working data bases. The data bases are described further in the following subsections.

3.8.1 Raw Data (Data Set 1)

The collective data from all components of the sampling and analysis made up the raw data set. Field, processing laboratory, and analytical laboratory personnel sent the original data forms to the QA staff at the Environmental Monitoring Systems Laboratory (EMSL) in Las Vegas for review, in order to ensure that data were correct and consistent. Completed forms were then forwarded to the Oak Ridge National Laboratory (ORNL), where the data were entered into the data base. To ensure accurate data transfer from the data forms to computer files, the information was double-entered into computer files and subjected to automated checking procedures (Rosen and Kanciruk, 1985). The raw data set was used to screen the data for problems, perform exploratory analysis, and evaluate the need for any adjustments in the data analysis plan.

3.8.2 Verification (Data Set 2)

The objectives of the data verification process were to identify, correct, and flag raw data of questionable or unacceptable quality and to identify data that might need to be corrected during or after data validation. These objectives were met by reviewing the QC data measured and recorded at the sampling site, at the processing laboratory, and at the analytical laboratories. The verification process was automated as much as possible through applicable computer programs. Data verification took place in two parts. First, the required numeric changes were identified, and then final numeric changes and flag setting were accomplished.

Verification began with receipt of the data forms from the field and processing laboratory. An NSS-I auditor reviewed the forms for completeness, agreement between field and laboratory forms, and proper assignment of sample identification codes and data qualifier tags. Data anomalies were reported to the field base site and processing laboratory coordinators for corrective action. Data reporting errors were usually corrected on the data forms before the data were entered into the raw data set. During verification, each sample was evaluated individually and by analytical batch. Individual values that were identified as exceptions (as a result of cation/anion balances, conductance balance, or protolyte analysis) or that did not meet the acceptance criteria, were flagged in the data base. Suspect values were also identified by examining QC data (blank, duplicate, and audit samples) measured and recorded at the processing and analytical laboratories. In addition, data qualifier flags were added when QC samples did not meet acceptance criteria, or when sample analysis holding time requirements or instrument detection limits were not met. Table 3-5 lists the computerized verification checks that were used to identify exceptions in the chemistry data. Table 3-6 shows the calculations performed for anion/cation balances, conductance estimates, and protolyte analysis.

The output from these checks, along with original data and field notebooks, was used to evaluate analytical results. Based on the evaluation of the analytical results reported for QC samples, analytical laboratories were directed to confirm reported values or to reanalyze selected samples. If a value was identified as an exception to expected results, a flag was placed in the data base to relay information about the disposition of this individual observation or value (Drouse et al., 1987).

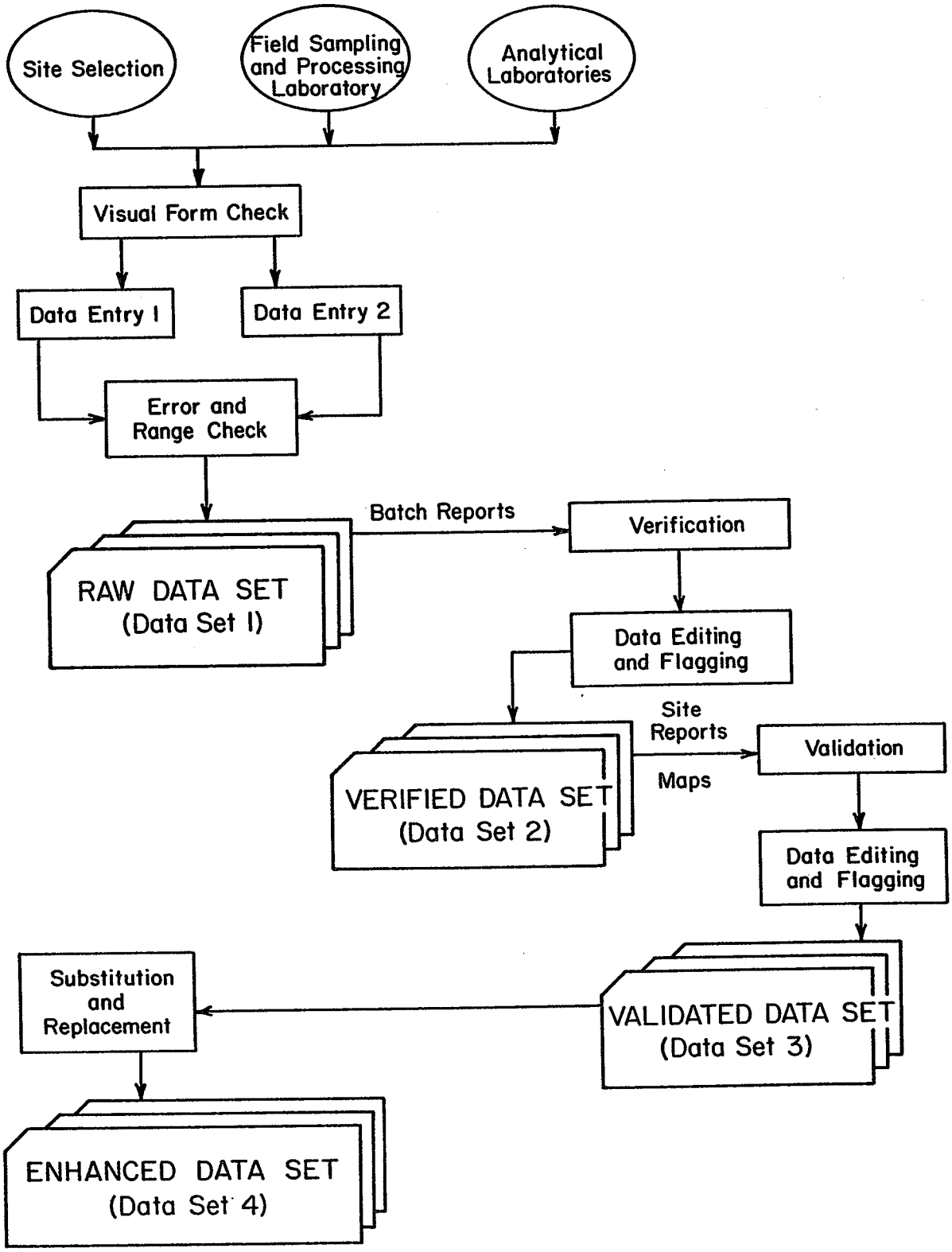

Figure 3-4. NSS-I data base development.

Table 3-5. Exception Generating Programs within the Verification System*

Verification Process	Data Evaluated
Audit Sample Evaluation	Field synthetic audit
	Laboratory synthetic audit
	Field natural audit
	Laboratory natural audit
Lab/Field Blank Evaluation	Field blank
	Laboratory blank
Field Duplicate Precision Evaluation	Routine field duplicate pairs
Instrumental Detection Limit Evaluation	All species
Holding Time Evaluation	All species
Conductance Check Calculations	All samples
Anion/Cation Balance Calculations	All samples
Protolyte Analysis	All samples
Reagent/Calibration Blanks and QCCS	All batches

* Summarized from Cougan et al., 1988.

Table 3-6. Calculations Performed as Part of Cation/Anion Balances, Conductance Estimates, and Protolyte Analysis in Verification

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Verification Checks

Anion/cation Balance

%Ion Balance Difference =

$$\frac{\text{ANC + Sum of Anions-Sum of Cations}}{\text{Total ion strength}} * 100$$

Sum of Anions= $[Cl^-] + [F^-] + [NO_3^-] + [SO_4^{2-}]$
Sum of Cations= $[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + [NH_4^+]$
Total ion strength = ANC + sum of anions + sum of cations + $2[H^+]$
ANC = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$ + [titrated organic anions] - $[H^+]$

Conductance Balance

% Conductance Difference =

$$\frac{\text{(calculated conductance - measured conductance)}}{\text{measured conductance}} * 100$$

Protolyte Analysis

Comparison of:

Measured ANC vs. carbonate alkalinity + organic anion
Measured BNC vs. CO_2 acidity + organic acid anions

Where:
Measured ANC and BNC were from Gran titrations
Carbonate alkalinity was calculated from DIC and pH variables
CO_2 acidity was calculated from DIC and pH variables
Organic anion was calculated from DOC using Oliver Model (Hillman et al., 1987; Oliver et al., 1983)

Figure 3-5 shows the verification process flow. Detailed information about verification procedures is found in Drouse et al. (1987) and Cougan et al. (1988).

3.8.3 Validation (Data Set 3)

Whereas the purpose of verification procedures was to evaluate data at the sample and batch level, validation was intended to compare samples within the population of units (all samples collected within a subregion). The validation process identified unusual data that would need special attention when used for statistical analysis, particularly for regional estimates concerning the target population of streams. The two main components of the validation process were (1) the identification of statistical outliers from subregional distributions of chemistry and (2) the evaluation of possible systematic errors in the measurement process. This approach is empirical in nature, as opposed to the geochemical and charge balance orientation of verification. Because NSS-I subregional boundaries generally group streams of similar geochemistry together, these empirical relationships reflect the geochemical trends of each subregion. Validation outliers may result from a number of conditions at the reach or from data base problems. Conditions that may cause outliers include:

1. The determination that the water sample was collected during a time that might be considered a precipitation episode event for a given reach.

2. The determination that a given reach is being influenced by factors beyond normal geochemical processes (e.g., pollution or watershed disturbance, including acid mine drainage, brine, or other nonpoint sources).

3. Unusual geochemical properties within a given subregion.

4. Impossible datum, clearly erroneous when reviewing chemistry for that reach.

5. Observation or identification inconsistencies (e.g., mislabelling of stream or batch ID).

Observations that surface as atypical during review of data at a subregional level are considered outliers from the rest of the data. Outliers in the data may result from the natural variability of streams in the set of sample reaches, from anthropogenic disturbances in the natural environment, and from errors in the sampling design, as well as from sampling and analytical errors. Although outliers may represent unusual data in comparison with other data, such values are not necessarily inaccurate in their representation of a sample stream reach. The validation process is, therefore, not meant to be a stringent pass/fail test, but rather a way to search for observations that may represent entry or analytical errors, or perhaps unusual water chemistry. Data outliers are not typical or common in the sample data sets. The unusual observations become apparent when the data are viewed as a set of information using univariate, bivariate, and multivariate analyses.

Figure 3-6 shows a flow diagram of the validation process. The statistical approaches and specific techniques summarized in Table 3-7 were applied to the validation of NSS-I data. During validation, a matrix for each subregion was constructed that depicted the results of validation checks on each individual water sample and datum. Using this matrix, outliers were identified and sent to the QA/QC group at EMSL-LV to be checked for possible entry errors. By means of principal component analysis, cluster analysis, and multivariate regression analysis,

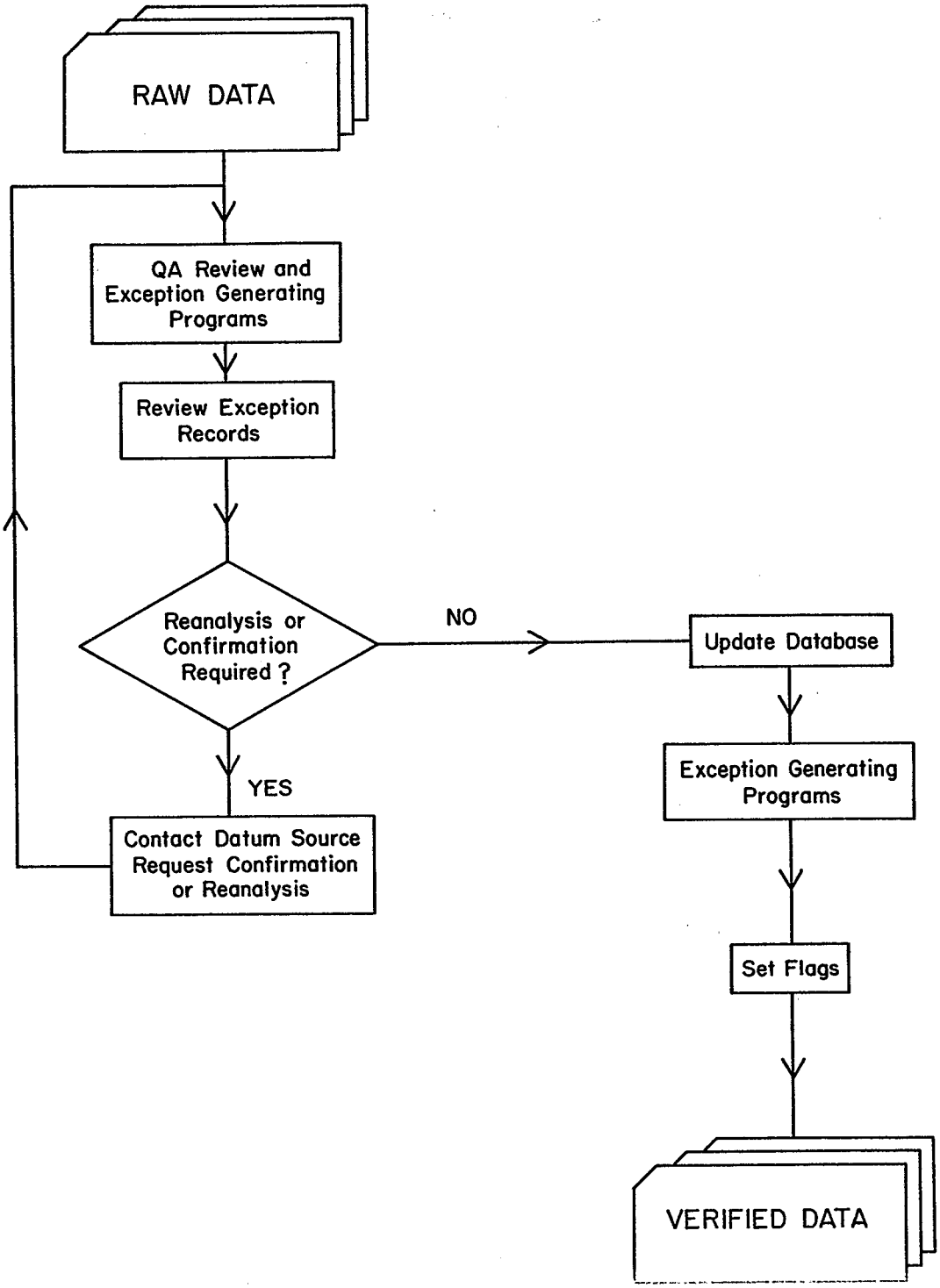

Figure 3-5. NSS-I data verification procedures.

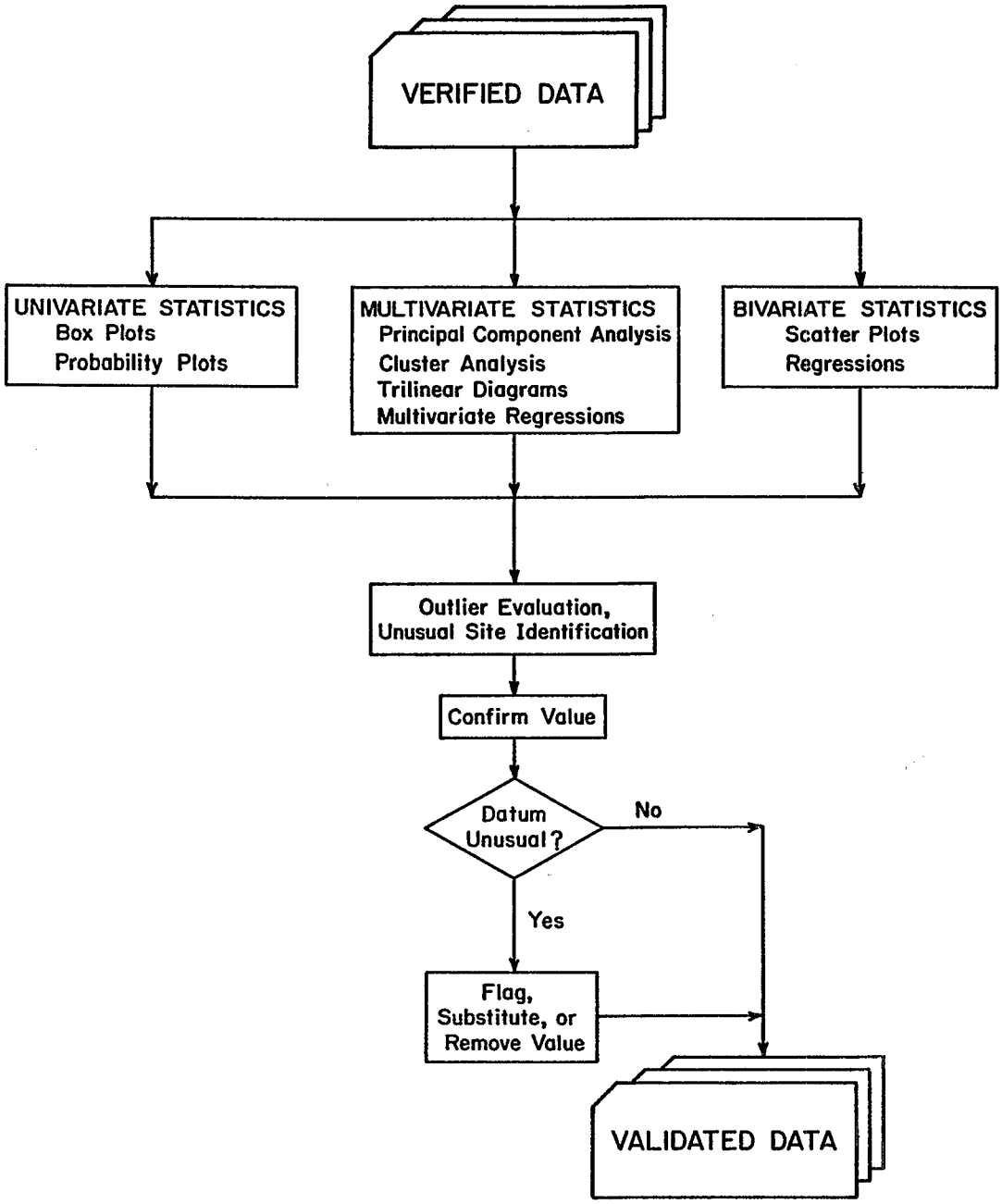

Figure 3-6. NSS-I data validation procedures.

Table 3-7. Types of Validation Analyses Performed on NSS-I Raw Data

UNIVARIATE ANALYSIS	
Univariate statistics:	Summary statistics, stem and leaf diagrams, probability plots, box plots, and quartile estimates, applying techniques of Velleman and Hoaglin (1981).
Spatial and Temporal Analysis	
Comparison of downstream vs. upstream differences and visit 1 vs. visit 2 differences.	
Difference ratios treated as univariates and subjected to standard univariate analyses.	
MULTIVARIATE ANALYSIS	
Principal Component Analysis:	Statistical relationships among data were identified using correlation coefficients and sets of eigenvectors. Within in each eigenvector, eigenvalues for each variable were calculated. From these eigenvector and eigen values, relationships between variables were identified and used to help explain data variability.
Regression Analysis:	Multi-linear regressions were performed from cross-correlation matrices, using statistical relationships among variables. A predicted versus a reported value for each variable observation was assessed and compared to a predicted value based on the relationship expected from the correlation matrices. Least squares regressions were performed that identifyed outliers at a particular residual threshold--standardized residuals (SAS, 1985). Removing outliers sequentially was useful in identifying outliers that might not have been apparent without removing aberrant values. Attention was given to leverage points, ordinate extremes, and abscissa extremes.
Cluster Analysis:	Agglomerative disjointed cluster analysis (SAS, PROC FASTCLUS) was performed using Euclidean distance with an iterative algorithm for minimizing the sum of squared distances from the cluster means.

sites having atypical chemistry compared with other sites in a subregion (unique multivariate relationships) were identified and evaluated as unusual sites (sites affected by acid mine drainage, agricultural impact, tidal influence, etc.). Data from unusual sites generally appeared as outliers in several analyses (regression, univariate statistics, etc.).

3.8.3.1 Episode Identification--

Besides identifying outliers, validation served to identify stream chemistry that might have been sampled during a precipitation or snowmelt episode (or influenced by it) and therefore would not provide an acceptable index of base flow chemistry. Although great care was taken not to collect samples during an episode, such conditions might have not been apparent to a sampling team. Episodes samples were identified according to the following criteria:

1. Site is identified as a validation outlier.

2. Change in stream gauge height of 7.5 cm or more, between site visits, supporting evidence of flood stage (except for Southeast Screening sites where no second visits to a site were made that would provide comparative stage height information).

3. Field comments indicated precipitation or snow melt activity (within 24 hours before sampling at one or other node).

4. Data for turbidity, total aluminum, manganese, and iron indicate possible episode at time of sampling (i.e., high turbidity and/or total aluminum relative to other visits at the same site or its corresponding upstream or downstream node).

3.8.3.2 Acid Mine Drainage--

Sites impacted by acid mine drainage represent a category of streams that must be identified in order to distinguish them from those impacted by acidic deposition (i.e., those with low alkalinity and pH and high sulfate). These sites were considered noninterest sites for calculation of NSS-I population estimates and were identified as satisfying all the following criteria, the rationale for which are discussed in subsection 9.3.1:

1. ANC < 0 μeq L^{-1}
2. Sum of base cations > 400 μeq L^{-1}
3. Sulfate/sum of anions $> 75\%$
4. DOC < 5 mg L^{-1}
5. $[SO_4^{2-}] > 300$ μeq L^{-1} in the Mid-Atlantic; $[SO_4^{2-}] > 200$ μeq L^{-1} in the Southeast.
6. Mining activity confirmed by means of maps, field visits, or aerial photographs.

3.8.3.3 Flagging of Unusual Values or Sites--

Values identified as unusual as a result of validation analyses were flagged in the validated data set. When data for an entire reach was considered unacceptable for the intended use of the data--to make population estimates, for example--a site flag code was placed in the data set. Examples include data from sites affected by acid mine drainage, pollution, tidal influence, and watershed disturbance.

3.8.3.4 Geographic Data Verification and Validation--

Concurrent with the verification and validation of chemical data, the NSS-I geographic data underwent a separate verification and validation process that examined data associated with the Stage I and II selection process, as well as data from reaches as they were sampled (e.g., elevation of actual sampling location versus intended location). The verification and validation of the geographic data included:

1. Comparison of total drainage area to sum of a_1, a_2, and a_3
2. Comparison of Stage I reach order to Shreve order
3. Comparison of Shreve versus Strahler orders
4. Examination of headwater reach length, watershed area, and order
5. Comparison of upper and lower node elevations
6. Comparison of Stage I and II geographic data versus geographic data of sites as sampled

3.8.4 Enhanced Data (Data Set 4)

An important aim of the NSS-I data base development process was the creation of a data base that could be used to calculate population estimates. This was accomplished by using a single index observation for each sample node (upstream and downstream). In cases where there were multiple visits, as in the mid-Atlantic, the index value was calculated as the average of the values reported from the separate visits. The mean of multiple pH values was calculated as the mean of hydrogen ion and converted into pH.

The calculation of population estimates and their confidence bounds is difficult if there are inconsistencies in the data (e.g., missing values). A final data set was prepared to resolve problems with erroneous data and missing values in the validated data set. When it was necessary, substitutions were performed according to the following criteria:

1. Values from duplicate samples were used whenever possible.

2. If a duplicate measurement was not available, a value from an alternate visit to the site was used.

3. If a duplicate measurement or a measurement from an alternate visit was not available, a substitution value was calculated by means of a linear regression model or ion balance estimate. This was done by calculating a predicted value based on observed relationships with other chemical variables or predicting a value based on relationships between upstream and downstream observations of the same chemical variable.

All substitute values were examined for acceptability before they were included in the final data set. In addition to the substitute values that were calculated, negative values for parameters other then ANC and base neutralizing capacity (BNC) were set equal to zero. All values modified in the final data set were flagged. Streams considered to be noninterest were flagged in a manner by which they could be excluded when using the enhanced data set for making regional estimates of the target population.

The NSS-I data base development process focused on providing data for calculating estimates of characteristics of the target stream population. The enhanced data set was structured in such a way to allow the easy inclusion or exclusion of data from noninterest (or nontarget) sites (e.g., tidal influence or acid mine drainage) in statistical analyses (Section 5.2). This is done by using a drop code variable (DRPCDE) as a criterion to subset data for making extensive estimates of NSS-I target population of streams. In addition, estimates can be made for the target population plus streams that did not meet exclusion criteria (i.e., those sites identified as noninterest). The drop codes are encoded as follows:

Drop Code	Exclusion Criteria Description
5	NSS-I special interest sites (Section 2.6).
4	Pilot Survey nonindex data (subsection 1.3.2.1).
3	Sites impacted by acid mine drainage (subsection 9.3.1).
2	Noninterest sites (Section 3.2).
1	Alternate node of noninterest site (discussion follows).
.	NSS-I target observation for both the upper and lower node.

The extensive estimates presented in Volume II exclude observations with exclusion criteria of "2" or greater. The data base and drop code variable allowed calculation of extensive estimates of upper and lower stream nodes as separate populations. However, in order to perform analyses requiring matched upper and lower node (e.g., interpolated length estimates), the data must be subset to remove observations that have a DRPCDE value of "1" or greater. The resulting data subset contains only data for sites that have matching upper and lower node observations.

Table 3-8 summarizes the total number of numeric changes to chemical variables during the NSS-I verification, validation, and enhancement process. The verification data include all samples--routine, duplicate, processing laboratory duplicate, audit, and blank. There was a total of 56,019 values. As a result of verification, 9,052 changes (16.2% of the data) were made. The changes were associated primarily with the following:

1. All alkalinity and acidity were recalculated after a refinement in the Gran titration regression curve fitting program.
2. Processing laboratory conductivity was recalculated for temperature compensation.
3. Chemical reanalyses were performed by the analytical laboratories.
4. Corrections were made to blank data reported from analytical laboratories.

Only data from routine and duplicate samples were examined during the validation process. Of these 44,975 values, 83 (less than 0.5% of the data base) were flagged. Only 34 values were actually substituted (enhanced) in data set 4. Of the 34 replaced values, 13 were replaced with data from an alternate visit. The remaining 14 values were replaced using multiple linear regression and ion balances. An additional step in creating data set 4 was the scoring of impossible negative values to zero for variables other than ANC and BNC. A total of 225 values (0.5%) of the data base) across 9 variables (extractable aluminum, total aluminum, DOC, iron, manganese, ammonium, nitrate, total dissolved phosphorus, and silica) had values scored to zero, with total dissolved phosphorus having the most scoring changes, at 99 values. The bias due to this adjustment did not affect the population estimates presented in this report.

Table 3-8. Numeric Changes Made in the NSS-I Data Base as a Result of Verification and Validation

Variable		No. of Numeric Changes from Verification	No. of Numeric Changes from Validation	No. of Numeric Changes from Enhancement
ACCO11	BNC	1642	0	0
ALDS16	Monomeric Al (PCV)	7	0	1
ALEX16	Extractable Al (MIBK)	4	7	0
ALKA11	ANC	1626	0	1
ALOR16	Nonexch. Monomeric Al (PCV)	11	2	1
ALTL16	Total Al	1298	0	1
CA16	Calcium	594	0	1
CL16	Chloride	10	0	1
COLVAL	True Color	3	0	0
COND11	Conductivity, Analytical Lab	19	1	2
CONIS	Conductivity, in situ	1	2	1
CONVAL	Conductivity, Processing Lab	1358	2	0
DICE11	DIC, air equilibrated	17	13	2
DICI11	DIC, initial	9	0	1
DICVAL	DIC, closed system	5	0	2
DO_IS	Dissolved Oxygen	0	0	6
DOC11	DOC	0	0	1
FE16	Iron	8	0	1
FTL16	Fluoride	6	0	0
K16	Potassium	92	0	0
MG16	Magnesium	65	0	0
MN16	Manganese	37	0	0
NA16	Sodium	4	0	1
NH416	Ammonium	369	45	2
NO316	Nitrate	17	0	2
PH_R	pH, in situ	0	1	0
PHAC11	pH, initial BNC	1073	0	0
PHAL11	pH, initial ANC	1072	0	0
PHEQ11	pH, air equilibrated	1	0	2
PHSTVL	pH, closed system	21	0	0
PTD16	Total Dissolved Phosphorus	72	0	0
SIO216	Silica	904	0	1
SO416	Sulfate	28	0	2
TURVAL	Turbidity	9	1	2

3.9 DIFFERENCES BETWEEN THE NSS-I AND THE PILOT SURVEY

A number of changes in methods and procedures were made for the NSS-I as a result of the Pilot Survey. Table 3-9 summarizes these changes.

3.9.1 Sample Holding Times - 24 Hours (NSS-I) vs. 12 Hours (Pilot Survey)

Holding times for Cubitainer and syringe samples (before aliquots were prepared and samples were analyzed upon arrival at the processing laboratories) were increased from 12 hours in the Pilot Survey to 24 hours in the NSS-I. The decision to increase sample holding times was based on the results of two experiments (Messer et al., 1986): (1) a laboratory study of CO_2 impermeability in syringe sample containers (Burke and Hillman, 1987) and (2) a field study of Cubitainer sample holding times (Stapanian et al., 1987; Knapp et al., 1987). Syringe experiments determined that holding times for DIC and pH held in syringes at 4°C, could be increased to 24 hours without significant change in these variables. Since pH changes and CO_2 degassing appear to be the most significant causes of changes in aluminum speciation, it was assumed that syringes for aluminum extraction can also be held for 24 hours. These Cubitainer experiments also demonstrated that increasing holding times to as much as 24 hours would not have a significant effect on determinations of the chemical characteristics involved.

3.9.2 Processing Laboratory Location

Because of the increased holding time criteria for syringes and Cubitainers during NSS-I, sample processing (aliquot preparation, preservation, and preliminary analyses) was centralized at the U.S. EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada. The relocation of the processing laboratory to a centralized location provided savings in resources and better QC, compared to the decentralized deployment of the laboratories at locations in the NSS-I subregions.

3.9.3 Field pH Measurement

Comparisons of closed- and open-system measurements made during the NSS-I Pilot Survey (Messer et al., 1986) indicated high comparability between the two field pH measurements and the processing laboratory pH measurements. The logistically simpler and less time-consuming open-system measurement was chosen to determine field pH for NSS-I.

3.9.4 Methods of Fractionation and Determination of Aluminum Species

A semi-automated colorimetric method for fractionation and determination of aluminum species (complexation with pyrocatechol violet) was used during the NSS-I because it was expected to be less expensive, less time consuming, and more reproducible than the 8-oxine method used during the NSS-I Pilot Survey (Messer et al., 1986). Automation of this method reduced the variability among analysts and eliminated the problems of reproducibility and precise timing inherent in the manual 8-oxine method. However, since the large-scale application of this method was being developed at EMSL-Las Vegas, total extractable aluminum measurements using the MIBK method were also continued throughout the NSS-I to permit comparison.

Table 3-9. Differences Between NSS-I and the Pilot Survey

Technique	Pilot	Phase I
Sample holding times	12 hours	24 hours
Processing laboratory location	Within subregion	Centralized at EMSL - Las Vegas
Field pH	Closed system	Open system
Methods of fractionation and determination of aluminum species	8-oxine method	Colormetric (pyrocatechol violet)
Matrix spike QC samples	Used	Not used
Phosphorus measurement	Unfiltered total phosphorus	Filtered dissolved phosphorus
Specific conductance in processing laboratory	Not measured	Measured

3.9.5 Matrix Spike Quality Assurance Samples

The purpose of the matrix spike samples was to establish a concentration matrix, similar to that of the samples collected, which could be used to verify the accuracy of analysis. An aliquot of a sample was spiked with a known quantity of analyte prior to analysis. The percentage of spiked analyte recovered (percent recovery) determined whether or not there was a matrix effect on the original sample. During the NSS-I Pilot Survey, the limits for spike recovery were met for every batch and no matrix interferences were observed (Drouse et al., 1987). In addition, matrix spike analyses from the Eastern and Western Lake Surveys showed no matrix interference. Because these QC samples did not appear to provide any additional information about the quality of the data, matrix spike samples were not used in the NSS-I full survey.

3.9.6 Total Dissolved Phosphorus (NSS-I) vs. Total Phosphorus (Pilot)

Recent studies (e.g., Young et al., 1985), have shown that particulate-bound phosphorus tends to have a wide range of bioavailability, depending on its source. Soluble (filterable) phosphorus, rather than total (unfiltered) phosphorus was selected for the NSS-I in order to provide a better measure of biologically active phosphorus.

3.9.7 Specific Conductance Measured in the Processing Laboratory for NSS-I

During both the Pilot Survey and the NSS-I, specific conductance was measured in the field and at the analytical laboratories. Since the equipment for the specific conductance measurement was already available in the processing laboratory, an additional conductivity measurement was made during the NSS-I to provide another comparison for the data user.

SECTION 4
DATA QUALITY ASSESSMENT

4.1 INTRODUCTION

An important objective of the National Stream Survey - Phase I (NSS-I) is that the data be of high quality, have low and quantifiable analytical error, have known precision, and be representative of the state-of-the-art attainable in high-volume contract analytical laboratories. The quality assurance and quality control (QA/QC) program of the NSS-I was designed to maximize the utility of the collected data and to minimize the likelihood of erroneous chemical data. This was accomplished through the establishment of data quality objectives (DQOs), which were used as guidelines in maintaining a high level of data integrity during the sampling, analysis, and data collection and recording.

This section describes the analytical approach, results, and conclusions for each of the five aspects of data quality (completeness, comparability, representativeness, accuracy, and precision), plus detectability, applicable to NSS-I data. Detectability was also analyzed because the low ionic strength of many of the NSS-I samples necessitated an evaluation of the background levels of analytes. For detectability, accuracy, and precision, data were evaluated at two levels. The analytical (method) level, for which specific target values or DQOs were identified for each analyte, evaluates performance of the measurement system under a high degree of process control. The second, or system level, for which target values were not specifically defined, was intended to evaluate the additional effects that the sampling design, sample collection, and sample handling and processing had on the analytical results.

Representativeness, completeness, and comparability were considered important data quality goals in the development of the statistical sampling design of the NSS-I and the QA plan. They were affected by uncontrollable events that influenced the number of samples actually collected and analyzed by the proper protocols during the course of the survey. Detectability, accuracy, and precision were quantitatively assessed by using the analytical results from QC samples.

Analysis of the QC samples (blanks, performance audits, and duplicates) described in Section 3.3 provided two kinds of information for the assessment of data quality. Sampling and laboratory performance could be gauged against the DQOs established for precision, accuracy, and detectability. In addition, unforeseen effects of the collection and measurement process on analytical results could be quantified and their impact on data interpretation discerned. For example, the addition of background levels of an analyte during sample collection and subsequent handling hinders the comparison and interpretation of data from streams having naturally low levels of that analyte. Interlaboratory bias also can confound statistical comparisons of data, because true differences may not be distinguishable from differences resulting from systematic measurement errors at the different laboratories.

4.2 COMPLETENESS

Of the 504 stream reaches initially selected for sampling, 500 (99%) were actually visited in the field. Four reaches were not sampled because of access permission difficulties or physical inaccessibility (two in the Southern Appalachians and two in Florida). Water samples were not collected from 39 upstream reach nodes and 39 downstream reach nodes because they were classified as noninterest sites at the time they were visited (subsections 3.2, 5.2; Hagley et al., 1988). In the context of the NSS-I statistical design, sampling is accomplished by visiting the stream and determining its target (interest) status, regardless of whether water samples were collected.

Thus, samples were collected from the required number of reaches for each sampling stratum in all subregions.

Of the 1,651 water samples collected during the NSS-I, 1,613 (97.7%) were analyzed for all physico-chemical variables. Missing or unacceptable values were replaced during data enhancement (subsection 3.8.4). Of the 31,185 chemical numeric values in the data base, only 34 were replaced in the enhanced data base (Table 3-8). The NSS-I data base has been shown to be sufficiently complete (both in terms of spatial representation and chemical completeness) to provide representative spring baseflow chemical indices to estimate the chemical status of streams as described in Sections 6 through 10.

4.3 COMPARABILITY

All the NSS-I field crews and laboratory personnel used standardized protocols (Hagley et al., 1988; Hillman et al., 1987), which maximized internal comparability within given streams or subregions. Similarly, the use of these standardized methods, combined with the quantitative results of QC sample analysis (Cougan et al., 1988), facilitated comparison with data from other studies, such as the National Lake Survey (NLS) (Linthurst et al., 1986; Landers et al., 1987), and detailed process oriented studies on NSS-I special interest site streams.

4.4 REPRESENTATIVENESS

Representativeness can be viewed in a hierarchical manner from specific analyses to the gereral representativeness of the group of sample streams. At the lowest level (analytical), representativeness refers to how well the chemical and physical analyses reflect chemical conditions in the stream at the instant of sampling. Analytical representativeness is largely defined by how well the analytical measurements reflect chemical conditions in the sample of water taken from the stream. This aspect of data quality is discussed under the subheadings of accuracy, bias, and precision (Sections 4.6, 4.7, and 4.8). An additional aspect of analytical representativeness is the degree to which the chosen set of chemical analyses describes the water in question. To assess acid deposition effects, we must be concerned primarily with major constituents of water chemistry that affect geochemical interpretation and toxicity to aquatic biota at low pH. Representativeness with regard to geochemical interpretation can be evaluated by examining the completeness of the analyses, that is, how well the anions and cations balance (subsection 4.9.1), how well the calculated conductivity agrees with that actually measured (subsection 4.9.2), and how well the calculated carbonate alkalinity agrees with that measured by Gran titration (subsection 4.9.3).

At a higher level (system level), the concept of representativeness refers to how well a water sample characterizes a specific reach of a particular stream. Representativeness in this context is influenced by the location of the sampling site within the reach, the specific location (or microhabitat) from which the sample was collected, and the local conditions at the time of collection. Standardized collection protocols directed sampling crews to collect the samples as near as possible to the upper and lower nodes of a reach, while avoiding areas influenced by tributary inflow or estuaries. Samples were collected in mid-stream from areas of flowing water to maximize sample representativeness. Sampling crews were instructed not to collect samples during precipitation events. Water samples are intended, therefore, to be representative of spring season base flow.

At the population level, representativeness refers to whether the NSS-I sample reaches were representative of the target population as a whole. The probability sampling design

employed by the NSS-I minimizes the likelihood of substantial bias that might result from seriously undersampling any particular geographic area or class of streams. The temporal and spatial aspects of the NSS-I sampling design are discussed in Section 2; the design and its implementation are believed to have produced data representative of spring season baseflow conditions in the target population.

4.5 DETECTABILITY

4.5.1 Method Level Detectability

Indices of detectability were calculated for the NSS-I at both the method level and the system level. Estimates of method level detectability were calculated from the results of calibration or reagent blank analyses. Limits of detection were estimated following the approach advocated by the American Chemical Society (Keith et al., 1983), based on the analyses of blank samples. The limit of detection was estimated as three times the standard deviation of blank sample measurements.

The NSS-I QA report (Cougan et al., 1988) evaluates method level detectability at each laboratory. Detectability for all variables except total aluminum and silica measured at one analytical laboratory were within the DQOs. Appendix A (Table A-1) contains the DQOs for each analyte. For reference, Appendix A (Table A-2) presents data from laboratory blank sample analyses and calculated method detection limits for all NSS-I chemical variables. Method level detectability primarily evaluates the degree to which analytical methods limit the overall ability of the sampling analysis system to detect analytes. System level detectablility includes the effects of data collection and processing, in addition to the limitation of the analytical methods, and thus is of greater interpretive value in relation to the distribution of chemistry in the regional stream populations.

4.5.2 System Level Detectability

Background levels of analyte added during the collection or handling of samples were estimated by computing a system decision limit (SDL). The SDL was estimated as the 95th percentile of the distribution of field blank measurements. The SDL represents the lowest measured quantity of analyte that can be distinguished (with 95% confidence) from the distribution of field blank measurements.

DQOs were not defined for system level detectability. SDLs (Table 4-1) were initially compared to method level decision limits to determine if the handling and processing of field blanks had resulted in the addition of analyte to the blank samples. SDLs for almost all NSS-I chemical variables were less than three times the method level limits of detection (Appendix A, Table A-2), indicating that background contamination was not a serious problem. Problems are not apparent with either detection or contamination in the analysis of the major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (SO_4^{2-}, NO_3^{-}, Cl^{-}). The SDLs (95th percentile of field blanks) for these ions were all ≤ 1 μeq L^{-1} (Table 4-1). SDLs and median field blank values for all NSS-I chemical variables are listed in Appendix A (Table A-3).

For extractable aluminum, DOC, and nitrate, SDLs were between three and four times the method limit of detection. In the case of extractable aluminum, the SDL (0.30 μM) is near the DQO for detectability (0.19 μM), and no data quality problem is indicated. For DOC, the background level (SDL = 0.45 mg L^{-1}) is low enough not to seriously impact data interpretation.

Table 4-1. Estimates of SDLs for the Primary NSS-I Chemical Variables Based on Analyses of Field Blank Samples Pooled Across Laboratories.

Variable	n	Median Field Blank Concentration	System Decision* Limit (SDL)
Aluminum (μM)			
Total	61	0.37	1.0
Extractable	61	0.04	0.30
Monomeric Aluminum (μM)			
Total	61	0.37	0.63
Nonexchangeable	61	0.52	0.93
Ca^{2+} (μeq L^{-1})	62	< 0.50	1.0
Cl^- (μeq L^{-1})	63	< 0.28	0.85
Conductivity (μS cm^{-1})	63	0.98	1.2
DOC (mg L^{-1})	63	0.17	0.45
K^+(μeq L^{-1})	62	< 0.26	0.41
Mg^{2+} (μeq L^{-1})	62	< 0.82	< 0.82
Na^+ (μeq L^{-1})	62	< 0.44	0.52
NO_3^- (μeq L^{-1})	62	0.08	0.56
SO_4^{2-} (μeq L^{-1})	63	0.21	1.0

*The system decision limit was estimated as the 95th percentile of field blank measurements.

Data for all NSS-I chemical variables is given in Appendix A (Table A-3).

The SDL for nitrate (0.56 μeq L^{-1}) was apparently affected by occasional contamination at the processing laboratory (Cougan et al., 1988). However the SDL is still very low and should not seriously affect data interpretation.

System level decision limits should be considered in the interpretation of chemical distributions in NSS-I regional stream populations. Population estimates of stream resources with concentrations at or below the SDL should be interpreted with caution. There can be little confidence that values reported at these very low analyte levels are significantly different from zero. It is likely, in fact, that variations in the distributions of observed values less than the SDL are artifacts of sample collection, handling, and analysis. For the same reason, groups of streams characterized by analyte levels below system decision limits should not be compared.

4.6 ACCURACY

4.6.1 Accuracy Within Laboratories

Accuracy within each of the laboratories was evaluated using the results from performance audit samples. Although not certified standard solutions, the performance audit samples provided a good means of understanding possible systematic errors. Data should not be corrected on the basis of the accuracy estimates presented here, but data interpretation should be conducted considering the potential for systematic errors in cases where estimates of accuracy are poor. Accuracy was estimated as percent accuracy for all analytes except pH by:

$$\text{Accuracy} = [(x - R)/R] \times 100$$

where x equals the mean of the measured values in an audit sample, and R equals the theoretical value, or an index value based on measured values at the laboratory where audit samples were prepared.

For pH, accuracy was expressed as the difference between the measured value and the index value. Negative estimates of accuracy imply that measured values were less than index values; positive estimates of accuracy imply that measured values were greater than index values.

Within-laboratory accuracy estimates for all chemical variables are detailed in Cougan et al. (1988), and are listed for each analytical laboratory in Appendix A (Tables A-4 and A-5). Accuracy estimates for specific conductance and calcium measured at laboratory #1 were not within the stated DQOs but the observed differences from the theoretical values were small (approximately 2 μS cm^{-1} for conductivity, 1.5 μeq L^{-1} for calcium). At the other analytical laboratory (#2), the accuracy estimates for DOC were not within the stated DQOs. The observed difference from the theoretical value for DOC was 0.3 mg L^{-1} and 0.1 mg L^{-1} in the two audit lots (Appendix A, Table A-5). Accuracy estimates were within the stated DQOs for all of the other primary NSS-I analytes.

4.6.2 Pooled Accuracy Estimates

Estimates of percent accuracy (pooled across lot and laboratory) for the primary NSS-I chemical variables (Table 4-2) showed that accuracy was good for the major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (SO_4^{2-}, NO_3^{-}, Cl^{-}). All of these ions had pooled percent accuracies less than 5%. All the synthetic audit samples for the aluminum species had significant deviations from the theoretical value. The theoretical value (0.74 μM), however, is close to the

Table 4-2. Percent Accuracy Estimates for the Primary NSS-I Chemical Variables Based on Synthetic Audit Samples Pooled Across Analytical Laboratories

Variable	Theoretical# Value	Measured Audit Value: Mean	Standard Deviation	n	Percent Accuracy	Data Quality Objective
Aluminum (μM)						
Total - Lot 14	0.74	1.26	0.823	19	70.3	10,20[a]
Total - Lot 15	0.74	1.11	0.267	31	50.0	10,20[a]
Extractable - Lot 14	0.74	0.889	0.393	9	20.1	10,20[a]
Extractable - Lot 15	0.74	0.556	0.074	26	-24.9	10,20[a]
ANC (μeq L^{-1})	106 $	114	8.75	56	7.55	10
Ca^{2+} (μeq L^{-1})	9.68	9.48	1.55	56	-2.07	10
Cl^- (μeq L^{-1})	9.67	9.31	0.818	56	-3.72	10
Spec. Cond.-Lab (μS cm^{-1})	17.5	18.5	1.58	56	5.71	5
DIC-closed sys. (mg L^{-1})	0.959	1.40	0.046	14	46.0	10
DOC (mg L^{-1})	1.00	1.1	0.27	56	10.0	5,10[b]
K^+ (μeq L^{-1})	5.19	5.12	0.20	56	-1.35	10
Mg^{2+} (μeq L^{-1})	36.8	35.4	2.63	56	-3.80	10
Na^+ (μeq L^{-1})	120	119	4.31	56	-0.83	10
NO_3^- (μeq L^{-1})	7.53	7.56	0.645	55	0.40	10
SO_4^{2-} (μeq L^{-1})	47.5	46.8	2.73	56	-1.47	10
					Accuracy evaluated as pH difference	
pH (air equilibrated)	7.25$	7.23	0.179	56	-0.02	0.1
pH (closed system)	7.25$	6.94	0.085	14	-0.31	0.1

The theoretical value is the expected value of the synthetic audit sample assuming no preparation error and no external effect.

$ The theoretical value was determined by measurements made at the support laboratory that supplied the audit samples.

a Lower limit represents the accuracy DQO for [Al] > 0.37 μM while the upper limit is for [Al] < 0.37 uM.

b Lower limit represents the accuracy DQO for DOC > 5.0 mg L^{-1} while the upper limit is for DOC < 5.0 mg L^{-1}.

SDL for these species (0.3 - 1.0 μM). The amount of aluminum in the audit samples, therefore, is approximately the same concentration as that just discernable from blank values (with 95% confidence). Also, synthetic audit samples sent to the processing laboratory were subject to loss of aluminum due to adsorption or precipitation between the time of preparation and the time the sample was filtered and preserved (Cougan et al., 1988).

There was also a large deviation from the theoretical value for audit sample measurements of closed-system pH (-0.31 pH units) and DIC (0.441 mg L^{-1}; Table 4-2). It is likely that the DIC overestimation in the closed-system sample resulted in underestimation of closed-system pH audit values. The synthetic audit samples were very sensitive to changes in CO_2 concentration, indicating that the pH and DIC values would not necessarily be stable in the synthetic audit samples. Data from circumneutral Bagley Lake and acidic Big Moose Lake indicated no serious inaccuracy problem with pH measurements at either the analytical laboratories or the processing laboratory. Thus, the most probable source of the pH deviation is the introduction of CO_2 into the audit samples between measurement in the support laboratory and measurement in the processing laboratory. This explanation agrees with the observation that there was almost no pH deviation (-0.02 pH unit) in the air-equilibrated pH measurement (Table 4-2). Furthermore, the relationship between field site pH measurements and closed-system processing laboratory pH in the NSS-I data base was very good: $r^2 = 0.991$, $n = 1290$; the mean pH difference (processing lab pH - field pH) was -0.047; 71.3% of the pH differences were within 0.1 pH units and 93.6% were within 0.2 pH units. This comparison indicates that transport conditions and processing did not cause a large pH shift. The NSS-I method of using sealed syringes appears to have succeeded in preventing pH change due to CO_2 degassing. The failure of the support laboratory to use syringe sampling and transporting containers for the audit samples, as were used in the NSS-I, makes it likely that inaccuracies observed in the audit samples are not applicable to the routine NSS-I samples.

4.7 LABORATORY BIAS

Seven of the eight different groups of audit sample types analyzed during NSS-I were used to test interlaboratory bias. These audit samples included two lots of low concentration synthetic audit samples and two types of audit samples from natural lake systems (Bagley Lake in Washington and Big Moose Lake in New York). Each lot or type of audit sample consisted of both field and laboratory samples (Figure 3-3). One of the low synthetic audits was analyzed at only one of the contract laboratories, thus it could not be used for evaluating interlaboratory bias.

Edland et al. (1987) have developed model-based approaches, based on the results of NSS-I audit sample analyses, to evaluate and possibly correct for biases among the laboratories. The authors of that report, however, do not recommend indiscriminate application of their techniques to the NSS-I data. Any correction applied to the NSS-I data, based upon audit sample analyses, will have an unknown effect on data quality because there is no information on bias over the entire range of analyte levels in the NSS-I data. Because accuracy estimates for most variables were within or near their DQOs (Cougan et al., 1988), interlaboratory differences should not seriously affect most data interpretation activities. In cases where accuracy estimates were outside the DQOs, the potential bias was most important at low concentrations, and thus may be eclipsed by problems of analytical precision at concentration ranges close to the detection limit for certain variables (e.g., total aluminum and extractable aluminum). The estimates of among-batch precision presented in Section 4.8 include the effects of interlaboratory bias.

4.8 PRECISION

The precision associated with various components of the NSS-I collection and measurement system was evaluated using the analytical results of performance audit samples, analytical and processing laboratory duplicate pairs, and field duplicate sample pairs (Cougan et al., 1988). No QC sample type provided all the information necessary to calculate a completely satisfactory estimate of the total measurement error associated with the collection, processing, and analysis of samples during the NSS-I.

Analysis of laboratory duplicate sample pairs was used to estimate the measurement precision of a particular analytical methodology within a sample batch (operationally defined as method level precision). Analysis of field duplicate pairs provided an estimate of overall precision within a batch, including the effects of sample collection and processing (operationally defined as system level precision). Performance audit samples (both synthetic and natural) provided estimates of among-batch precision within a laboratory, and when pooled across the two laboratories, this included the effects of interlaboratory bias (operationally defined as among-batch precision). A batch refers to a batch of samples grouped together at the processing laboratory and kept together throughout the analytical process with the same batch ID.

Because of the dilute nature of the waters sampled during the NSS-I, a single estimate of pooled precision for the entire range of analyte values may be misleading because of the effects of concentration on precision. Model based approaches to estimating precision as a function of concentration (e.g., Mericas and Schonbrod, 1987) were not used because the range of concentrations represented by duplicate sample pairs was not evenly distributed over the entire range of measured values, and models may be unduly influenced by outlying measurements.

To minimize the effect of concentration on precision estimates, and to provide data users with estimates of precision relevant to particular ranges of interest, pooled precision estimates were calculated for subset ranges over the total range in analyte concentration. For some variables, the range subsets were defined in terms of biologically or chemically relevant limits, while for other variables the ranges are arbitrary. Scatterplots of the standard deviations of sample pairs versus mean concentration of a pair indicated that there were no trends in the relationship between concentration and variance within each range subset.

Data from both analytical laboratories were combined before calculating pooled precision estimates. A total of 68 laboratory duplicate pairs and 65 field duplicate pairs were analyzed for most analytes. Field or laboratory duplicate pairs having values identified as unacceptable during the verification process were not included in calculating precision estimates. For each range subset, precision was estimated as a pooled standard deviation based on the means and variances of the sample pairs included in that subset. The individual variances of each sample pair were summed to calculate a pooled variance, and a pooled standard deviation was calculated as the square root of the pooled variance divided by the sample size. The percent relative standard deviation (%RSD) was then calculated as:

$$\%RSD = \frac{\text{pooled standard deviation}}{\text{pooled mean.}} * 100$$

Method level estimates of precision were compared to the DQOs. For all variables, pooled method level precision estimates were within the DQOs for all range subsets greater than the SDL (Appendix A, Table A-6).

Pooled (across laboratory) system level and among-batch precision estimates and associated summary statistics for the primary NSS-I chemical analytes are presented in Table 4-3. Data for all NSS-I analytes is given in Appendix A (Table A-7). System level precision was estimated for all field duplicate measurements. The distribution of field duplicate pairs among concentration range subsets was not uniform because duplicate sample pairs were not purposefully selected to cover the concentration range of samples. For the among-batch estimates, when more than one audit sample type was present within a concentration subset, the sample type that had the largest %RSD is presented (Table 4-3).

At concentrations above the SDL, the %RSDs for the system level precision of the major cations and anions were all less than 5%, except for the lowest subranges where they were all less than 10% (Table 4-3). The %RSD tended to be higher in the lowest concentration range subset. At concentrations below the SDL, precision was usually poor (%RSD = 6% - 56%), as would be expected for samples at the detection limit. Values of %RSD were not calculated for pH and ANC because ANC can have a value of zero and pH values are logarithmic. Instead, pooled standard deviation values were used to evaluate precision. ANC had a system level precision of < 5 μeq L^{-1} for values less than zero and a precision of 6 - 8 μeq L^{-1} for values between 0 and 200 μeq L^{-1}. The system level pooled standard deviations for pH values below 6.0 were less than 0.1 pH unit, whereas at pH values greater than 6.0, they were less than 0.2 pH unit. Aluminum species and DOC had rather high %RSDs (15% - 36%) in concentration subsets just above their SDLs, indicating a lack of precision at these low concentrations. Total aluminum had %RSD greater than 22% in all concentration subsets; population estimates for total aluminum should be interpreted with this in mind.

Among-batch precision was estimated for each of the three different types of audit samples by pooling the measurements from both analytical laboratories. The among-batch precision was expressed as the standard deviation of the pooled measurements. Among-batch precision within each laboratory is discussed more fully in Cougan et al. (1988). In almost all concentration range subsets, for all variables, the among-batch variance estimates (pooled standard deviations) were larger than the corresponding system level (within batch) precision estimates. This finding suggests that variation among batches within a laboratory, or among laboratories, contributed more to overall measurement error than sample collection or processing. These differences result from differences in calibrations from batch to batch (day to day), either within a laboratory or among laboratories. Aluminum species and DOC had relatively high among-batch %RSD (> 20%) in the lower concentration range subsets (Table 4-3). The poor among-batch precision for DOC and aluminum is in a large part due to their poor within-batch precision.

Above the SDL, all of the among-batch %RSDs for the major cations and anions were less than 10% (Table 4-3), except for the lowest concentration range subset for calcium, chloride, conductivity, and closed system DIC (%RSD = 10% to 16%). A small interlaboratory bias (or between-batch bias within each laboratory) may exist at low concentrations for these analytes (1-2 μeq L^{-1} for Ca^{2+} and Cl^-; 2 μS cm^{-1} for conductivity; 0.06 mg L^{-1} for DIC). In general, the magnitude of interlaboratory bias does not appear to be an important problem in the NSS-I data base. For interpreting the NSS-I data, the most conservative estimate of precision (among-batch precision) should be used as the best estimate of measurement error, because it is the largest variance and it takes into account biases between laboratories.

Table 4-3. System Level and Among-Batch Precision Estimates for Primary NSS-I Chemical Variables

		System Level Precision#			Among-Batch Precision&			
Variable	Concentration Range Subset	Number of pairs	Pooled SD	%RSD	Number of samples	SD	%RSD	Sample type$
Total Aluminum (μM)	< 1.0 (SDL)	5	0.400	56.4	38	1.48	148	BL
	1.0 to 5.0	26	0.900	29.4	50	0.550	47.0	S
	5.0 to 10.0	14	1.38	22.0	--	--		
	> 10.0	20	5.75	31.5	37	0.945	9.3	BM
Extract. aluminum (μM)	< 0.30 (SDL)	34	0.0590	43.5	38	0.126	48.6	BL
	0.30 to 2.0	20	0.237	35.7	35	0.209	32.6	S
	> 2.0	11	0.523	6.9	37	1.22	15.3	BM
Total monomeric Alum. (μM)	< 0.63 (SDL)	35	0.0801	19.6	13	0.271	73.2	S
	0.63 to 2.0	19	0.143	16.9	--	--		
	> 2.0	11	0.178	2.5	24	0.434	6.0	BM
Nonexchang. monomeric Alum. (μM)	< 0.93 (SDL)	51	0.124	20.1	13	0.311	55.9	S
	> 0.93	14	0.263	14.9	24	0.471	21.9	BM
ANC ($\mu eq\ L^{-1}$)	< 0	7	2.94	--	39	4.88	--	BM
	0 to 50	9	7.83	--	--	--		
	50 to 200	20	6.10	--	38	11.73	--	BL
	> 200	29	13.7	--	--			
Ca^{2+} ($\mu eq\ L^{-1}$)	< 50	4	0.749	2.7	56	1.55	16.4	S
	50 to 250	35	2.84	2.2	39	3.84	4.1	BM
	250 to 500	19	4.49	1.3	--	--		
	> 500	7	80.0	5.6	--	--		
Cl^- ($\mu eq\ L^{-1}$)	< 30	8	0.508	2.6	39	1.44	11.9	BM
	30 to 55	18	0.931	2.2	--	--		
	55 to 150	24	1.21	1.4	--	--		
	150 to 275	6	2.06	1.0	--	--		
	> 275	9	20.7	4.0	--	--		

SDL = System decision limit.
%RSD = Percent relative standard deviation.
Overall within-batch precision calculated from field routine duplicate sample pairs.
& Among-batch precision calculated from performance audit samples.
$ Audit sample types from which precision estimate was derived. S = Synthetic audit sample; BL = Bagley Lake natural audit sample; BM = Big Moose Lake natural audit sample.

Table 4-3. System Level and Among-Batch Precision Estimates for Primary NSS-I Chemical Variables (Continued)

		System Level Precision#			Among-Batch Precision&			
Variable	Concentration Range Subset	Number of pairs	Pooled SD	%RSD	Number of samples	SD	%RSD	Sample type$
Spec. Cond	< 25	6	0.87	4.2	38	1.91	14.6	BL
Lab Value	25 to 50	24	0.27	0.7	39	0.89	3.6	BM
(μS cm^{-1})	50 to 100	24	0.42	0.6	--	--		
	> 100	11	1.22	0.6	--	--		
DIC	< 1.0	7	0.020	4.3	27	0.062	11.7	BM
Closed	1.0 to 2.0	9	0.063	4.4	27	0.061	3.6	BL
System	2.0 to 5.0	31	0.092	2.7	--	--		
(mg L^{-1})	5.0 to 10.0	13	0.184	2.8	--	--		
	> 10.0	5	0.365	1.5	--	--		
DOC	< 0.45 (SDL)	2	0.02	6.1	39	0.42	105	BL
(mg L^{-1})	0.45 to 2.0	41	0.24	20.8	56	0.27	24.5	S
	2.0 to 5.0	15	0.44	14.3	39	0.28	7.2	BM
	5.0 to 10.0	7	0.58	8.1	--	--		
K^+	< 10	8	0.0824	1.3	39	0.409	5.3	BL
(μeq L^{-1})	10 to 25	20	0.346	2.2	39	0.563	5.1	BM
	25 to 50	28	0.773	2.2	--	--		
	> 50	9	3.60	4.4	--	--		
Mg^{2+}	< 80	19	1.07	2.0	56	2.63	7.4	S
(μeq L^{-1})	80 to 160	23	1.15	0.9	--	--		
	160 to 400	18	4.77	1.9	--	--		
	> 400	5	19.9	2.6	--	--		
Na^+	< 20	4	0.0435	0.5	--	--		
(μeq L^{-1})	20 to 42	4	1.30	3.6	39	1.83	4.9	BL
	42 to 90	24	1.22	1.9	--	--		
	90 to 225	25	1.61	1.1	56	4.31	3.6	S
	> 225	8	4.22	1.0	--	--		

SDL = System decision limit.
%RSD = Percent relative standard deviation.
Overall within-batch precision calculated from field routine duplicate sample pairs.
& Among-batch precision calculated from performance audit samples.
$ Audit sample types from which precision estimate was derived. S = Synthetic audit sample; BL = Bagley Lake natural audit sample; BM = Big Moose Lake natural audit sample.

Table 4-3. System Level and Among-Batch Precision Estimates for Primary NSS-I Chemical Variables (Continued)

		System Level Precision#			Among-Batch Precision&			
Variable	Concentration Range Subset	Number of pairs	Pooled SD	%RSD	Number of samples	SD	%RSD	Sample type$
NO_3^-	< 0.56 (SDL)	8	0.0660	24.0	38	0.305	158	BL
(μeq L^{-1})	0.56 to 50	45	0.739	5.7	55	0.645	8.5	S
	> 50	12	5.22	2.2	--	--		
pH	4.00 to 5.00	6	0.032	--	--	--		
Proc. Lab	5.00 to 6.00	13	0.036	--	27	0.059	--	BM
Closed	6.00 to 7.00	24	0.036	--	14	0.085	--	S
System	7.00 to 8.00	19	0.036	--	27	0.049	--	BL
	>8.00	3	0.026	--	--	--		
pH	4.00 to 5.00	6	0.017	--	--	--		
Anal. Lab	5.00 to 6.00	4	0.041	--	39	0.071	--	BM
Air	6.00 to 7.00	11	0.113	--	--	--		
Equil.	7.00 to 8.00	40	0.171	--	56	0.179	--	S
	> 8.00	4	0.083	--	--	--		
SO_4^{2-}	< 50	18	1.10	3.6	56	2.73	5.8	S
(μeq L^{-1})	50 to 100	10	1.69	2.1	--	--		
	100 to 275	24	2.66	1.5	39	3.48	2.6	BM
	> 275	13	5.06	1.1	--	--		

SDL = System decision limit.
%RSD = Percent relative standard deviation.
Overall within-batch precision calculated from field routine duplicate sample pairs.
& Among-batch precision calculated from performance audit samples.
$ Audit sample types from which precision estimate was derived. S = Synthetic audit sample; BL = Bagley Lake natural audit sample; BM = Big Moose Lake natural audit sample.

4.9 CHEMICAL DATA QUALITY OVERVIEW

Another way to test the quality of the NSS-I chemical data is to examine the ionic relationships between the analytes in the data base. By examining the charge balance between anions and cations, measured versus calculated conductivity, and measured ANC versus calculated carbonate alkalinity (from DIC and pH), one can get an overall impression of the quality of the chemical data. The enhanced data set (data set 4, subsection 3.8.4) was used to make these comparisons, because it is the data set from which all of the results presented in this report are derived.

4.9.1 Charge Balance

Because of the electroneutrality constraint, the sum of positively charged ions (i.e., cations) in water must equal the sum of those with a negative charge (i.e., anions). Major discrepancies between the sum of measured anions and cations thus reflect analytical errors, failure to measure all ions with significant concentrations, or a combination of both. Although charge balances alone cannot identify the cause of a charge imbalance, they can serve as a QC check on the completeness and accuracy of the ion chemistry data.

To assess the quality of the data for the ionic species in water, ion charge balances, involving a comparison of the sum of cations and anions, were determined for all stream samples with chemical data. The sum of the cations is defined as the equivalent sum of Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+ + H^+, and the sum of anions is SO_4^{2-} + NO_3^- + Cl^- + F^- + (ANC + H^+). ANC + H^+ includes the carbonate protolytes (HCO_3^- + CO_3^{2-}), hydroxide (OH^-), plus any noncarbonate protolytes (e.g., weak organic anions, metal oxides) that react with hydrogen ions during the titration of ANC.

A charge balance plot for all NSS-I Mid-Atlantic and Southeast Screening stream samples is shown in Figure 4-1. Some deviation from the one-to-one line (i.e., y = x) is expected because the analytical errors associated with the measurement of the individual anions and cations are additive in the calculation of the sum of cations and anions. Although random analytical errors would tend to cancel in calculating the sum of anions or cations, the analytical accuracy and precision differ for each of the ions measured. Hence some charge imbalance may occur because of the differences in the analytical precision and accuracy between methods.

In most cases, the discrepancies in the charge balance are relatively small and are within the combined limits of precision of the analytical methods used to measure the respective ions. Percent ion balances ([cation sum - anion sum]/[cation sum + anion sum] * 100) were calculated for all of the NSS-I routine stream samples. Of the 1,342 samples, 86.4% had ion balance differences less than 5% and 94.7% had ion balance differences less than 10%. The charge balance plot, however, does show some bias, with more of the samples having an anion deficit (i.e., sum of cations > sum of anions) than a cation deficit. This bias suggests a small systematic analytical error (e.g., an underestimate of one or more anions or an overestimate of cations), failure to include one or more anions in the charge balance, or a combination of both.

Although the calculated charge balances do not include all ions that could potentially contribute to the sum of the cations and anions, those included generally contribute most of the total ionic strength in freshwater environments. Inorganic ions not included, such as phosphorus and trace metals, are generally present in low concentrations in most streams, and hence are not significant contributors to the total ionic concentration. Silica is not included in the charge balance, but this should not make a serious difference because in most natural waters, silica exists predominantly as o-silicic acid ($H_4Si(OH)_4$; Stumm and Morgan, 1981) and is not charged.

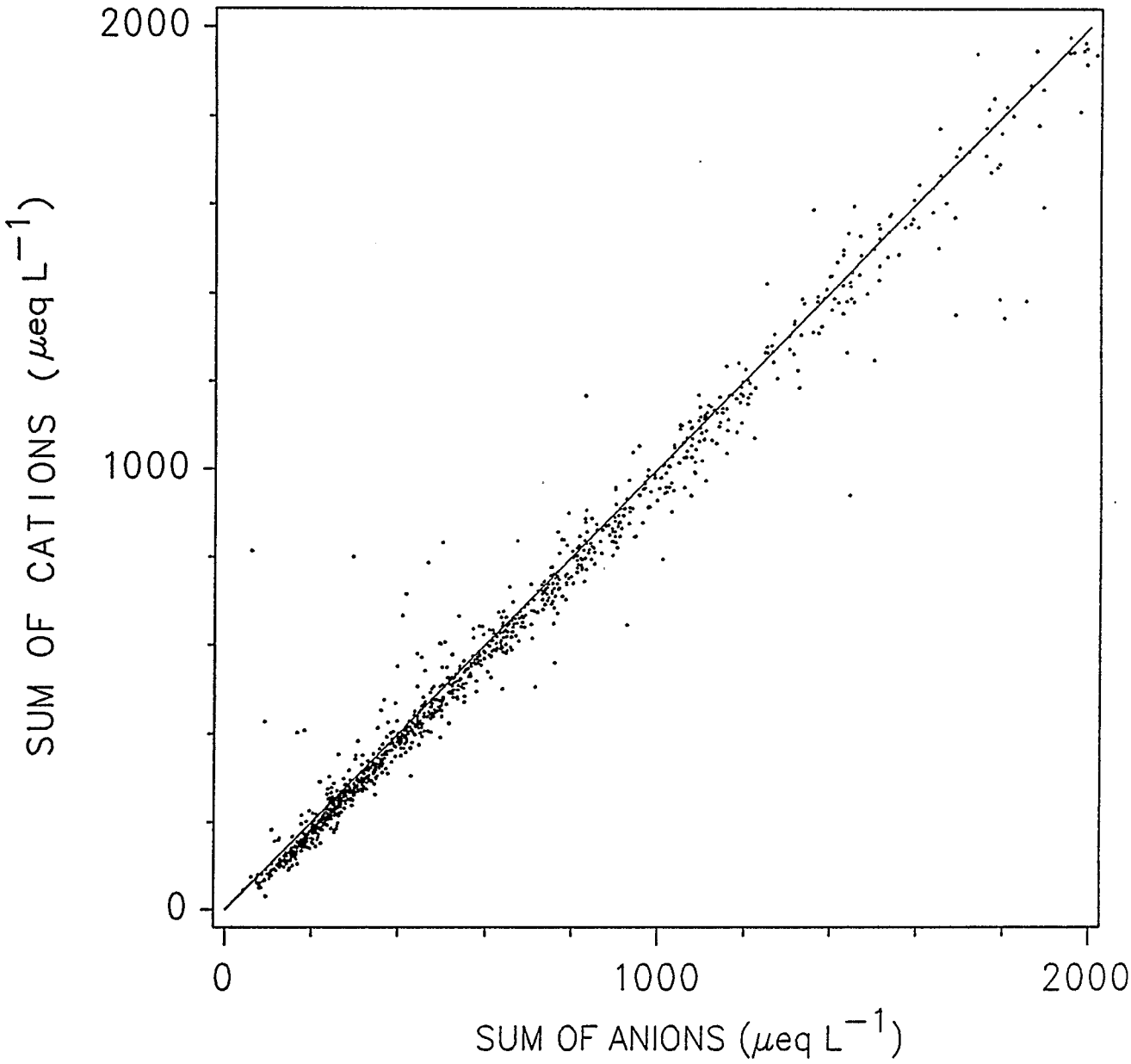

Figure 4-1. Charge balance plot for all NSS-I Mid-Atlantic and Southeast Screening streamwater samples. The line is y = x.

Aluminum, which becomes more soluble with decreasing pH, may be a major contributor to the cation sum in acidic environments. However, failure to include aluminum in the charge balance would most likely cause a cation deficit rather than an anion deficit because cationic species of aluminum [Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$] would be favored at the acidic pH where aluminum solubility is maximum. Thus, it is unlikely that failure to include silica, phosphorus, and trace metals in the cation and anion sums is the reason for the observed anion deficits. Aluminum, however, may account for some of the observed cation deficits.

Another potential cause of the observed anion deficits is unmeasured strong organic anions that do not react with hydrogen ions during the ANC titration. This deficit is particularly large (> 150 μeq L^{-1}) for some of the streams in Florida and in the Mid-Atlantic Coastal Plain (Figure 4-2). As discussed in Section 8.6, many of the streams in these two subregions have relatively high concentrations of DOC (median concentration of DOC at the upper and lower node of 8 and 4 mg L^{-1}, and 5 and 4 mg L^{-1} in Florida and the Mid-Atlantic Coastal Plain, respectively) compared to those in streams of the other subregions. Naturally occurring organic solutes can exhibit a wide range of dissociation constants (pK_a) and the extent to which they affect the charge balance of surface waters depends on their concentration in water, the pK_a of the organic acids, and the pH of the water. For example, naturally occurring organic acids that are strongly acidic (i.e., $pK_a < 4.0$) will behave like strong mineral acids, in that the protons are completely dissociated, resulting in a depression in the ANC. Because there is no direct measure of the anions associated with these strong organic acids, they are not included in the anion sum. Hence, if they are present in significant concentrations, anion deficits would exist.

Weak (nonprotolytic) organic acids ($pK_a > 5.0$) may also influence the ANC and the ionic strength of water, depending on their concentration and pK_a, and on the pH of the stream water. However, the anions of the weak organic acids that are titrated in the measurement of ANC would be included in the charge balance as noncarbonate ANC, and hence would not contribute to the observed anion deficits.

To assess whether anions of strong organic acids could account for the anion deficit in the streams in Florida and the Mid-Atlantic Coastal Plain, the calculated deficit was regressed against the measured DOC concentration in these two subregions (Figure 4-2). The latter was used as a surrogate variable for strong organic anions because there was no direct measurement of strong acid organic anions in NSS-I samples. The results for individual subregion/node regression showed that variation in the concentration of DOC accounts for a large percentage of the variation in the anion deficit among streams in Florida ($r^2 = 0.54$ and 0.87) and a smaller percentage in the Mid-Atlantic Coastal Plain ($r^2 = 0.33$ and 0.03 at the lower and upper nodes, respectively). This result is consistent with the conclusion that unmeasured organic anions that behave as strong mineral acids contribute to the observed anion deficit in many streams in these subregions. The contribution of strong and weak organic acids to the ANC and BNC in streams is discussed in more detail in Section 8.6.

In higher conductivity waters, not all of the ions that contribute to ionic strength were included in the calculated anion and cation sums. For example, acid mine drainage waters contain significant amounts of heavy metals (Fe, Mn, Cu, Pb, etc.) that may be responsible for some of the cation deficits observed in Figure 4-1 at high ionic strength. The exact speciation of iron, manganese, aluminum, and DOC was not measured in the NSS-I, so exact charge balances cannot be calculated using these species. Their equivalent strength, however, can be approximated. The charge balances were reanalyzed using approximations for iron, manganese, aluminum, and DOC. Organic anion equivalents were calculated from DOC using the Oliver model

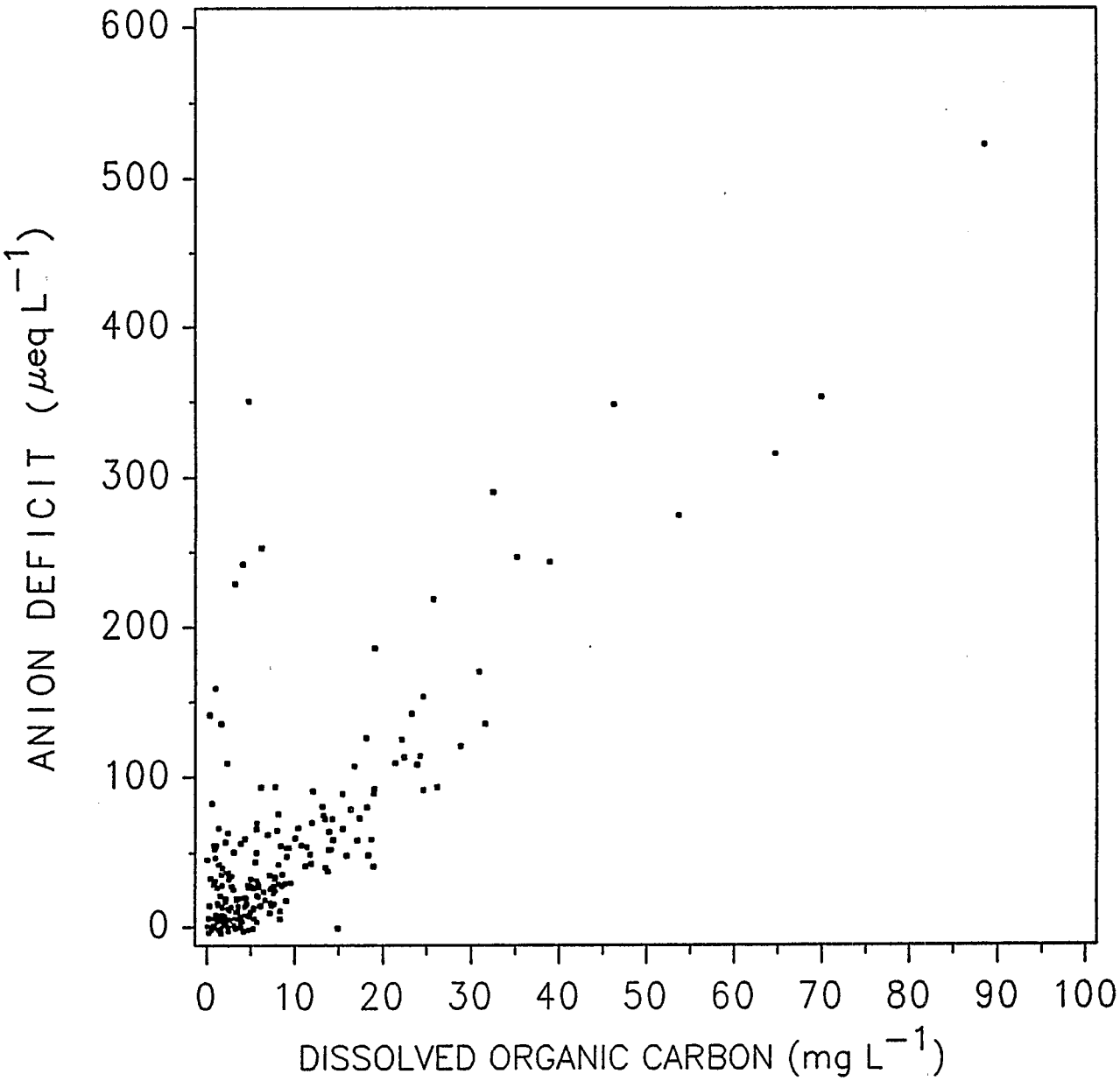

Figure 4-2. **Relationship between anion deficit and DOC for all NSS-I stream samples in Florida (3C) and the Mid-Atlantic Coastal Plain (3B).**

(Oliver et al., 1983). Iron and manganese equivalents were approximated from total dissolved iron and manganese measurements using a charge of +2. Aluminum equivalents were calculated from total aluminum measurements assuming an average charge of 0.87 per total aluminum ion (Driscoll et al., 1984). The (ANC + H^+) term was removed from the anion sum and replaced with measured values of HCO_3^-, CO_3^{2-}, and OH^- (calculated from pH and DIC measurements), because the organic component of ANC is now included in the Oliver model approximation.

In the new charge balance plot shown in Figure 4-3, which includes the approximations for DOC, Fe, Mn, and Al, deviations from the equality line were smaller at anion concentrations less than 1000 μeq L^{-1} than those present in the first charge balance plot (Figure 4-1). There were, however, larger deviations from equality at anion concentrations greater than 1000 μeq L^{-1}. The overall ion balance differences were roughly the same (95% of the samples had ion balance differences less than 10%) for both figures. The fact that the revised charge balance was better in dilute systems indicates that in these systems some of the charge balance discrepancies observed in Figure 4-1 were caused by not measuring all of the ions that contribute to ionic strength. It is likely that at high ionic strengths the approximations used in Figure 4-3 are less valid, causing the observed increase in charge balance deviations.

4.9.2 Calculated vs. Measured Conductance

The presence of ionic species in water increases the electrical conductance of that aquatic solution. Conductance, therefore, provides an indication of ion concentration. Further, since the relationship between ion concentration and specific conductance is known for most ionic species, the measured conductance of water samples can be used as an internal check on both the accuracy and the completeness of measurement of ionic species by comparing the measured and expected conductance. The expected conductance is calculated as the sum of the product of the ionic concentration and the molar conductivity (mho cm^{-2} mol^{-1}) of each of the measured ions in water. Because the molar conductivity constants are valid only in dilute (infinite dilution) solutions, they were corrected for concentration effects using the Debye-Hyckel-Onsager equation (Atkins, 1978):

$$M_c = M_c^\circ - (A + BM_c^\circ)\, C^{\frac{1}{2}}$$

where M_c is the corrected molar conductivity, M_c^o is the molar conductivity at infinite dilution, C is concentration, and A and B are constants. In water at 25°C, A equals 60.2 mho cm^2 $mol^{-1}/(mol\ L^{-1})^{\frac{1}{2}}$ and B equals 0.229 $(mol\ L^{-1})^{\frac{1}{2}}$.

A plot of the calculated vs. measured conductances for all NSS-I Mid-Atlantic and Southeast Screening stream samples is shown in Figure 4-4. Agreement between the expected (calculated) and observed conductance is excellent. The coefficient of variation (r^2) for the relationship was 0.987. The slope of the regression line was 0.981 (SE = 0.00314) and the y intercept was 4.87 (SE = 0.522). Differences between the observed and expected conductances can be attributed to analytical errors in the measurement of the ions or of the conductance (or both), the inclusion of electrostatically neutral species in the calculated conductance, or the failure to measure ions that may contribute to the total conductivity.

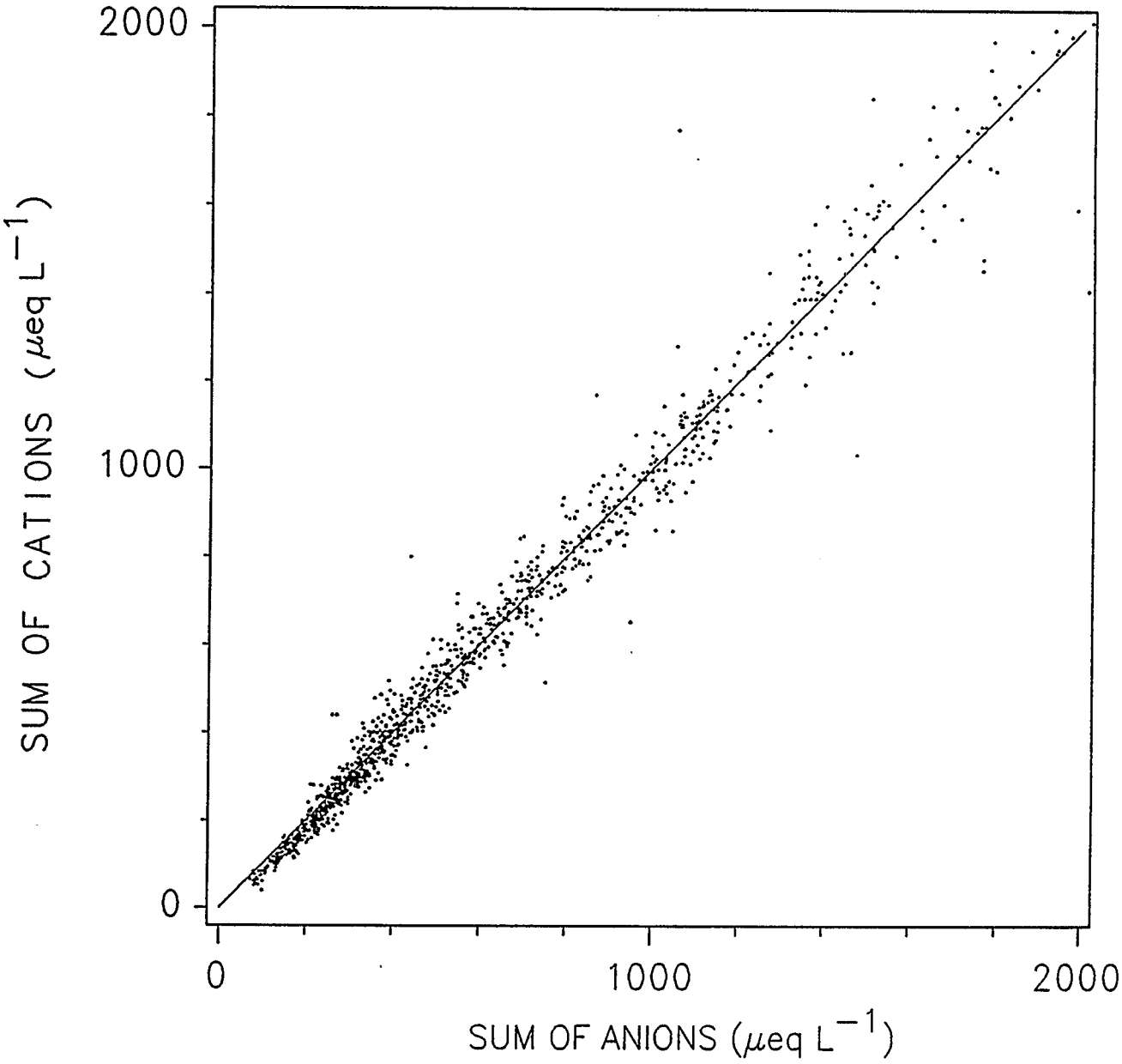

Figure 4-3. Charge balance plot for all NSS-I Mid-Atlantic and Southeast Screening samples that include approximated equivalent concentrations for DOC, Fe, Mn, and Al. The line is y = x.

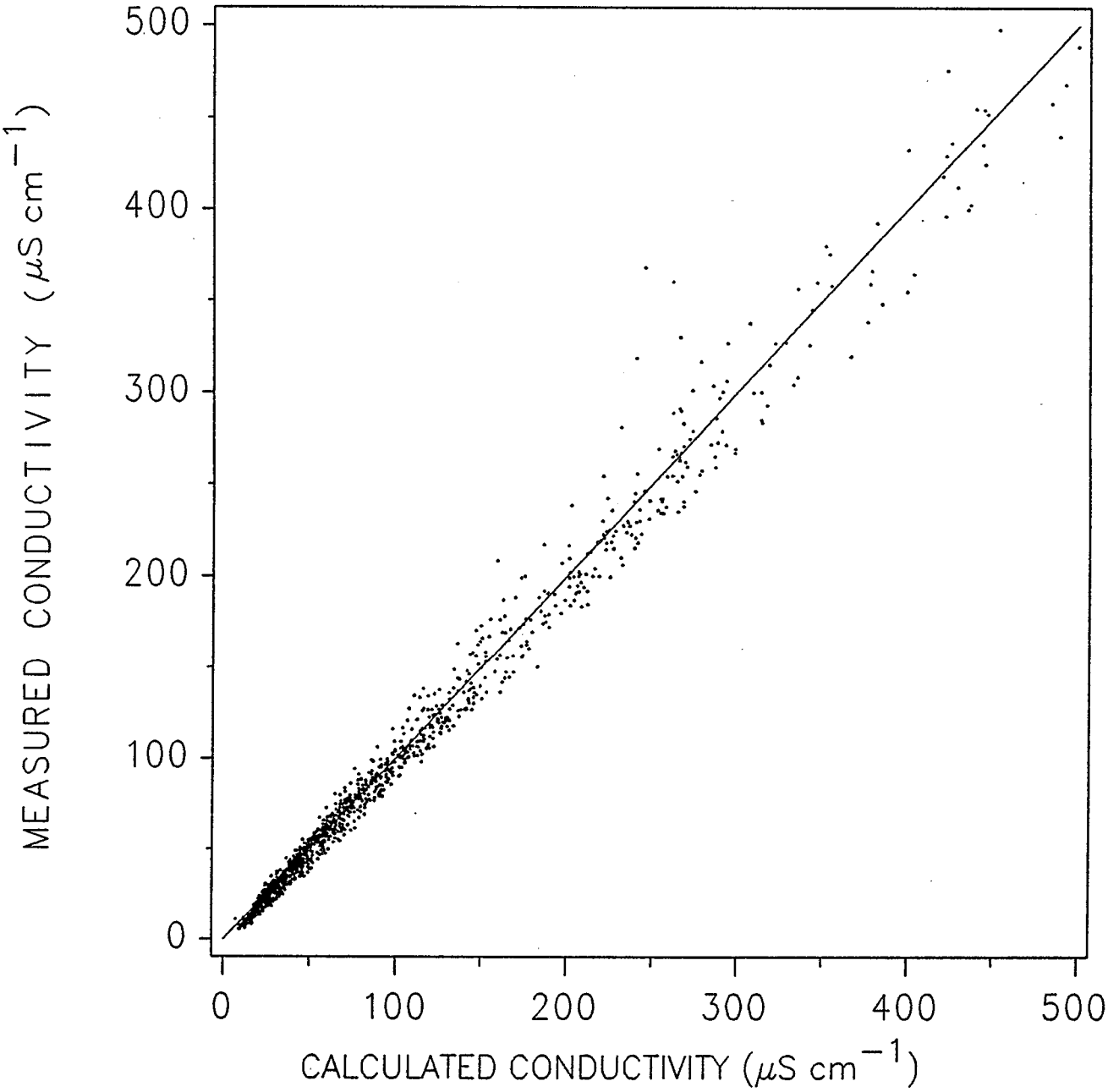

Figure 4-4. Measured vs. calculated conductance of NSS-I Mid-Atlantic and Southeast Screening stream water samples. The line is y = x.

4.9.3 Calculated vs Measured ANC

A third method for assessing the quality of the stream survey data involves comparisons of the calculated carbonate alkalinity with the measured ANC. The carbonate alkalinity is the protolyte (i.e., reacts with hydrogen ions) portion of the carbonate system only and is defined as

$$[Alk]_C = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+].$$

Carbonate alkalinity ($[Alk_C]$) was calculated from the initial pH and DIC concentration measured at the analytical laboratory (Hillman et al., 1987). ANC is a measure of the sum of protolytes for a defined pH titration range that includes the bicarbonate system. Thus [ANC] must be greater than or equal to $[Alk_C]$ because $[Alk_C]$ is a portion of the titrated [ANC]. Any discrepancy between the calculated carbonate alkalinity and the measured ANC must be due to analytical errors in the measurement of ANC, pH, or DIC, the presence of noncarbonate protolytes in the water, or a combination of both. Comparisons of the calculated alkalinity and measured ANC thus can serve as a QC check on the measured pH, DIC, and ANC.

Comparisons of the calculated carbonate alkalinity and the measured ANC for all NSS-I stream samples are shown in Figure 4-5. In general, the measured ANC is greater than or equal to the calculated carbonate alkalinity as indicated by the predominance of the data plotting on or below the one-to-one line. Since the ANC must account for at least the carbonate protolytes in water, the fact that few of the data are above this line indicates that the pH, DIC, and ANC data for most of the streams are reliable.

The ANC in a few of the samples is less than the carbonate alkalinity, indicating some analytical error in the measured ANC and/or in the DIC and pH, both of which were used to compute the carbonate alkalinity. At most sites, however, the ANC equals or exceeds the carbonate alkalinity, suggesting the presence of noncarbonate protolytes, a systematic overestimate of the ANC or underestimate of the carbonate alkalinity, or some combination of the above. Assuming there is no systematic error in the estimates of ANC and bicarbonate alkalinity, there appear to be few cases in which the analytical error exceeds the effect on ANC of noncarbonate protolytes.

Potential noncarbonate protolytes include dissolved and particulate organic carbon, aluminum and other proton-reacting metal complexes, and particulate aluminosilicates and metal oxides. The potential contribution of weak organic anions to the ANC of stream water is discussed in Section 8.6 of this report.

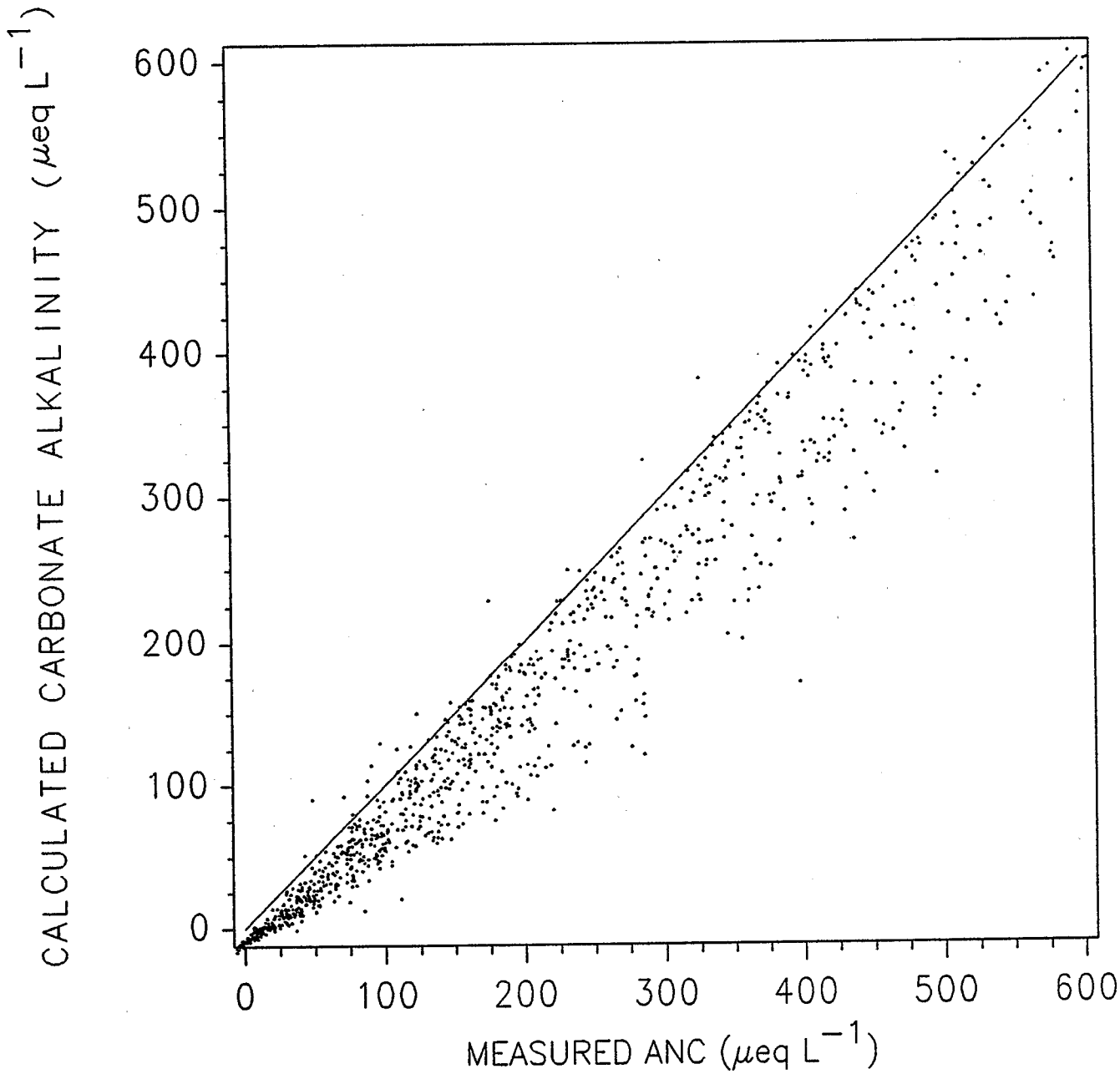

Figure 4-5. Measured ANC vs. the calculated carbonate alkalinity for NSS-I stream water samples. Data below the line of equality (y = x) indicate the presence of noncarbonate species that react with hydrogen ions, whereas data above the line indicate anlaytical error.

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SECTION 5
TARGET POPULATION--PHYSICAL CHARACTERISTICS

5.1 OVERVIEW

Section 5 describes how the National Stream Survey - Phase I (NSS-I) target population was refined from the population initially identified from map criteria to the refined target population whose chemical characteristics are described in Sections 6 through 10. This section presents the total numbers and the combined length of target stream reaches, and provides statistics that describe the distribution of physical characteristics of the reaches (e.g., drainage area, elevation, channel width). Population estimates are included for those categories within the initial target population not of interest in an assessment of acid deposition effects.

5.2 REFINEMENT OF THE TARGET POPULATION

The set of stream reaches intended for field visitation was selected in two stages, as discussed in Section 2.4. Site inclusion criteria were applied at the first stage (the examination of reaches selected by grid points). These criteria excluded lakes, reservoirs, wetlands, and other nonflowing water selected by map grid points, as well as reaches too large, too urban, or too greatly affected by ocean tides to be of interest for this survey. Because map-based criteria may not adequately exclude some types of noninterest streams, further refinement of the target population was accomplished by means of site or sample exclusion criteria applied in the field (Section 3.2). These criteria specified that sampling was not to be undertaken during storm episodes. The criteria also enabled samplers to identify and avoid reaches severely affected by acid mine and oil field brine drainage, those influenced by ocean tides, those with no defined channel, and those in which flow was insufficient for clean sampling.

The target population was further refined after field sampling through examination of stream chemistry data and field comments. Reaches with severe point-source pollution were identified, along with those with acid mine drainage, tidal, or storm episode effects not readily apparent during field sampling. Stream reaches where acid mine drainage was suspected, but where evidence was ambiguous, were revisited the following spring (1987). The analytical criteria used for these after-the-fact refinements of the target population are described in subection 3.8.3 and the basis for the criteria in subsection 9.3.1. Figure 5-1 illustrates the process of target population refinement.

During the first stage of NSS-I sample reach selection, all 3,305 sites identified by the grid point sampling frame were evaluated with respect to inclusion in the target population. This evaluation according to map criteria was the first attempt to refine the sample population identified by the grid point sampling frame. From 51 to 76 percent of the stream reaches defined by the grid points (64 mi^2 or 166 km^2 per grid point) were identified, depending on the subregion, as having characteristics that tentatively placed them in the category of target reaches (Section 2, Table 2-3). These 2,301 reaches comprised a sample of the initial target population (selected solely on mapped information); a subsample of 500 of these were visited during the spring baseflow period of 1986 (spring and summer 1985 for the Pilot Survey in subregion 2As). As a result of field visits and chemical data analysis, additional stream reaches or sampling locations (upstream or downstream nodes) were subsequently classified as representative of noninterest subpopulations (Section 3.2). A total of 445 upper, and 446 lower, reach nodes were retained as representative of the refined target population. Population estimates of target and noninterest reaches (Figure 5-2) show that 80% to 100% of the initial target population in all

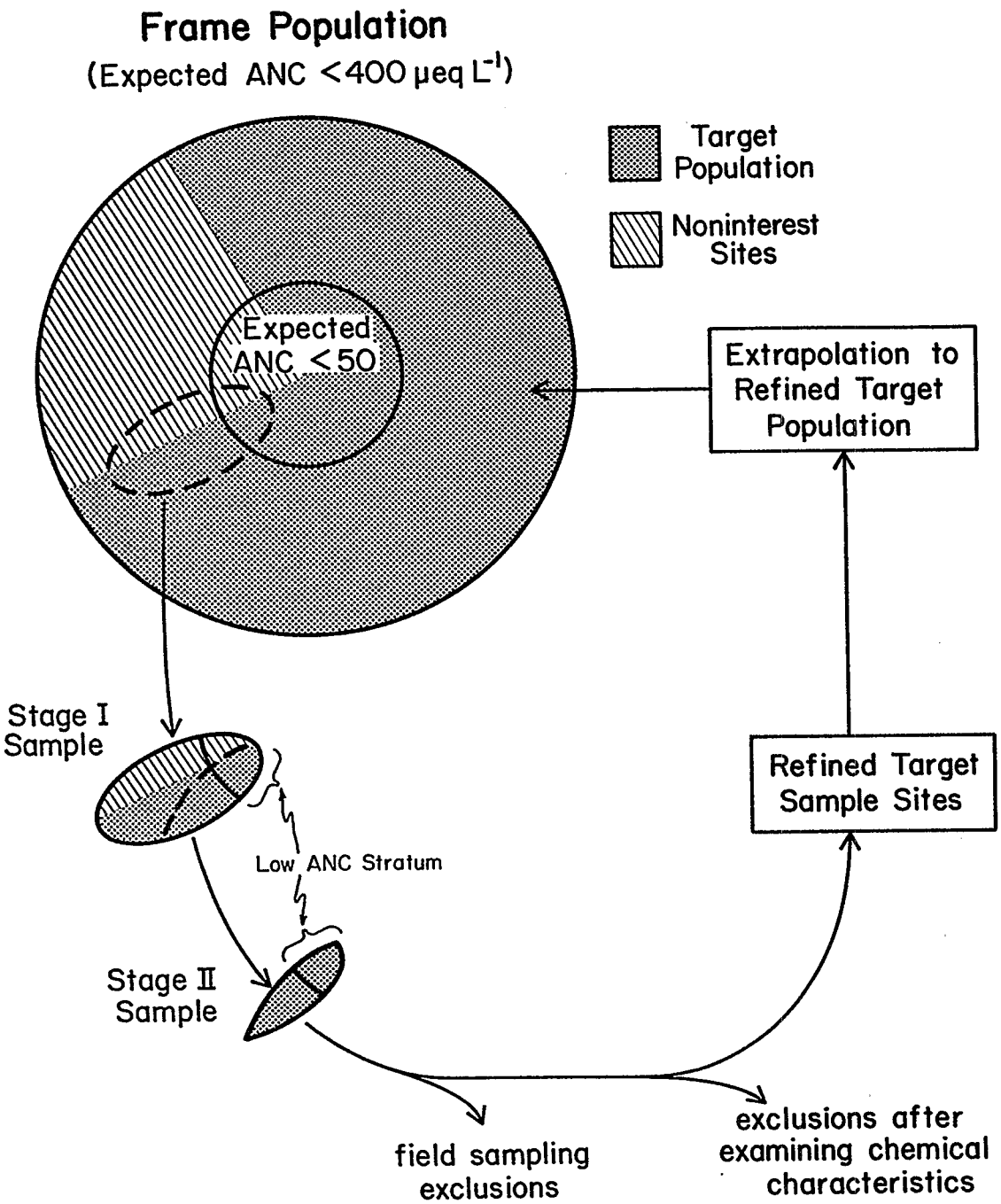

Figure 5-1. NSS-I target population refinement concept.

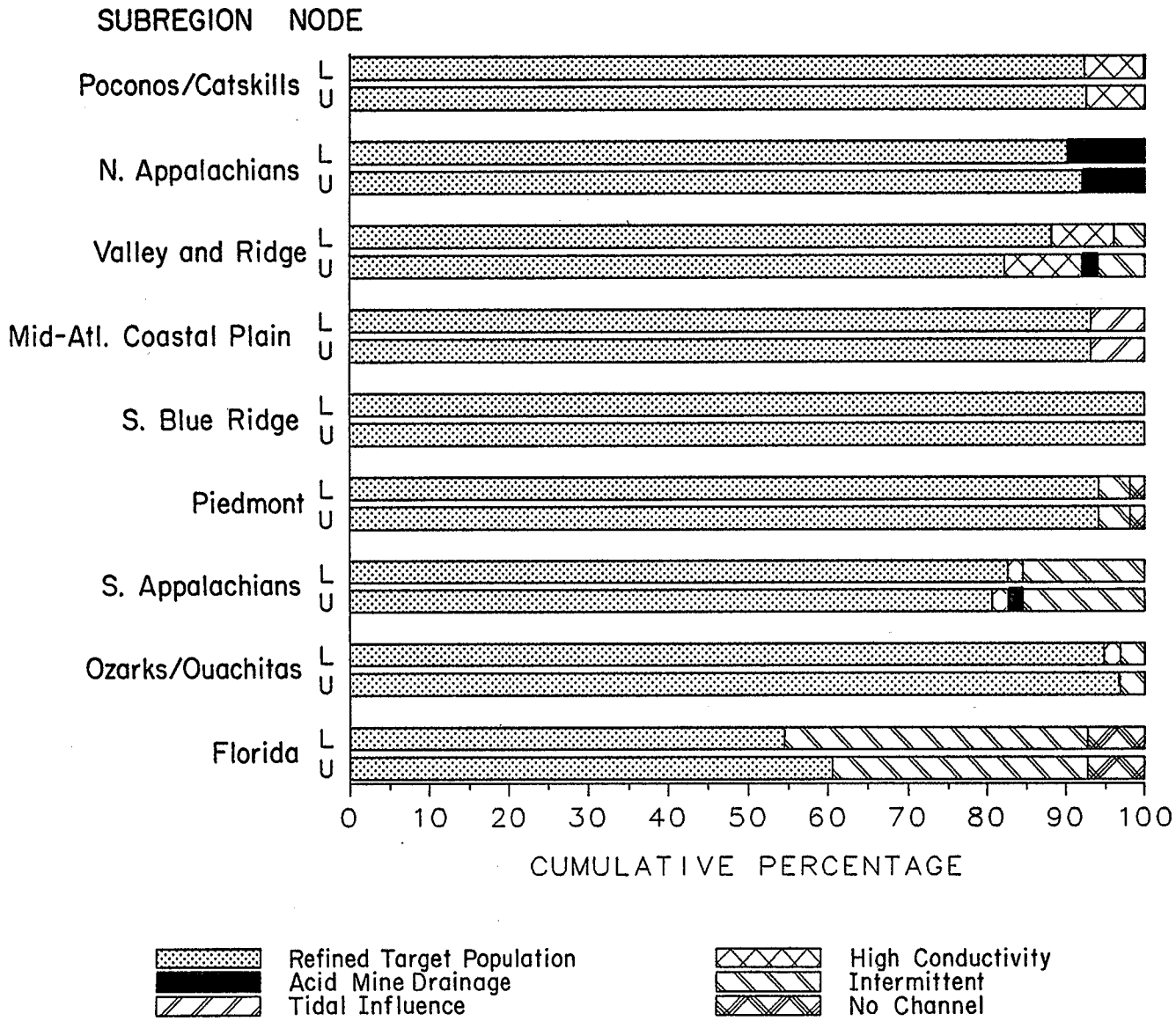

Figure 5-2. **Estimated percentages of refined target and noninterest stream reaches in NSS-I subregions.**

subregions except Florida was retained in the refined target population for which population estimates are given in Section 6.

In Florida, 61% of upstream and 54% of downstream reach ends were retained. The major cause for exclusion of reaches after field visitation in Florida and most other subregions was insufficient flow or imperceptible flow with no defined channel. Drought conditions in parts of the survey area during 1986 may have caused streams that usually flow during the spring to run dry. Another major reason for excluding streams was the extremely high conductivity or low pH resulting from accelerated weathering of alkaline or acid generating minerals exposed by mining activities. Chemical data from eight visits to five separate stream reaches were identified after-the-fact as having been influenced by storm episodes (subsection 3.8.3.1); however, substitute data from alternate site visits were available to provide baseflow chemistry at those sites. No population estimates of the chemical impacts of episodes can be provided, as the project design specified that index chemical samples from the target population exclude storm episodes.

Substantial portions (32% and 38%) of upstream and downstream ends of reaches in the Florida subregion (3C) were excluded from the refined target population because of insufficient depth or flow velocity for sampling during spring 1986. An estimated 15% of upstream and downstream reach ends in the Southern Appalachians (2X) were dry or too shallow for sampling. Only 3% to 6% of reaches in the Piedmont (3A), Ozark/Ouachita (2D), and Valley and Ridge (2Bn) subregions were similarly excluded.

An estimated 8% of the upstream and 10% of the downstream ends of the initial target reach population in the Northern Appalachian subregion (2Cn) were acidic and were affected by acid mine drainage. The rationale for this classification is discussed in subsection 9.3.1. Smaller proportions (2% or less) of the initial target population were excluded from the refined target population because of acid mine drainage in the Valley and Ridge (2Bn), the Southern Appalachians (2X), and the Poconos/Catskills (1D). It has been estimated that 4,594 km, or 2%, of the combined length of stream reaches in the initial target population of the combined NSS-I subregions were acidic at either node because of mine drainage (Section 9.4).

Seven to ten percent of upstream and downstream reach ends in subregions 1D and 2Bn had temperature corrected field conductivities higher than 500 $\mu S\ cm^{-1}$ but were not acidic. Of the sample streams in this category for which chemistry was measured, most had acid neutralizing capacity (ANC) > 1000 $\mu eq\ L^{-1}$. These cases may have occurred because of oil field brine drainage or strip mining in geologic formations containing carbonate minerals.

In the Mid-Atlantic Coastal Plain (3B), approximately 7% of upper and lower reach ends in the initial target population were eliminated because of tidal influence. Other stream reaches were excluded from the refined target population because sampling points represented wetland conditions where no defined channel could be identified. In still other cases, stream channels were inundated by impoundments, or there was no evidence that water had ever flowed in the sample location.

5.3 TOTAL TARGET POPULATION RESOURCE ESTIMATES

Estimates of the total number of upper and lower reach ends and the combined length of reaches in the refined target population are presented in Table 5-1. Both the target population chemical distributions based on reach numbers described in Section 6, and those based on number and length presented in Volume II of this report use these total resource estimates. Length-based population estimates employing interpolation of upstream and downstream reach chemistry (Section 6) are based upon that portion of the total stream length that includes both the upstream and downstream reach ends in the refined target population.

The NSS-I sample reaches are representative of a total population of 55,918 reaches for which both the upstream and downstream nodes are included in the refined target population (Table 5-1). These reaches have a combined length of 200,652 km. The four Mid-Atlantic subregions contain 36,045 of these reaches (109,865 km), whereas the five Southeast subregions contain 19,873 reaches with a combined length of 90,787 km.

5.4 TARGET REACH PHYSICAL CHARACTERISTICS

Population frequency distributions of target reach drainage areas and Strahler Order (Strahler, 1957) (Figures 5-3a and 5-3b) confirm that NSS-I reaches comprise a population of streams best described as small to mid-sized. At the upstream ends, 46% of these reaches are classified as headwater reaches (Strahler Order = 1) on 1:24,000-scale maps. At the downstream ends, most reaches (67%) are of Strahler Order 2 and 3. Streams managed by fishery agencies are typically of Strahler Order 1 to 4 (TIE, 1981; Higbee, 1986; Johnson, 1986). Median drainage areas at the upstream ends of the target reaches range from 0.44 to 5.0 km^2 in the nine NSS-I subregions, with lower 20th percentiles between 0.10 and 1.1 km^2. Downstream medians range from 5 to 16 km^2 with 80th percentile values between 19 and 55 km^2.

Stream width and depth distributions (Figures 5-4a and 5-4b) further support the description of NSS-I target streams as small to mid-size, which is the size range of interest for management of sport fisheries. The nine subregion median widths range from 1.6 to 3.0 m at the upper reach nodes, and from 2.4 to 4.8 m at the lower nodes. Depending on the subregion, at least 20% of the reaches are narrower than 0.9 m at their upper ends and 2.7 m at the downstream ends. Fishery management agencies (e.g., Pennsylvania Fish Commission) typically manage streams between 4 and 20 m in width (Higbee, 1986; Johnson, 1986).

Median depths of NSS-I target stream reaches are between 0.09 and 0.27 m at the upstream ends, and between 0.16 and 0.31 m at the downstream ends. Figure 5-4a illustrates that, depending on the subregion, at least 20% of the target stream reaches are shallower than 0.12 m at their upstream node. Similarly, depending on the subregion, no more than 20% of the stream reaches are deeper than 0.76 m at the lower node. The shallowest upstream and downstream medians are in subregions such as the Northern Appalachians (2Cn), where many target streams are of relatively high gradient. The median gradient is 3% in subregion 2Cn, for example. Conversely, the deepest upstream medians are in the Florida (3C) and Mid-Atlantic Coastal Plain (3B) subregions, where median gradients are considerably less than 0.5%. Subregions with the greatest median depths at the downstream ends of their target reaches are in the low-elevation subregions (e.g., 3C and 3B) and also in the Pocono/Catskill (1D) and Ozark/Ouachita (2D) subregions. These latter two subregions have particularly large median downstream node drainage areas when compared with the other subregions (Figure 5-3a).

Population frequency distributions of target reach elevation (Figure 5-5a) show considerably greater variation among and within subregions than between upstream and downstream ends of reaches. This result reflects the broad range of target reach drainage areas and the broad geographical extent of the NSS-I subregions (compared with smaller differences between upstream and downstream drainage areas on single reaches). The 20th to 80th percentile ranges indicate, for each subregion, the elevation range containing the majority (60%) of target reaches. More than 60% of the reaches in the Florida (3C) and Mid-Atlantic Coastal Plain (3B) subregions are found at low elevations between 4 and 76 m. In the Valley and Ridge (2Bn), Ozark/Ouachita (2D), and Piedmont (3A) subregions, target reaches are of moderately low elevation, with the majority found between 96 and 390 m. The Southern Appalachian (2X) and Pocono/Catskill (1D)

Table 5-1. Refined Target Population Total Stream Resource Estimates[&]

NSS-I Subregion	Reach Nodes*				Length[#]
	Downstream		Upstream		(km)
	$\hat{N}$	(n)	$\hat{N}$	(n)	$\hat{L}$
1D (Poconos/Catskills)	3,235	(56)	3,244	(58)	15,144 - 15,270
2Cn (N. Appalachians)	8,488	(61)	8,663	(67)	21,738 - 22,373
2Bn (Valley and Ridge)	13,992	(47)	13,038	(44)	32,687 - 36,405
3B (Mid-Atlantic Coastal Plain)	11,287	(58)	11,284	(57)	40,296 - 40,344
2As (Southern Blue Ridge)	2,031	(54)	2,031	(54)	9,036 - 9,036
3A (Piedmont)	7,515	(47)	7,515	(47)	33,531 - 33,531
2X (Southern Appalachians)	5,057	(40)	4,936	(39)	21,892 - 23,015
2D (Ozarks/Ouachitas)	4,117	(48)	4,204	(49)	22,480 - 22,753
3C (Florida)	1,555	(34)	1,727	(31)	3,848 - 5,284
Subtotal Mid-Atlantic	37,002	(222)	36,229	(226)	109,865 - 114,392
Subtotal Southeast	20,275	(223)	20,413	(220)	90,787 - 93,619
Total NSS-I	57,277	(445)	56,642	(446)	200,652 - 208,011

& $\hat{N}$ refers to the population estimate of the total number of reaches; n is the sample size; standard errors for the population estimates are tabulated in Appendix C.

* The number of upstream and downstream reach ends may not agree because differing numbers of upstream and downstream ends may be assigned to noninterest subsets of the target population.

\# The smaller number represents all target reaches for which both ends met the site inclusion criteria. The larger number includes additional reaches for which one end was a noninterest point.

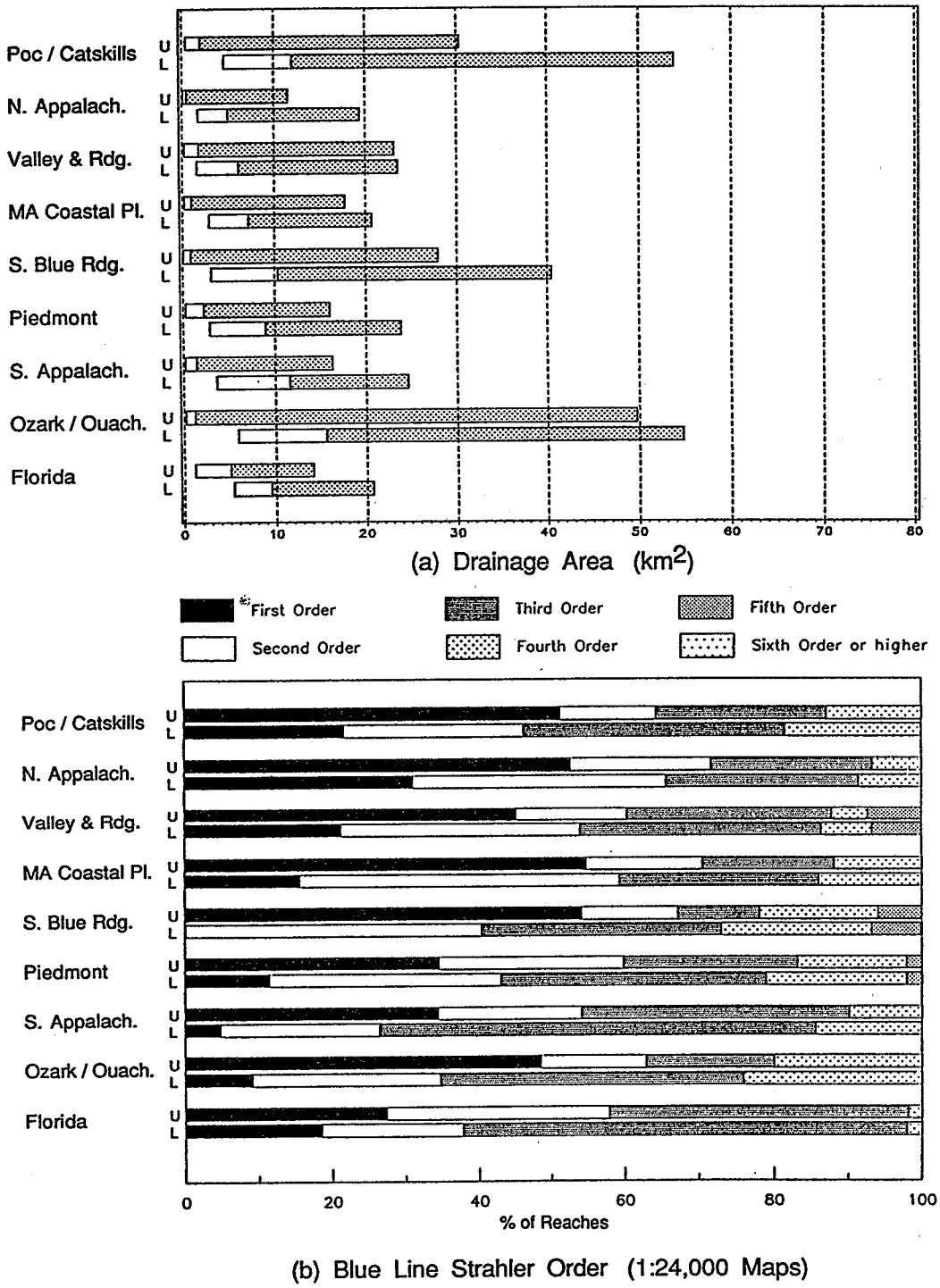

Figure 5-3. Population frequency distributions for (a) drainage area (20th percentile, median, 80th percentile) and (b) population frequency histograms, Strahler Order (1:24,000-scale maps) at NSS-I target reach upper and lower nodes.

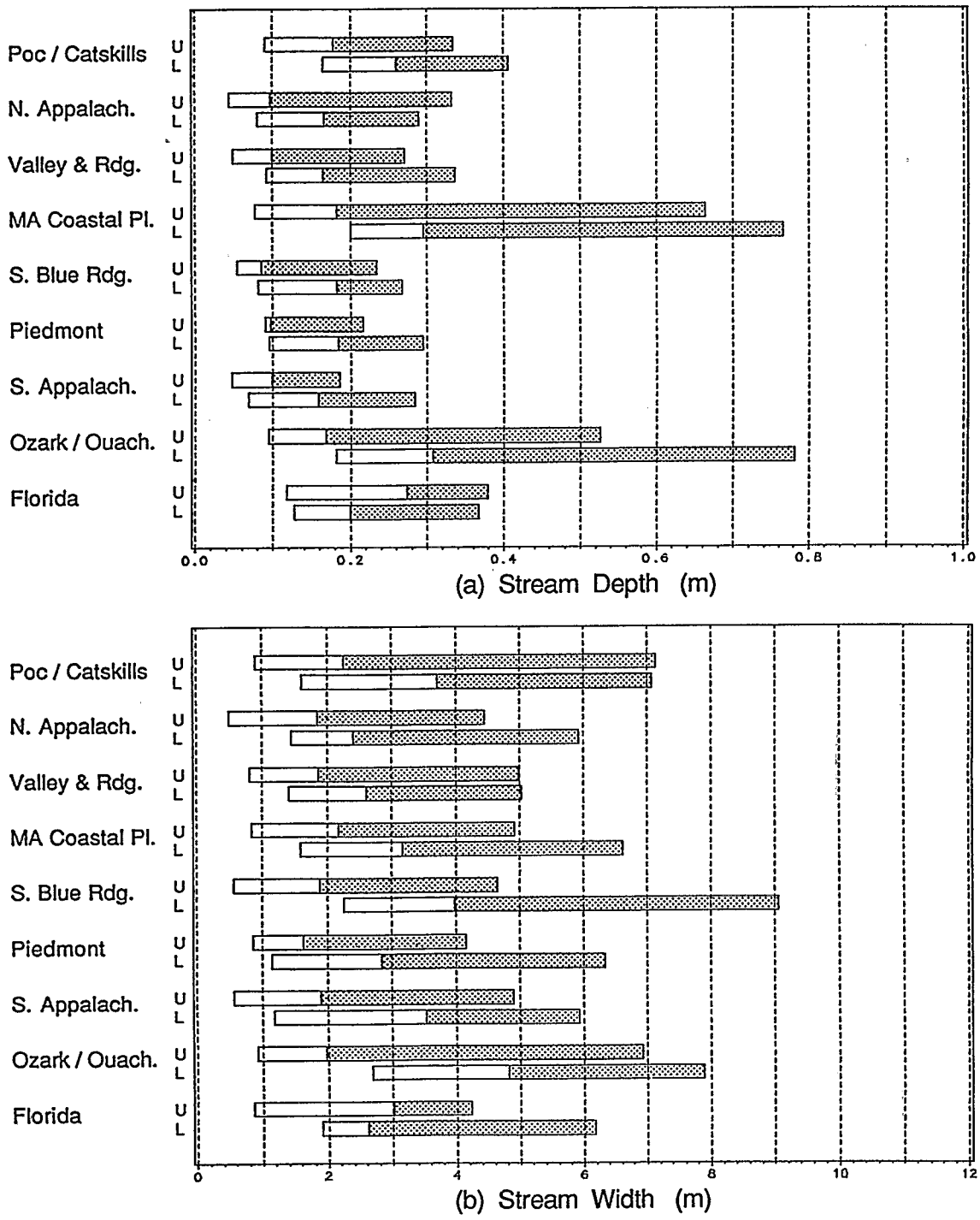

Figure 5-4. Population frequency distributions (20th percentile, median, 80th percentile) for (a) depth and (b) width of NSS-I target reaches at upper and lower nodes.

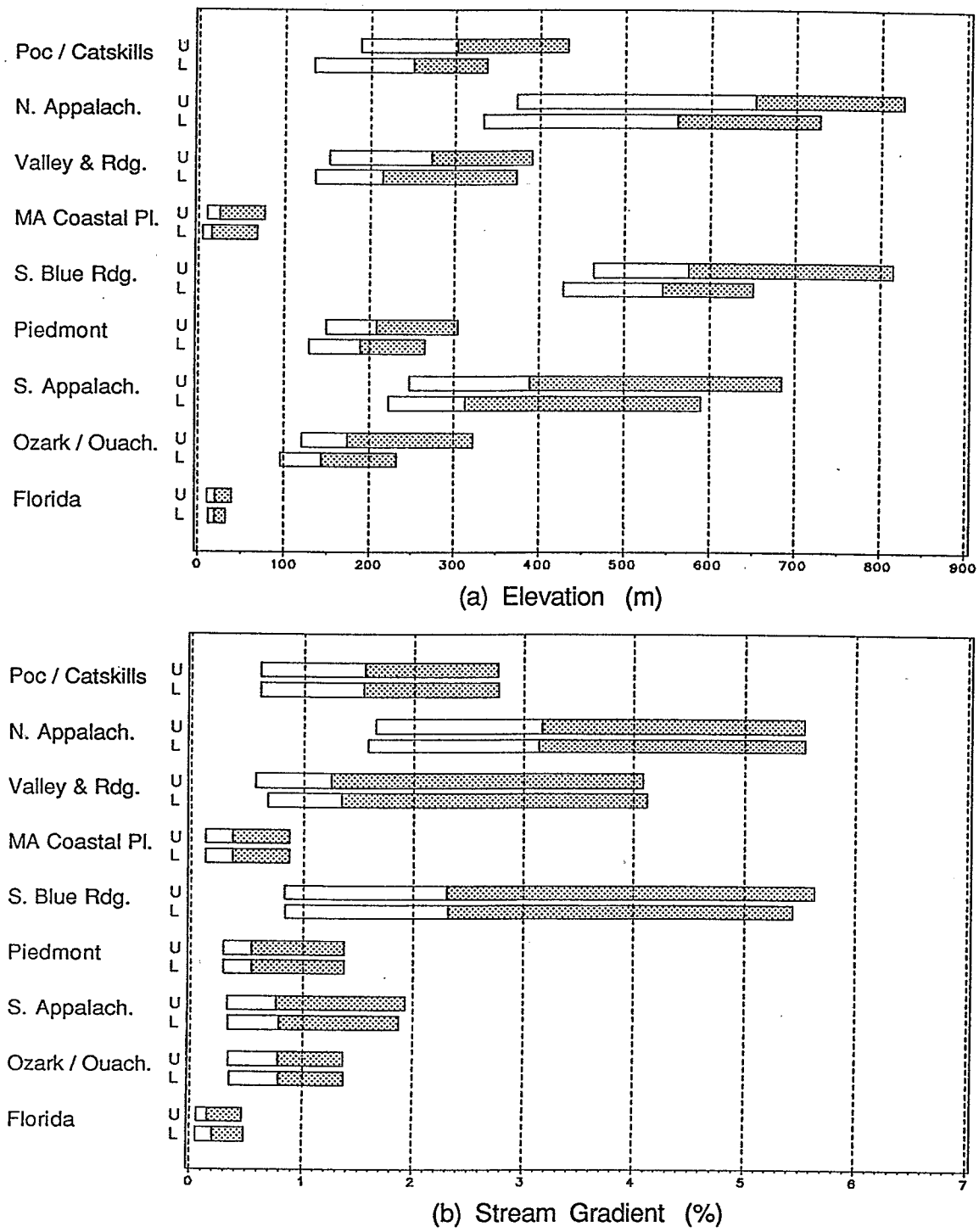

Figure 5-5. Population frequency distributions (20th percentile, median, 80th percentile) for (a) upper and lower node elevation, and (b) gradient between nodes of NSS-I target reaches.

target reaches are of moderately high elevation, with most between 130 and 685 m. The Northern Appalachian (2Cn) and Southern Blue Ridge (2As) subregions have target reaches at relatively high elevation, with most reaches between 334 and 861 m.

Target population gradient distributions (Figure 5-5b) reflect the elevation distributions, with the lowest gradients (medians less than 0.5%) found in subregions 3C, 3B, and 3A. Those subregions with the highest elevations (2Cn, 2As, 2X, and 1D) have higher median gradients (0.8% to 3.0%).

5.5 GEOGRAPHIC CLASSIFICATION OF SAMPLE SITES

Examination of regional patterns and associations between stream chemistry and site characteristics revealed that in many cases the NSS-I subregions encompass a large amount of geographic variability. To improve the interpretation of the influence of watershed characteristics on stream chemistry, it was necessary to reclassify NSS-I sites on the basis of geographic characteristics alone. The NSS-I subregion boundaries (Section 1, Figure 1-2) were drawn with consideration for topography, geology, soils, climate, vegetation, land use, and presence or absence of lake resources, but also with respect to the rate of atmospheric acid deposition. The subregion names refer to the dominant geographic or physiographic feature or unit within each subregion. However, subregion boundaries do not always correspond with the recognized boundaries of the physiographic units for which these subregions are named. For example, NSS-I subregion 1D, the Pocono/Catskill subregion, contains glaciated portions of the Northern Appalachian Plateau and the extreme northern portion of the Valley and Ridge Province (Fenneman, 1946), in addition to the Catskill and Pocono Mountains (Table 5-2). The Mid-Atlantic Coastal Plain subregion (3B) includes a number of sites from the northern Piedmont physiographic province, in addition to those on the Coastal Plain itself. Similarly, the Blue Ridge Mountains physiographic province (Fenneman, 1946) is largely contained within NSS-I subregion 2As, the Southern Blue Ridge, but the northern Blue Ridge sample sites are contained within NSS-I subregion 2X, the Southern Appalachians. A few sites of the Southern Blue Ridge physiographic province are contained in NSS-I subregion 3A, the Piedmont.

NSS-I sites were reclassified solely upon geographic considerations--largely according to the physiographic regions of Fenneman (1946). Individual sites within these larger regions were subclassified according to geology, local elevation, vegetation cover, and land use (Tables 5-2 and 5-3). The geographic classes (Table 5-2) are properly treated as substratifications within the NSS-I subregions when calculating population distribution estimates and their variance (Section 9.5; Appendix D). Throughout this report, population estimates of the distributions of target reach physical or chemical characteristics (e.g., Section 6) refer to the NSS-I subregion strata unless explicitly stated otherwise (e.g., Section 9.5).

Table 5-2. Distribution of Refined Target Population Upper and Lower Reach Nodes by Geographic Site Class in NSS-I Subregions

Geographic Site Class	SUBREGION ID 1D	2Cn	2Bn	3B	2As	3A	2X	2D	3C	Total
Allegheny Plateau										
High Plateau	-	13	-	-	-	-	-	-	-	13
Forested Plateau	-	56	-	-	-	-	-	-	-	56
Forested Agric. Plat.	-	47	-	-	-	-	7	-	-	54
Northeast Mid-Atlantic										
Pocono/Catskill Mts.	16	-	-	-	-	-	-	-	-	16
Glaciated Agric. Plat.	31	-	-	-	-	-	-	-	-	31
Glaciated Forested Plat.	13	-	-	-	-	-	-	-	-	13
Valley and Ridge Province										
Ridges	9	6	32	-	-	-	9	-	-	56
Valleys	45	6	40	-	6	-	27	-	-	124
Arkansas/Oklahoma										
Boston Mts.	-	-	-	-	-	-	-	20	-	20
Ouachita Mts.	-	-	-	-	-	-	-	30	-	30
Arkansas R. Valley	-	-	-	-	-	-	-	29	-	29
Piedmont Province										
Piedmont	-	-	9	18	-	68	4	-	-	99
Piedmont Lowlands	-	-	10	7	-	-	-	-	-	17
S. Appalachian Highlands										
Blue Ridge Mts.	-	-	-	-	94	4	14	-	-	112
Cumberland Plateau	-	-	-	-	-	2	18	-	-	20
French Broad R. Valley	-	-	-	-	8	-	-	-	-	8
Coastal Plain										
Eastern Mid-Atlantic	-	-	-	18	-	-	-	-	-	18
Western Mid-Atlantic	-	-	-	50	-	-	-	-	-	50
New Jersey Pine Barrens	-	-	-	22	-	-	-	-	-	22
Eastern Gulf	-	-	-	-	-	20	-	-	-	20
Western Gulf	-	-	-	-	-	-	-	18	-	18
Florida										
Panhandle Upland	-	-	-	-	-	-	-	-	36	36
Peninsula Upland	-	-	-	-	-	-	-	-	9	9
Panhandle Swamp	-	-	-	-	-	-	-	-	9	9
Peninsula Swamp	-	-	-	-	-	-	-	-	11	11
Total	114	128	91	115	108	94	79	97	65	891

Table 5-3. Characteristics of NSS-I Geographic Site Classifications

ALLEGHENY PLATEAU

High Plateaus
- Land Use: Forest
- Geology: Sandstone
- Relief: Shallow to steep
- Soils: Sandy loam, deep, well-drained

Forested Plateau
- Land Use: Forest with several strip mines throughout the region
- Geology: Sandstone, shales, and siltstones
- Relief: Moderate
- Soils: Silt loam to sandy loam, good drainage

Mixed Forest and Agriculture Plateau
- Land Use: Mixed forest and agriculture
- Geology: Sandstones and shales
- Relief: Moderate
- Soils: Silt loam to sandy loam, good to well drained

NORTHEASTERN MID-ATLANTIC

Pocono/Catskill Mountains
- Land Use: Forest or woodland
- Geology: Sandstone, shales, quartz conglomerates
- Relief: Moderate to Steep
- Soils: Silt loam, shallow to deep

Glaciated Agricultural Plateau
- Land Use: Agriculture, extensive transportation development throughout the region
- Geology: Sandstone, siltstone, and shales
- Relief: Moderate
- Soils: Silt loam, loam, poor to good drainage

Glaciated Forested Plateau
- Land Use: Forest or woodland
- Geology: Sandstones, shales, siltstones, and coal
- Relief: Moderate
- Soils: Silt loam, loam, good to well drained

Table 5-3. Characteristics of NSS-I Geographic Site Classifications (Continued)

VALLEY AND RIDGE PROVINCE

Ridges
- Land Use: Forest
- Geology: Sandstone, shales, and siltstones
- Relief: Moderate to steep
- Soils: Silt loam to sandy loam, good to well drained

Valleys
- Land Use: Agriculture and urban
- Geology: Limestones, calcareous shales, dolomites, glacial till
- Relief: Shallow in lower watershed, moderate in upper watershed
- Soils: Silt loam to sandy loam, good to well drained

ARKANSAS/OKLAHOMA

Boston Mountains
- Land Use: Forested with < 10% of the watershed in agriculture
- Geology: Shales and sandstones
- Relief: Steep

Ouachita Mountains
- Land Use: Forested with < 5% of the watershed in agriculture
- Geology: Sandstone and shales
- Relief: Moderate in the West, steep in the East

Arkansas River Valley
- Land Use: Mixed forest and agriculture
- Geology: Shales and sandstones
- Relief: Shallow

PIEDMONT

Piedmont
- Land Use: Mixed forest and agriculture
- Geology: Schist, gneiss, small number of watersheds with granite or phyllite
- Relief: Shallow to moderate
- Soils: Clays of clayey loam, moderate well drained, deep to shallow

Piedmont Lowlands
- Land Use: Agriculture with patches of forest
- Geology: Limestone, schist, and gneiss
- Relief: Little or none
- Soils: Silty loam, sandy loam, clays

Table 5-3. Characteristics of NSS-I Geographic Site Classifications (Continued)

SOUTHERN APPALACHIAN HIGHLANDS

Blue Ridge Mountains

Land Use: Forest with some agriculture isolated in valley bottoms
Geology: Phyllite, quartzite, graywacke, conglomerates
Relief: Shallow to steep
Soils: Loam, good drainage

Cumberland Plateau

Land Use: Forested with some mixed forest and agriculture
Geology: Sandstones and shales
Relief: Shallow
Soils: Loamy soils, well drained, strongly acid

French Broad River Valley

Land Use: Agricultural
Geology: Phyllite, quartzite, graywacke, conglomerates
Relief: Shallow
Soils: Deep loam, good drainage

COASTAL PLAIN

Eastern Mid-Atlantic

Land Use: Agriculture, urban, small patches of forest
Geology: Sands, mix of sands, gravels, clays, and silts
Relief: Little or none
Soils: Sandy, increasing amounts of clay to the south

Western Mid-Atlantic

Land Use: Mixed forest and agriculture in north, increasing forest cover in the southern portions of the region
Geology: Sands in the northern portion, fossilerous clays and sands in the southern portion
Relief: Shallow to moderate (swampy in the 3B070 sites)
Soils: Fine loamy with a small percentage of sites with coarse loamy or fine silty, well drained

New Jersey Pine Barrens

Land Use: Forested with some urbanization, cranberry bogs
Geology: Sandstone, gravel and sandstone
Relief: Very shallow
Soils: Quartz sands

Table 5-3. Characteristics of NSS-I Geographic Site Classifications (Continued)

Eastern Gulf of Mexico

Land Use: Mainly forest with some agriculture along stream reach
Geology: Sandstone, shales, clays, gravels, lignite, and coal
Relief: Shallow
Soils: Loamy, well drained, deep to moderately deep

Western Gulf of Mexico

Land Use: Mixed forest and agriculture
Geology: North - shales and sand; south - alluvium
Relief: Shallow

FLORIDA

Panhandle Upland

Land Use: Forest or mixed forest and agriculture
Geology: Gravel, sand, micaceous kaolinitic clay
Relief: Shallow
Soils: Sandy, well drained

Peninsula Upland

Land Use: Mixed forest and agriculture
Geology: Coastal sands, sand and clayey fine sands
Relief: Shallow
Soils: Sandy, well drained

Panhandle and Peninsula Swamp Sites

Land Use: Forest
Geology: Sands over clayey sands
Relief: Shallow or none in most watersheds
Soils: Sands to sandy loam, poor to well drained

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SECTION 6
TARGET POPULATION REGIONAL CHEMISTRY

Section 6 addresses the National Stream Survey - Phase I (NSS-I) primary objectives of estimating the regional extent of acidic and low acid neutralizing capacity (ANC) streams and describing their chemical characteristics. Further interpretation of the NSS-I data is contained in the four subsequent sections. Section 7 addresses uncertainty in the population estimates due to temporal variability. Section 8 discusses the chemical characteristics of the target population in greater detail, examining the relationships among chemical constituents. Section 9 classifies acidic and low ANC streams according to probable sources of acid anions, and Section 10 examines evidence of acidification in streams of the target population.

6.1 INTERPRETING NSS-I POPULATION DISTRIBUTIONS

The subjects discussed in subsections 6.1.1 through 6.1.6 are relevant to interpretation of the NSS-I regional population distribution data presented throughout Section 6.

6.1.1 Target Population of Interest

The target population as defined in the discussion of the statistical sampling frame (Section 2.4) has been refined to encompass a slightly more restrictive population in most of the NSS-I subregions. In Florida (3C), where a substantial proportion of intended sample reaches were dry, the difference between the original and refined target populations is greater. This refined sub-population of interest within the target population of the nine NSS-I subregions excludes sites affected by acid mine drainage but not previously excluded on the basis of low field pH (< 3.3) or high field conductivity (> 500 μS cm^{-1}). Stream reaches that were without discernable flow or that were too shallow to sample were also excluded. Section 5.2 discusses the process of excluding sample reaches in more detail and estimates the population proportions of these types of noninterest categories in the nine NSS-I subregions.

6.1.2 NSS-I Subregions

Throughout Section 6 and the remainder of this report, population estimates for distributions of target reach physical or chemical characteristics refer to the NSS-I subregion strata shown in Figure 2-2 and the inside of the front cover, not the geographic classification of target streams, unless explicitly stated otherwise. Except in Section 9, the geographic site classes within NSS-I subregions are used in a descriptive way to aid interpretation of the observed geographic patterns in chemistry. In Section 9, population estimates show the distribution of target reaches according to geochemical types within each geographic class.

6.1.3 The Florida Subregion

The Florida subregion (3C) was surveyed as a feasibility study to evaluate the point-frame sample reach selection procedure and site inclusion criteria in a coastal lowland setting. Sampling was concentrated on a geographic region expected to contain surface waters with ANC less than 200 μeq L^{-1}, rather than 400 μeq L^{-1}, as was the case in the other NSS-I and Eastern

Lake Survey (ELS) subregions. NSS-I results for Florida are discussed separately in Section 6.2.4 because results are not strictly comparable with those from other subregions.

6.1.4 The Southern Blue Ridge Subregion

A Pilot Survey was undertaken in the Southern Blue Ridge in 1985, a year before field activities in the remaining NSS-I subregions. Population estimates given in this section based on the average downstream chemistry during spring baseflow are as reported and discussed by Messer et al. (1986, 1988), with very small changes resulting from a minor modification in the procedure used to calculate ANC from titration curves. Spring season samples were collected only at the upstream nodes on 20 of the total 54 sample reaches in this subregion. However, the full set of downstream nodes was sampled in both spring and summer, and the full set of upstream nodes was sampled in the summer. To provide population distribution estimates for the Southern Blue Ridge that are comparable to spring upstream estimates for other subregions, highly predictive empirical relationships have been employed using available data to synthesize upstream spring values for the 34 missing sites (Appendix B). These synthesized values are not included in the enhanced data base, but can be provided in a separate small data set.

6.1.5 Index Sample

The spring baseflow chemical index concept and the rationale for its selection and use are discussed in Section 2.5. All population distributions are based on spring baseflow index chemistry. In the Southeast, measurements from single visits to each upstream and downstream sample site comprise the spring index for each node of the sample reaches. In the mid-Atlantic, the spring index at each reach node is calculated as the average from two separate visits. Indices for pH were calculated by averaging hydrogen ion concentrations from the separate visits. Because a trend of decreasing acidity between visits was observed in some subregions, population distribution estimates based on the separate values of pH and ANC observed on each visit are provided in subsection 7.4.2.

It is important to understand the limitations as well as the strengths of the chemical index approach. For example, the number of stream reaches that are acidic due to episodic pH depressions during storm runoff, or to seasonal variability at other times of the year, cannot be obtained or inferred directly from the distribution of index chemistry provided by the NSS-I. The number of streams experiencing acidic episodes may be much greater than the number estimated to be acidic during spring baseflow. Further studies of short-term and seasonal variability are expected to demonstrate a useful predictive relationship between index chemistry and chemistry during other times of the season or year, as has been shown for the Adirondack Lakes (Driscoll, 1986) and other eastern Lakes (Newell, 1987), in the United States.

6.1.6 Distributions Based on Upstream and Downstream Chemistry

This report provides separate regional chemical distributions calculated from chemical data collected at upstream and downstream ends of NSS-I sample reaches. The population distribution estimates based on upstream and downstream sampling comprise two spring baseflow "snapshots" focusing at different positions within the streamflow network represented by blue lines on 1:250,000-scale topographic maps (Figure 6-1). Each upstream reach end (upper node) is paired

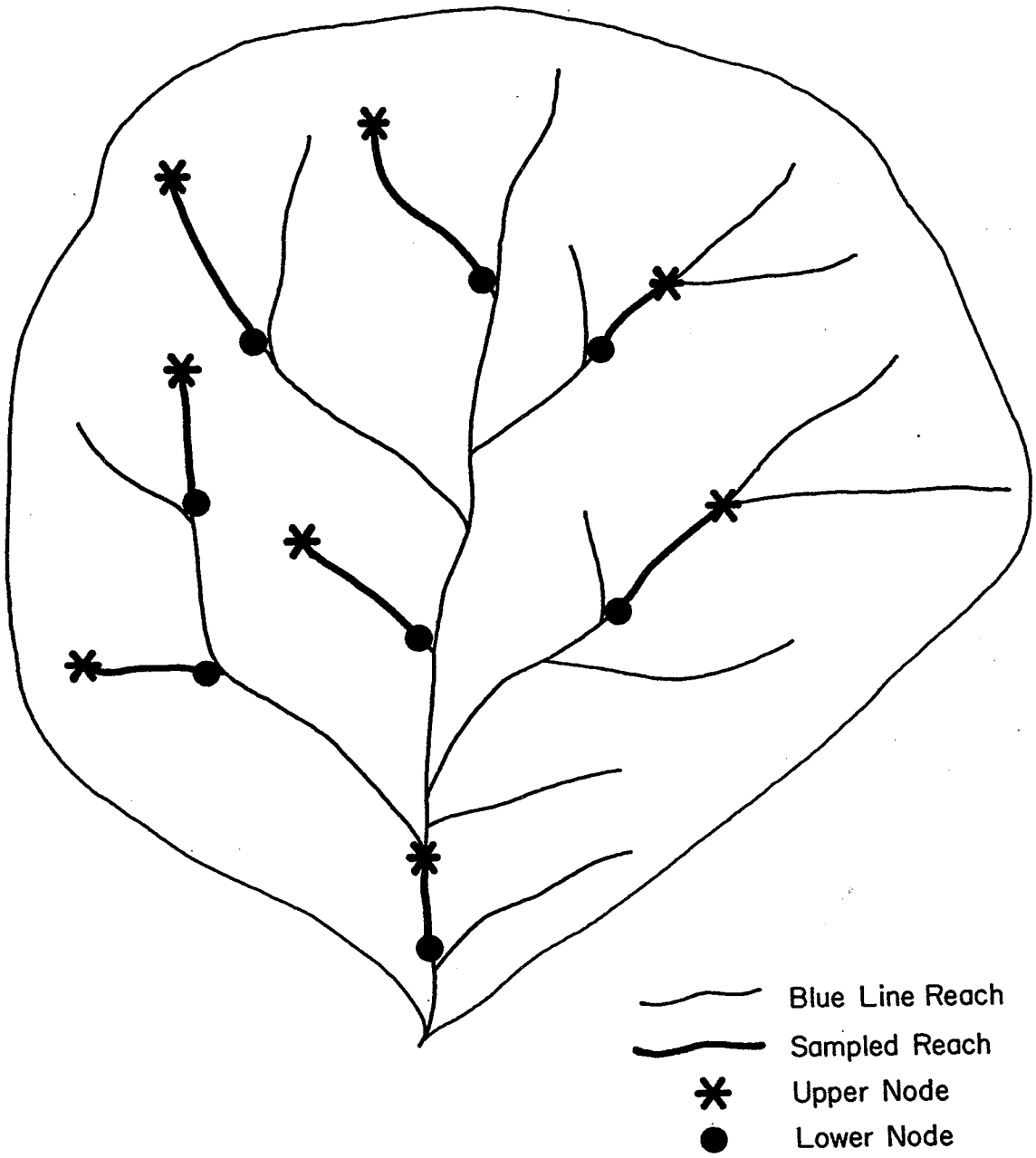


Figure 6-1. Conceptual representation of upper and lower reach node samples and populations.

with a corresponding lower node at the downstream end of the reach. Because roughly two-thirds of the NSS-I target population is made up of headwater reaches (on 1:250,000-scale maps), the population of upper reach nodes is located largely upstream of the lower node population (i.e., for two-thirds of the population, there is no overlap). However, the other one-third of the target reaches that are not headwaters have upstream nodes farther downstream in the network than lower nodes of reaches higher up in the drainage network.

One can think of the downstream sampling points as representing stream water at a given moment in time as it exits the population of target reaches that form the total blue-line network. (This is not the same thing as the water quality leaving the whole network, however, because the population of target reaches is a hierarchical network in which smaller target reaches are nested within the network as tributaries to larger reaches). Downstream ends of the target reach population are typically of Strahler Order 2 and 3 (sensu Strahler, 1957, based on 1:24,000-scale maps) and drain land areas primarily in the range from 1.2 to 56 km^2. Upstream ends are located, on the average, 3 km upstream from lower ends of target population reaches. Water quality samples taken at the upstream ends of the sample of target reaches are therefore representative of water draining a range of watershed areas that overlaps the range of the lower ends, but is somewhat smaller. Upstream ends of target reaches are typically of Strahler Order 1 and 2 with drainage areas primarily in the range from 0.1 to 47 km^2.

6.1.7 Interpolated Length Distributions

Separate distributions and scatter plots of chemistry at the upstream and downstream ends of target stream reaches provide a fairly complex picture of their status. Similar graphs depicting chemical distributions based on the length and other attributes of the stream resource are provided in the data compendium comprising Volume II of this report. The length and total drainage area (discharge index) plots in Volume II are based on the chemistry at one reach node (lower node). It is perhaps of greater interest to combine upstream and downstream chemical measurements and to report the status of stream resources in terms of the combined length of streams within reference categories of pH and ANC. Such estimates may have more utility for fish habitat quality assessment. It is possible now to present population estimates of this nature, but the statistical confidence bounds provided for them are somewhat crude at this time. These interpolated length estimates are based on a simplistic model that assumes that chemical concentrations change in a linear fashion from the upstream sampling point to the lower one. Concentrations of ANC and hydrogen ion for positions on stream reaches between sampling locations have been linearly interpolated between sampling points to produce the population distributions of ANC and pH reported in the bar charts presented in subsection 6.2.5.

6.2 DISTRIBUTIONS OF pH AND ANC

6.2.1 Regional Overview

Population proportions are reported within ranges defined by reference values. The value of ANC = 0 is of significance because waters at or below this level have no capacity to neutralize acid inputs--they are acidic by definition.

The 50 $\mu eq\ L^{-1}$ reference value forms an upper bound of the range of aquatic systems between 0 and 50 $\mu eq\ L^{-1}$ that may be considered to have very low ANC. Although there may be no special significance to the 50 $\mu eq\ L^{-1}$ level, some scientists term surface waters with ANC $< 50\ \mu eq\ L^{-1}$ as "extremely acid sensitive" (Schindler, 1988). There is some evidence that

certain groups of streams and lakes with spring baseflow ANC (streams) or fall turnover ANC (lakes) below this level may be prone to acidic episodes during storm events or snowmelt (Driscoll, 1986; Eshleman, in press). Low ANC is probably a necessary condition predisposing acidic episodes, but certainly not a sufficient one. Streams or lakes experiencing acidic episodes are also often subject to high atmospheric acid deposition rates, and may have watersheds that are more susceptible to episodic pH depressions due to their hydrology (Marmorek, et al., 1986).

The 200 μeq L^{-1} ANC reference value is of interest because it has been frequently cited in acid deposition literature as a value below which streams or lakes are often defined or hypothesized to be sensitive to acidification (Schindler, 1988). Some researchers appear to define all waters with ANC < 200 μeq L^{-1} as sensitive (Johnson, 1986), whereas most consider 200 μeq L^{-1} as a threshold above which aquatic systems are unlikely to be sensitive. It should be kept in mind that "sensitivity" to acid deposition impacts depends on factors other than the ANC of the stream water itself. A stream is an integral part of its watershed; as such, its sensitivity to acid deposition depends on the ability of watershed geology, soils, and vegetation to neutralize incoming acidity.

Before proceeding with an overview of ANC population distributions in the NSS-I regions, it is appropriate to keep in mind that the system level precision of ANC measurements was 3 to 8 μeq L^{-1} (pooled SD of field duplicate pairs) for ANC ranges $\leq$ 200 μeq L^{-1} (Table 4-3). Precision estimates that take into account laboratory bias and day-to-day variation in procedures had a %RSD of approximately 11% in the ANC range of 50 to 200 μeq L^{-1} (Table 4-3).

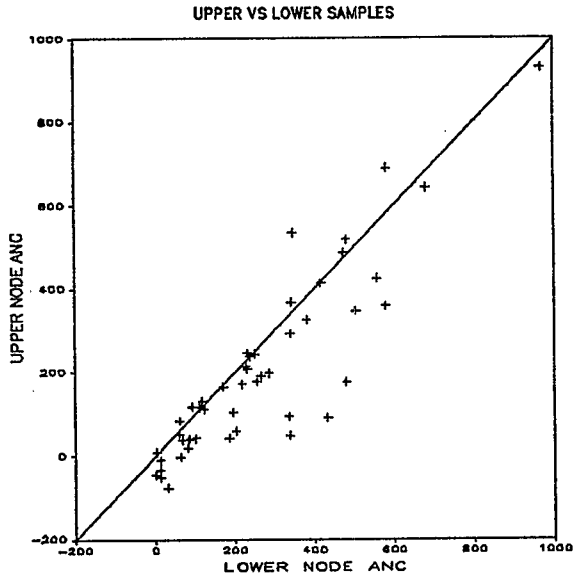
The proportions of the target stream reach population with spring index ANC values of 200 μeq L^{-1} or less were similar in the Mid-Atlantic (MA) and Southeast (SE) regions surveyed by the NSS-I. Excluding Florida, 51% (18,542) of MA reaches and 52% (9,642) of SE reaches had ANC $\leq$ 200 μeq L^{-1} at their upstream ends. After flowing an average of 3 km to their downstream ends, an estimated 41% (15,060) of MA reaches and 47% (8,682) of SE reaches were at or below this index ANC value. In the Mid-Atlantic Region, 7.4% of reaches (2,677) were acidic (ANC $\leq$ 0 μeq L^{-1}) at their upstream ends and 3% (1,098) were acidic at their downstream ends. In the NSS-I Interior Southeast subregions, however, reaches that were actually acidic during spring baseflow were rare. (Note that Florida is not included and will be discussed separately.) An estimated 0.6% of SE reaches (121 reaches in the Cumberland Plateau of the Southern Appalachians) had acidic upstream ends. No reaches with ANC less than zero (upstream or downstream) were observed in the NSS-I in the remaining SE subregions (Southern Blue Ridge, Piedmont, and the Ozarks/Ouachitas). Cumulative frequency distributions for ANC in the upstream and downstream reach node populations of individual subregions are presented in Figures 6-2 (a - i).

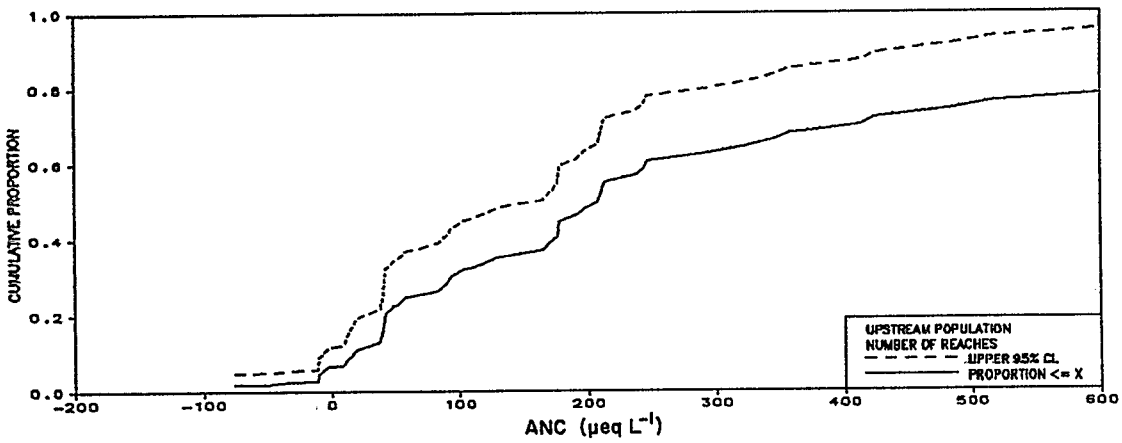
Discussion of the pH distribution in the regions surveyed by the NSS-I refers to several reference pH values (5.0, 5.5, and 6.0). These are defined partially for convenience, and partially for comparison with other studies (e.g., Linthurst et al., 1986; Landers et al., 1987; Messer et al., 1986) that have reported results referencing such values. These reference values bear some relationship to critical values below which populations of different types of fish in freshwater ecosystems are not sustained. Because of the influence of pH on the solubility and speciation of aluminum (Stumm and Morgan, 1981), it is difficult to separate the effects of low pH and aluminum toxicity. However, it has been reported that waters with pH chronically below 4.0 are virtually devoid of fish (Harvey, 1980; Leuven et al., 1984; Wendelaar-Bonga and Dederen, 1986). Similarly, waters with pH chronically below 4.5 are reported to contain few fish species (Cooper and Wagner, 1973). Cooper and Wagner (1973) conclude that pH values less than 5.0 may limit the distribution of brook trout (Salvelinus fontinalis), one of the most tolerant species (Haines, 1981; Magnuson et al., 1984; Johnson et al., 1987).

ANC

POCONOS / CATSKILLS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	-76.4	1.5
20%	41.3	114.4
40%	173.7	230.2
MEDIAN	206.9	257.4
60%	245.0	357.1
80%	635.0	655.5
MAX	4580.8	4871.4
MEAN	431.7	526.1
STD	697.9	747.6
SAMPLE(n)	58	56
POP EST(N)	3244	3235
SE(N)	347	347





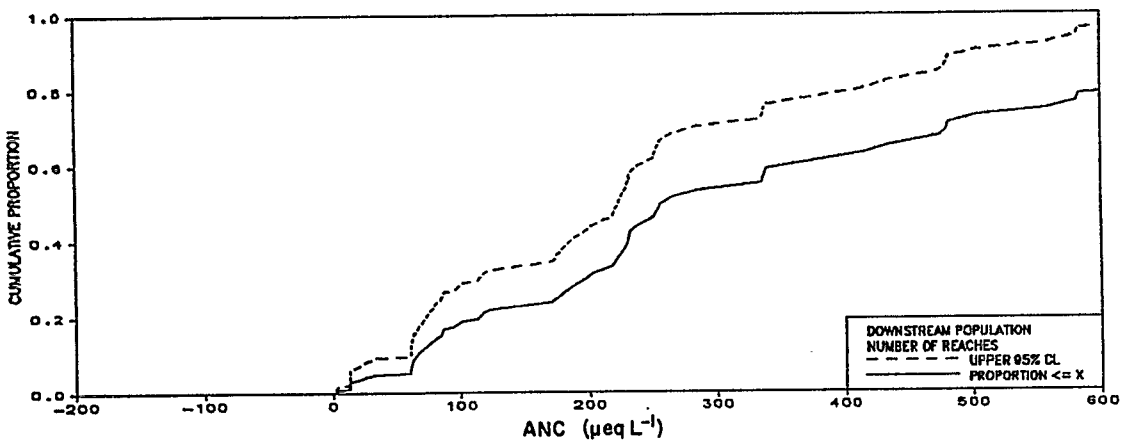
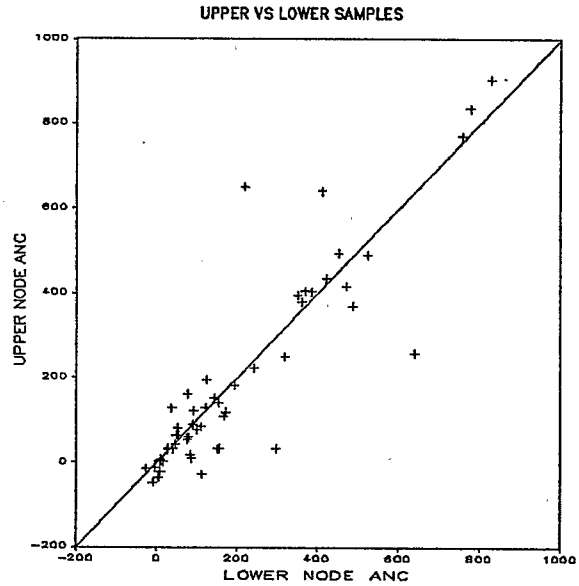


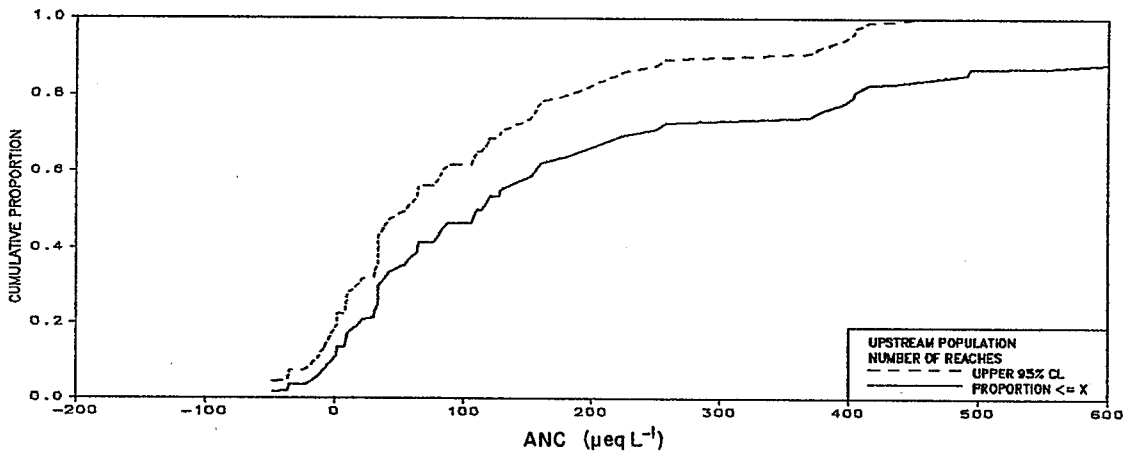
Figure 6-2a. Population distributions and comparison of index ANC at upper and lower reach nodes in NSS-I subregion 1D (Poconos/Catskills).

ANC

NORTHERN APPALACHIANS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	-48.0	-26.0
20%	19.6	43.5
40%	64.4	85.9
MEDIAN	110.5	127.6
60%	155.1	171.7
80%	404.3	445.4
MAX	2702.3	2150.3
MEAN	296.4	312.5
STD	519.9	452.5
SAMPLE(n)	67	61
POP EST(N)	8663	8488
SE(N)	807	814





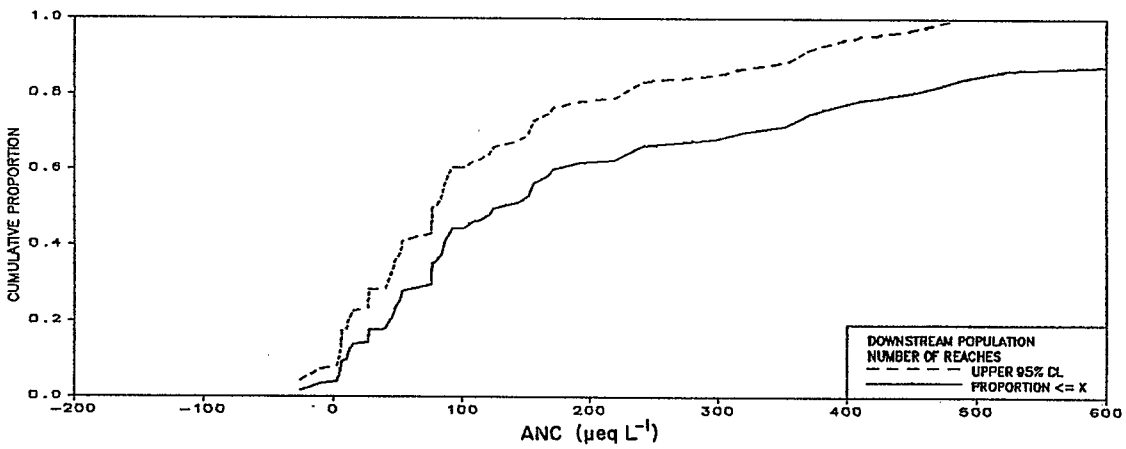
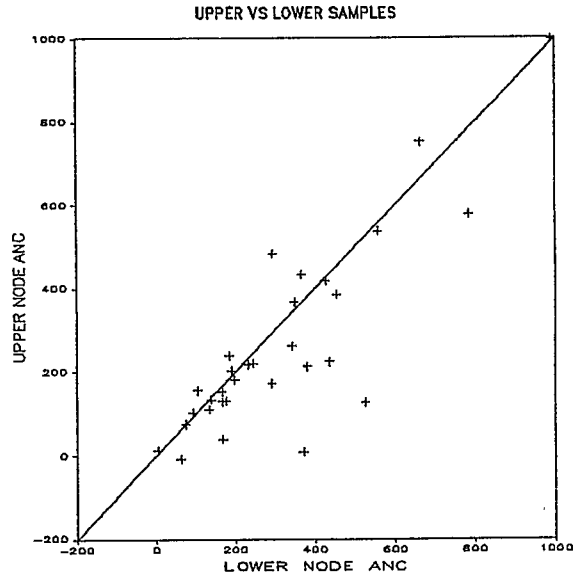


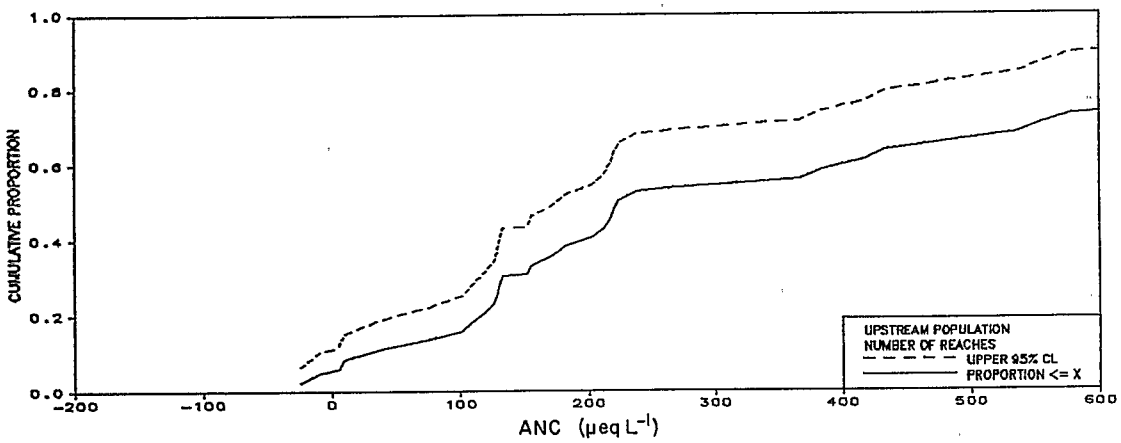
Figure 6-2b. **Population distributions and comparison of index ANC at upper and lower reach nodes in NSS-I subregion 2Cn (Northern Appalachians).**

ANC

VALLEY AND RIDGE

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	-24.0	5.0
20%	115.8	172.9
40%	196.3	337.5
MEDIAN	223.4	395.7
60%	402.5	549.0
80%	1005.2	1135.1
MAX	4924.8	4909.9
MEAN	644.8	819.9
STD	932.2	993.2
SAMPLE(n)	44	47
POP EST(N)	13038	13992
SE(N)	1249	1213





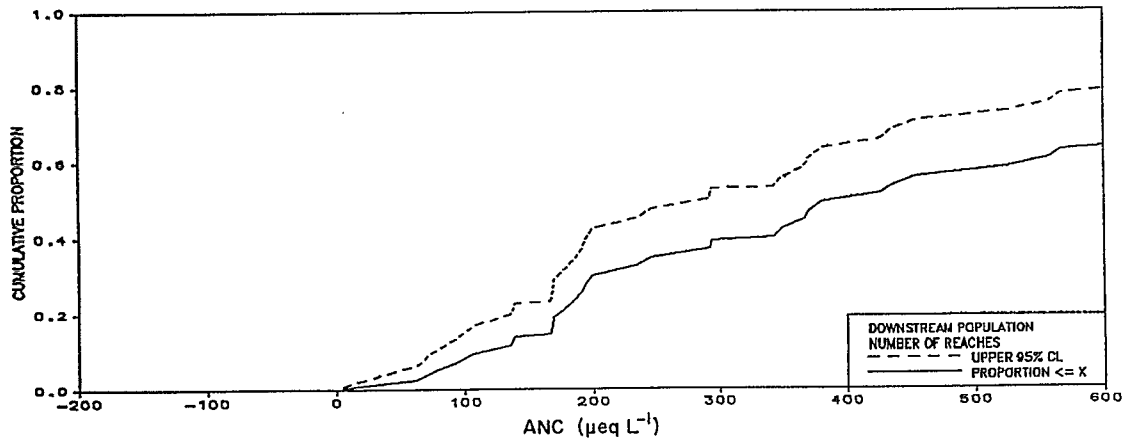
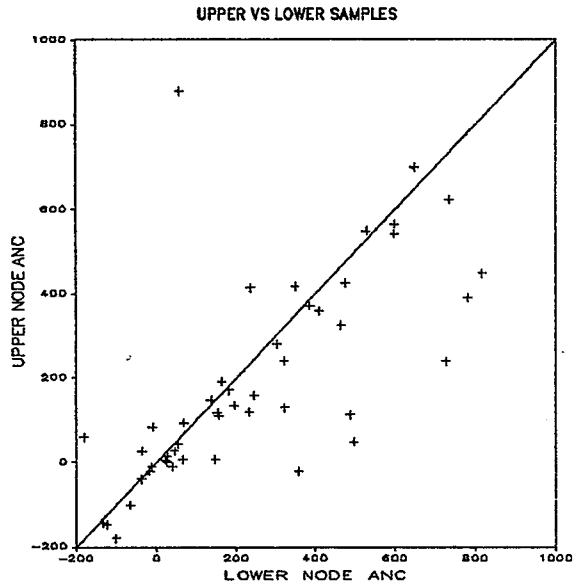


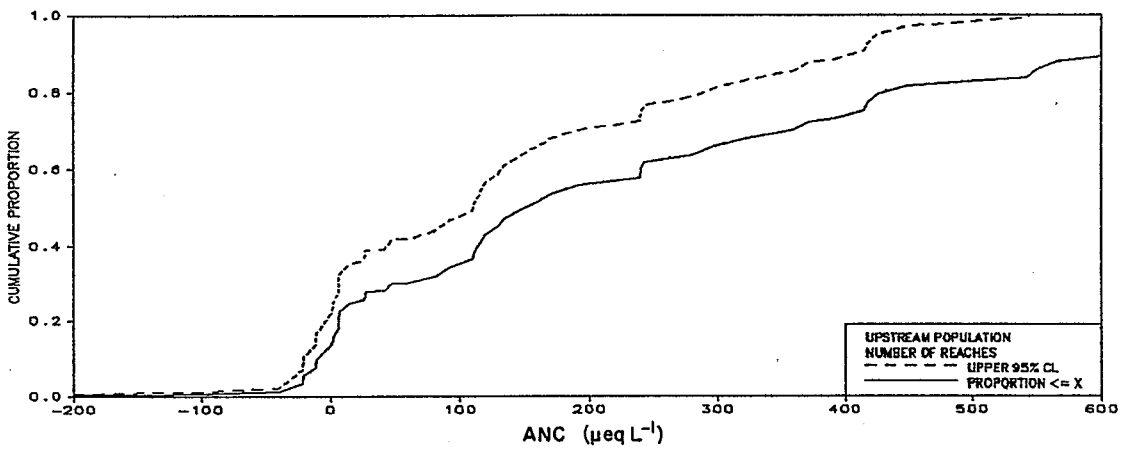
Figure 6-2c. Population distributions and comparison of index ANC at upper and lower reach nodes in NSS-I subregion 2Bn (Valley and Ridge).

ANC

MID-ATLANTIC COASTAL PLAIN

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	-442.3	-181.5
20%	6.5	54.4
40%	114.2	188.6
MEDIAN	150.5	308.7
60%	240.2	387.6
80%	431.2	657.6
MAX	1117.1	2196.1
MEAN	258.8	452.4
STD	282.9	506.0
SAMPLE(n)	57	58
POP EST(N)	11284	11287
SE(N)	1078	1078





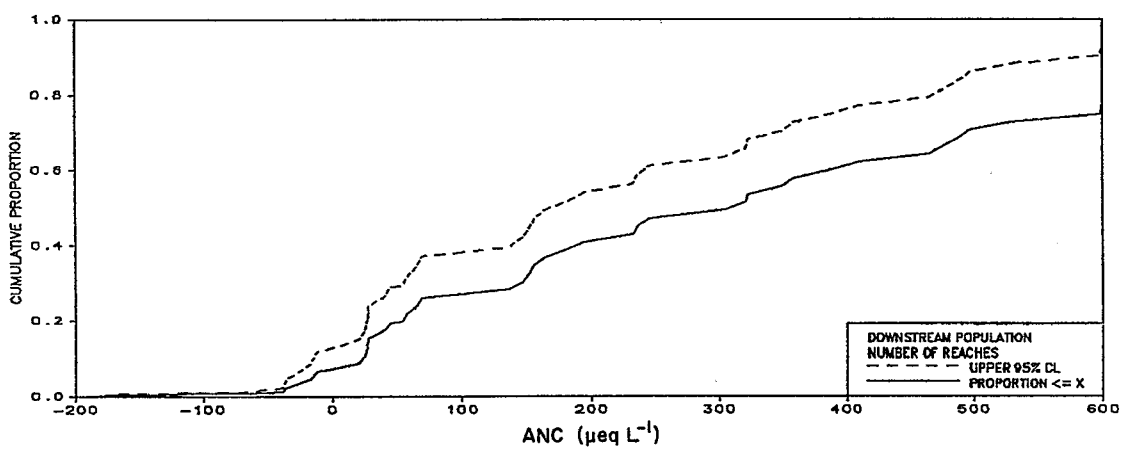
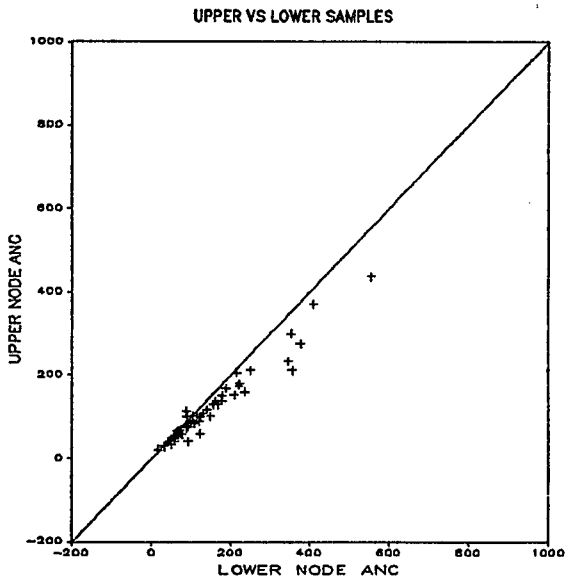


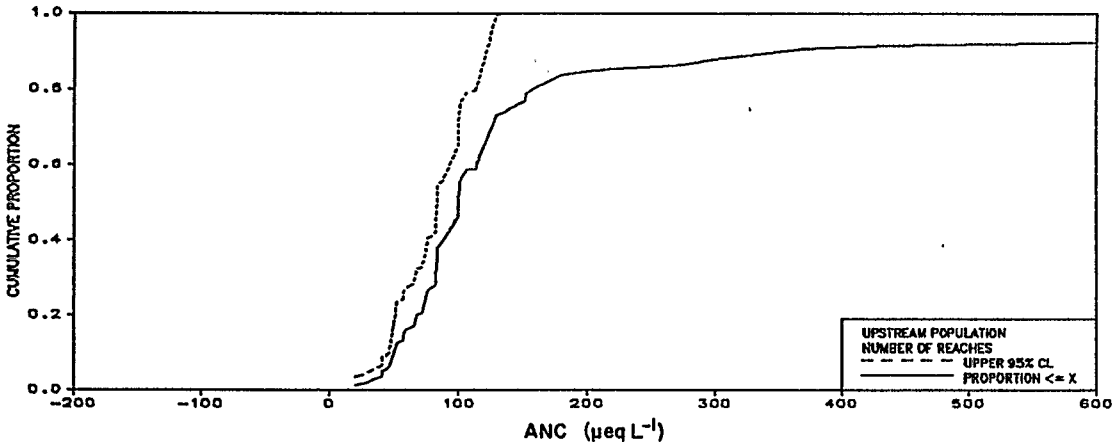
Figure 6-2d. Population distributions and comparison of index ANC at upper and lower reach nodes in NSS-I subregion 3B (Mid-Atlantic Coastal Plain).

ANC

SOUTHERN BLUE RIDGE

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	20.9	16.5
20%	67.7	88.4
40%	88.5	104.4
MEDIAN	99.6	121.6
60%	114.3	137.5
80%	157.1	206.7
MAX	2227.9	1730.4
MEAN	241.3	257.2
STD	451.7	403.1
SAMPLE(n)	54	54
POP EST(N)	2031	2031
SE(N)	326	326





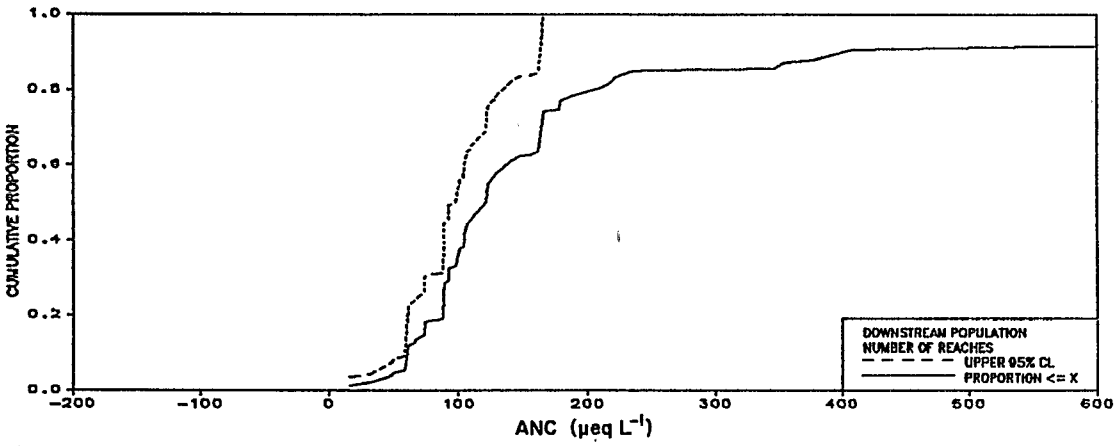
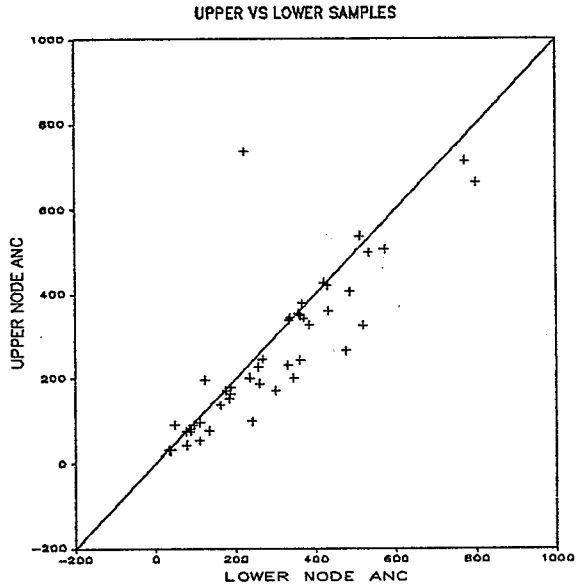


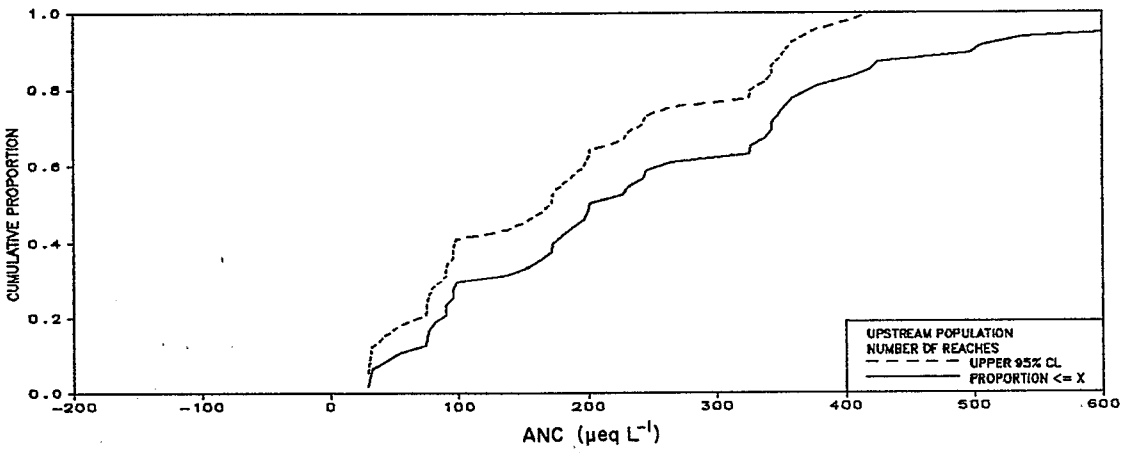
Figure 6-2e. Population distributions and comparison of index ANC at upper and lower reach nodes in NSS-I subregion 2As (Southern Blue Ridge).

ANC

PIEDMONT

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	29.7	33.6
20%	86.0	101.9
40%	173.0	188.4
MEDIAN	201.4	259.3
60%	256.1	335.3
80%	372.1	426.2
MAX	736.1	799.9
MEAN	256.2	285.3
STD	179.6	183.5
SAMPLE(n)	47	47
POP EST(N)	7515	7515
SE(N)	650	650





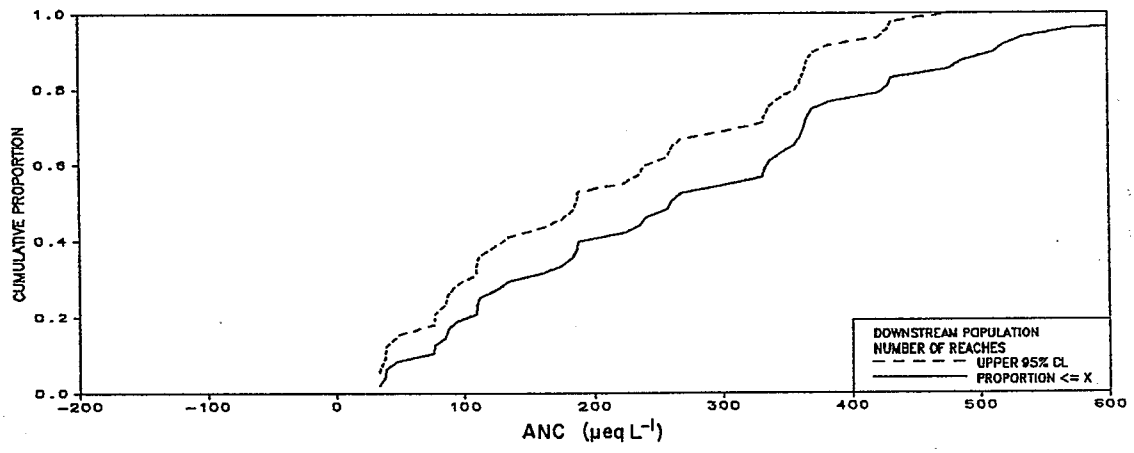
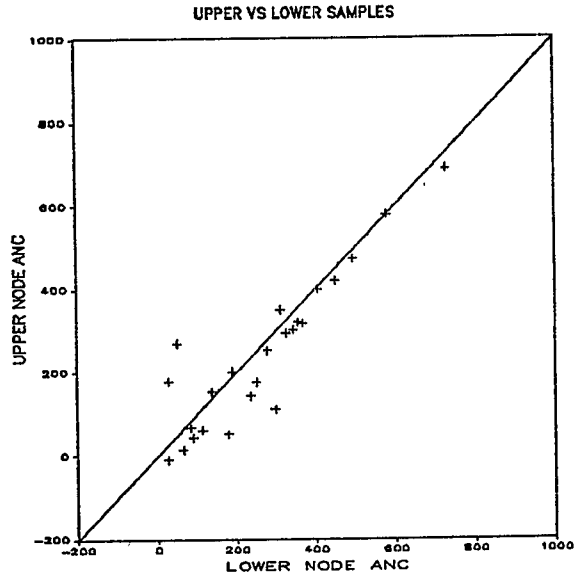


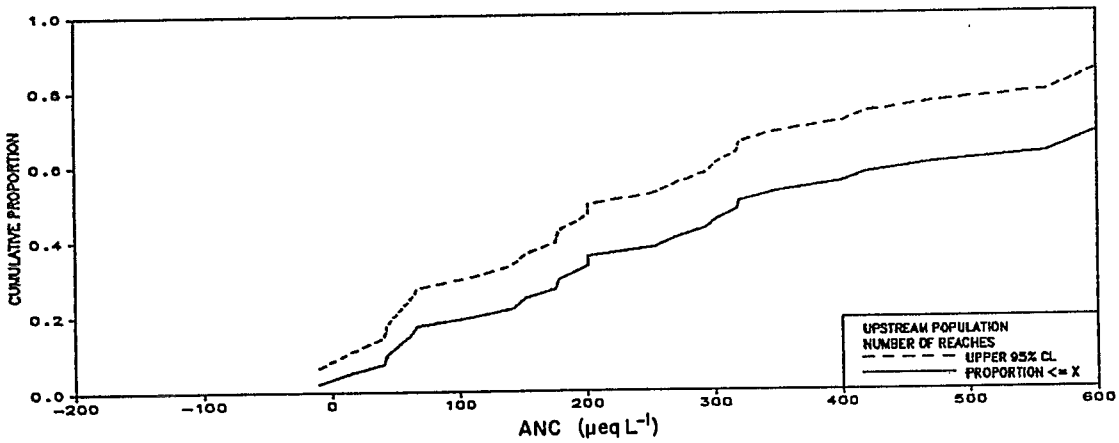
Figure 6-2f. Population distributions and comparison of index ANC at upper and lower reach nodes in NSS-I subregion 3A (Piedmont).

ANC

SOUTHERN APPALACHIANS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	-9.9	26.0
20%	114.8	151.6
40%	266.8	314.9
MEDIAN	319.5	382.6
60%	469.0	548.9
80%	1318.4	2224.4
MAX	3827.6	4041.8
MEAN	796.0	1001.8
STD	979.5	1119.1
SAMPLE(n)	39	40
POP EST(N)	4936	5057
SE(N)	529	526





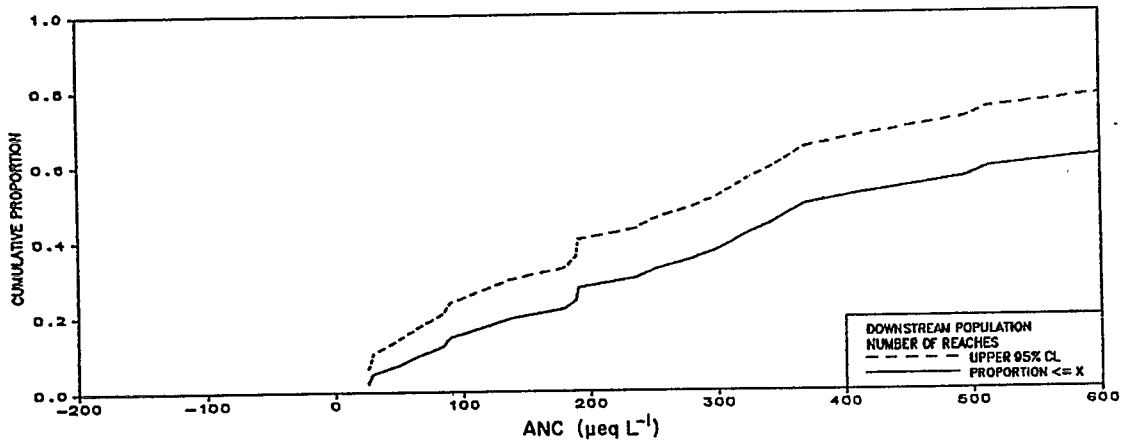
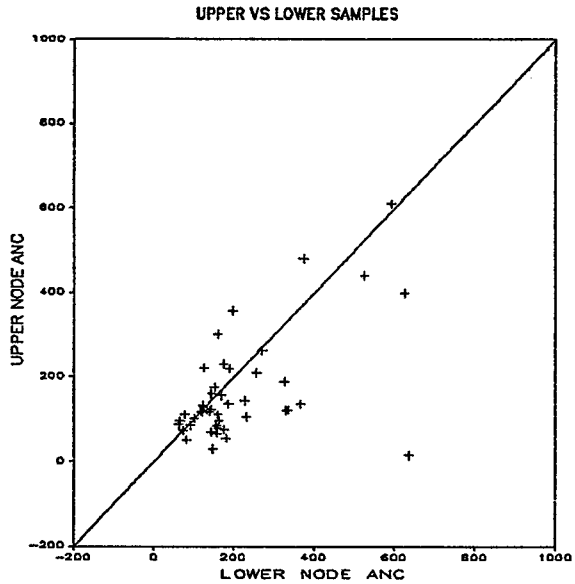


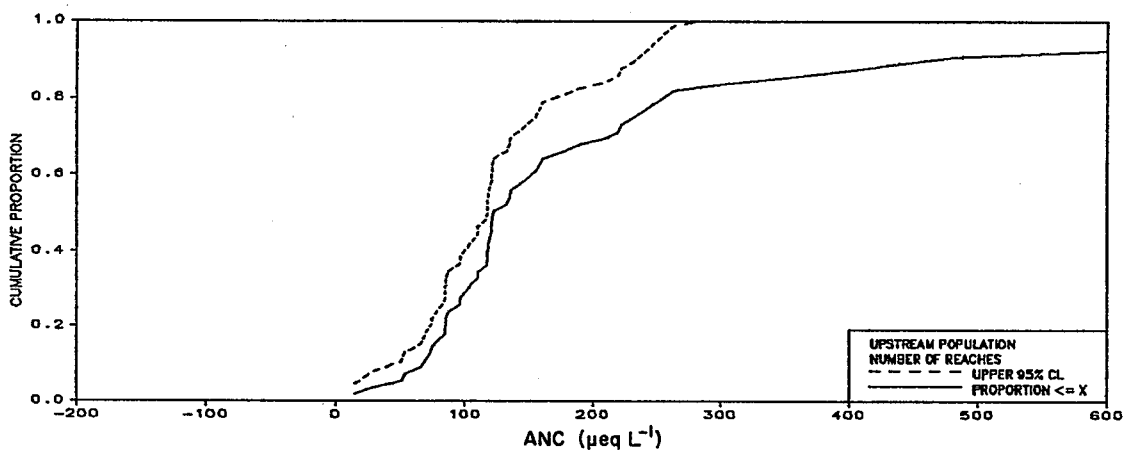
Figure 6-2g. Population distributions and comparison of index ANC at upper and lower reach nodes in NSS-I subregion 2X (Southern Appalachians).

ANC

OZARKS / OUACHITAS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	15.2	63.2
20%	85.2	120.2
40%	118.1	151.8
MEDIAN	122.6	161.9
60%	151.9	180.1
80%	254.7	327.1
MAX	2089.5	2987.8
MEAN	245.6	303.2
STD	336.4	453.0
SAMPLE(n)	49	48
POP EST(N)	4204	4116
SE(N)	406	410





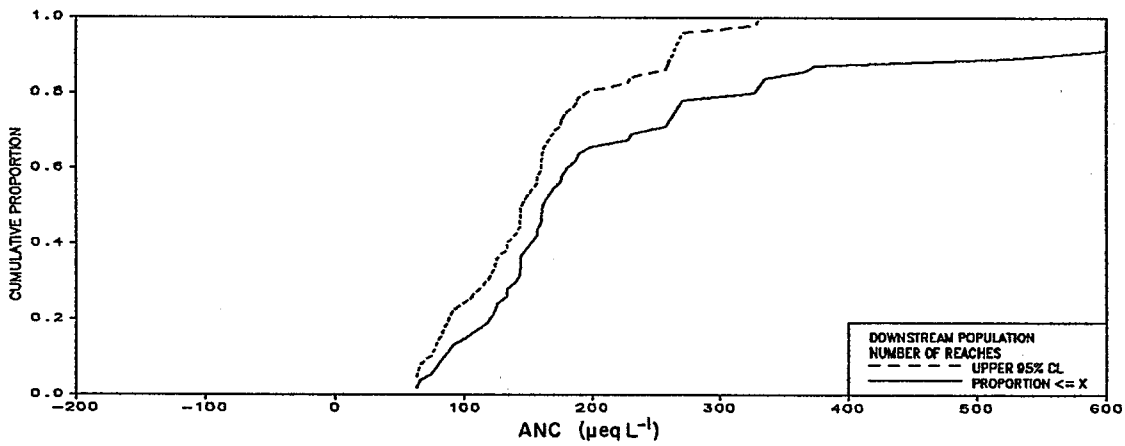
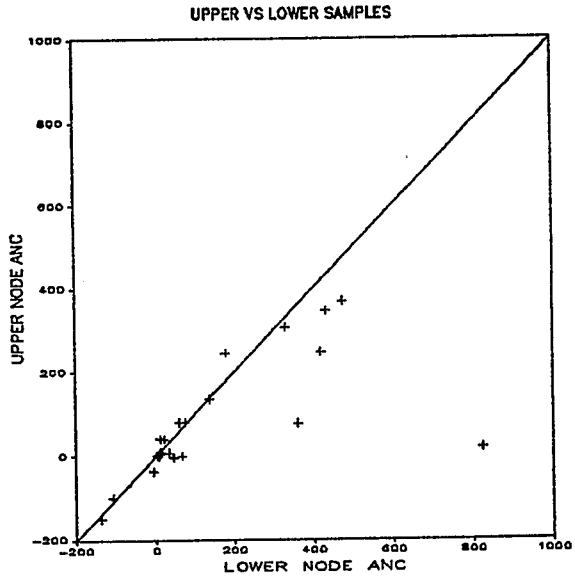


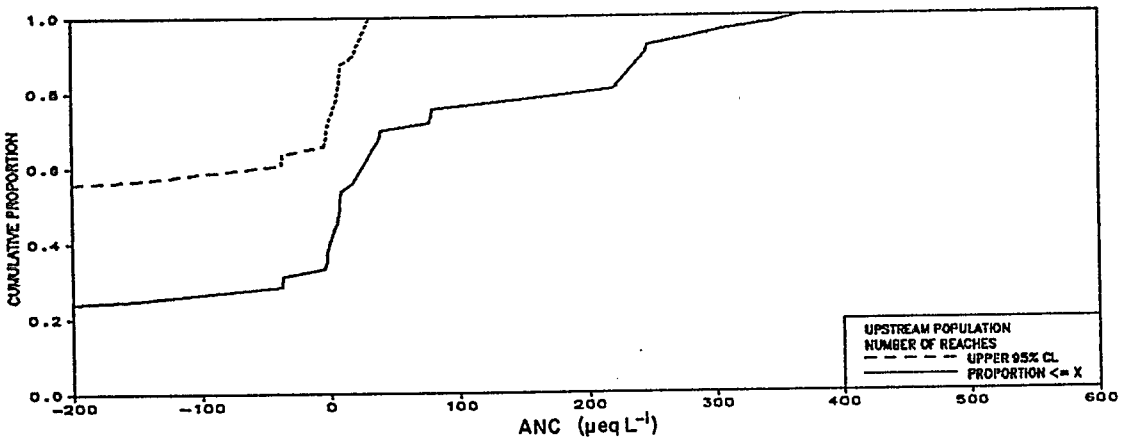
Figure 6-2h. Population distributions and comparison of index ANC at upper and lower reach nodes in NSS-I subregion 2D (Ozarks/Ouachitas).

ANC

FLORIDA

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	-645.2	-138.3
20%	-545.0	7.0
40%	-0.4	18.1
MEDIAN	7.6	33.2
60%	25.3	60.5
80%	207.0	174.1
MAX	368.0	1801.1
MEAN	-69.3	156.6
STD	313.4	323.4
SAMPLE(n)	31	34
POP EST(N)	1727	1555
SE(N)	437	306





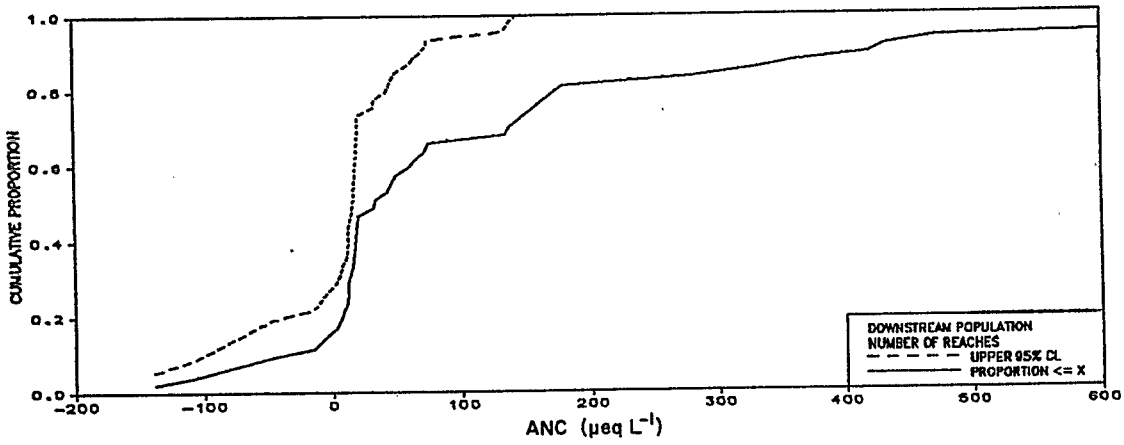


Figure 6-2i. **Population distributions and comparison of index ANC at upper and lower reach nodes in NSS-I subregion 3C (Florida).**

Blueback herring (Alosa aestivalis), an important anadromous fish that spawns in small tributaries entering Chesapeake Bay, like many other warm water fish species, is apparently more sensitive to low pH and elevated aluminum concentrations than are brook trout and brown trout (Klauda and Palmer, 1987; Klauda et al., 1987). Blueback herring eggs and larvae experienced high mortality when exposed to acid pulses or prolonged exposure at pH 5.0 to 5.7 and calculated total monomeric aluminum concentrations between 0.03 and 0.09 mg L^{-1}.

Klauda and Palmer (1987) inferred, from a review of field and laboratory studies, a general ranking of the relative sensitivity of several fishes to pH and aluminum. They report, without attempting a life-stage-specific comparison, that percids (e.g., darters), cyprinids, flagfish (Jordanella floridae), desert pupfish (Cyprinodon n. nevadensis), and striped bass appear to be more sensitive than blueback herring. On the other hand, some percids (e.g., yellow perch Perca flavescens and walleye Stizostedion vitreum, centrarchids, esocids, catostomids, and salmonids) are apparently less sensitive to low pH and high aluminum than are blueback herring.

Haines and Baker (1986) have summarized a large volume of literature concerning pH-toxicity bioassays and the occurrence of various fish species in lakes and streams over a range of pH. Estimates for critical values below which salmonid fish populations are not sustained range from pH 4.7 to 5.5 (Haines and Baker, 1986). Estimates for Smallmouth Bass are between pH 5.2 and 5.5. Except for effects reported on several species of dace, shiners, and minnows, pH levels above 6.0 have not been associated with adverse impacts on fish populations. However, the recent blueback herring bioassays by Klauda and Palmer (1987) and Klauda et al. (1987) and others (Hall et al., 1985, 1987; Hall, 1987) employing striped bass (Morone saxatilis) further suggest that, under certain conditions of aluminum concentration, pH between 6.0 and 6.5 can lead to increased egg and larval mortality.

Several types of pH measurements were made in the NSS-I (Section 3). The measurements that most accurately reflect pH in the stream at the time of sampling are the closed-headspace measurements made in the processing laboratory. These measurements are recorded in the NSS-I data base as the variable PHSTVL. Before proceeding with an overview of population distributions of pH in the NSS-I regions, it is helpful to briefly review some quality assurance information from Section 4 regarding the precision and accuracy of pH measurements. System level precision estimates were 0.026 to 0.036 pH unit (Table 4-3), depending on the pH range of samples. Precision estimates incorporating day-to-day variability in the processing laboratory were less than 0.1 unit.

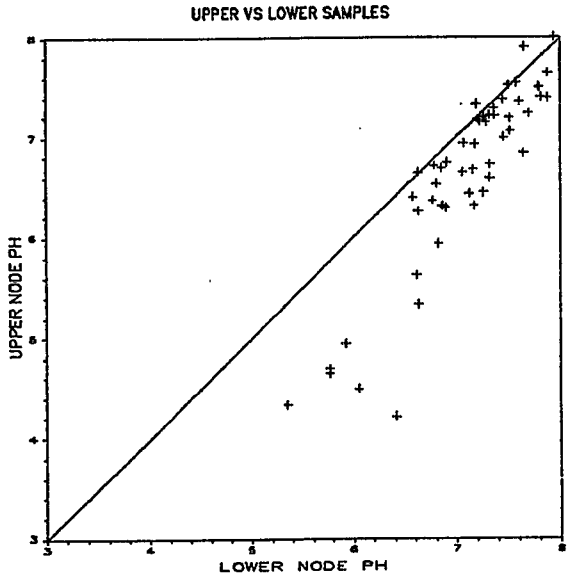
In the Mid-Atlantic Region, an estimated 13% of the reaches (4,770) had spring base flow pH $\leq$ 5.5 at their upstream ends. At their downstream ends, 5.4% (1,991) were at or below this pH level. In the portions of the Southeast Region surveyed during NSS-I (excluding Florida), 2% (347) had pH $\leq$ 5.5 at their upstream ends and less than 1% had pH at or below 5.5 at their downstream ends. The Florida subregion (3C) stands out as a geographic area with relatively high percentages of acidic and low ANC streams. It is also an area, like the Mid-Atlantic Coastal Plain subregion (3B), in which there are many highly colored streams with high concentrations of dissolved organic material that may ameliorate to some extent the adverse effects of aluminum on fish in these streams (by complexing aluminum ion). Cumulative frequency distributions for pH (closed headspace, measured in the processing laboratory) in the upstream and downstream reach node populations of the NSS-I subregions are presented in Figures 6-3 (a - i).

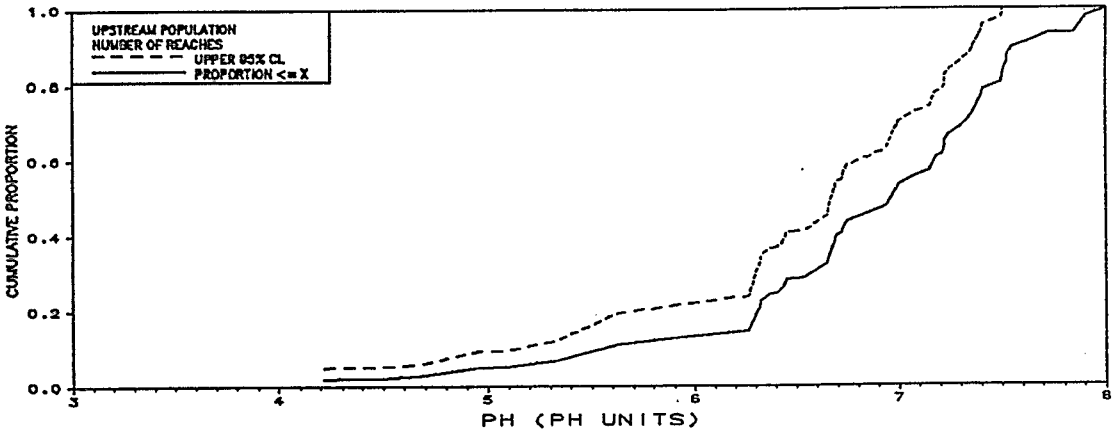
Table 6-1 compares population median pH, ANC, and SO_4^{2-} based on both upstream and downstream sampling locations across the nine subregions sampled by the NSS-I and the Pilot Survey. It is evident that there is a consistent pattern of higher ANC and pH at downstream ends of target stream reaches, supporting a hypothesis that streamflow tends to acquire chemical weathering products in the downstream direction due to the increased time and opportunity for

PH

POCONOS / CATSKILLS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	4.21	5.35
20%	6.31	6.84
40%	6.70	7.18
MEDIAN	6.96	7.28
60%	7.18	7.38
80%	7.48	7.65
MAX	8.01	8.23
MEAN	5.70	6.90
STD	5.05	6.49
SAMPLE(n)	58	56
POP EST(N)	3244	3235
SE(N)	347	347





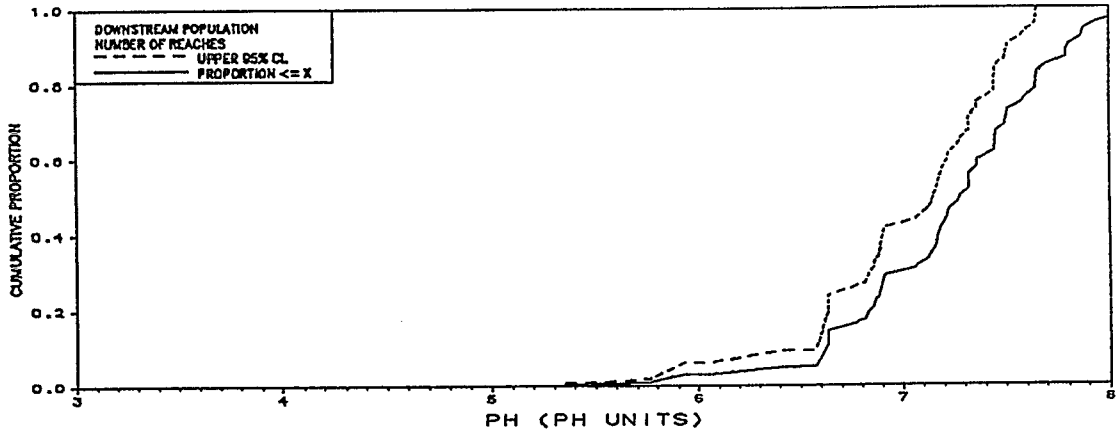
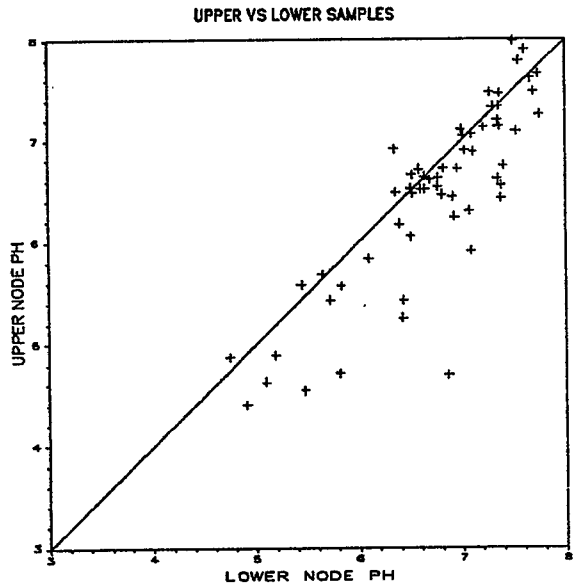


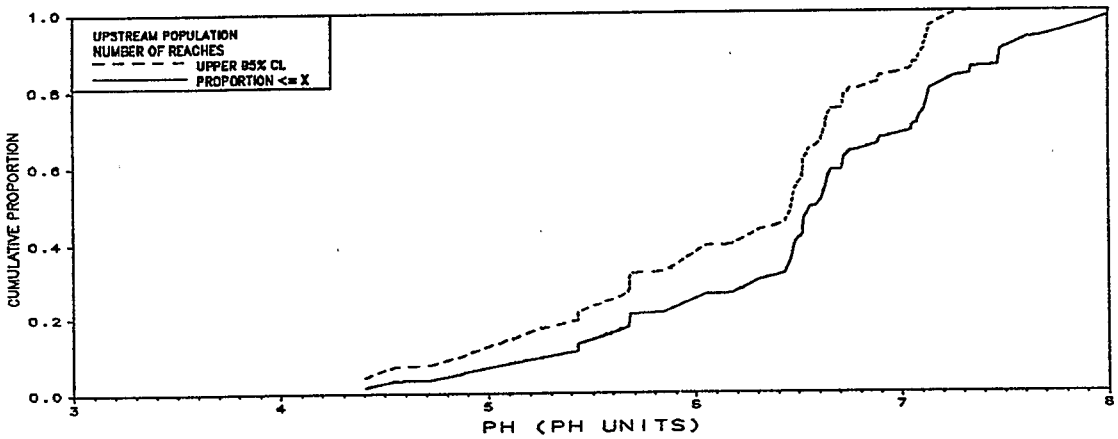
Figure 6-3a. Population distributions and comparison of index pH at upper and lower reach nodes in NSS-I subregion 1D (Poconos/Catskills).

PH

NORTHERN APPALACHIANS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	4.40	4.74
20%	5.68	6.42
40%	6.49	6.66
MEDIAN	6.60	6.91
60%	6.72	7.07
80%	7.14	7.37
MAX	8.00	8.25
MEAN	5.66	6.05
STD	5.19	5.55
SAMPLE(n)	67	61
POP EST(N)	8663	8488
SE(N)	807	814





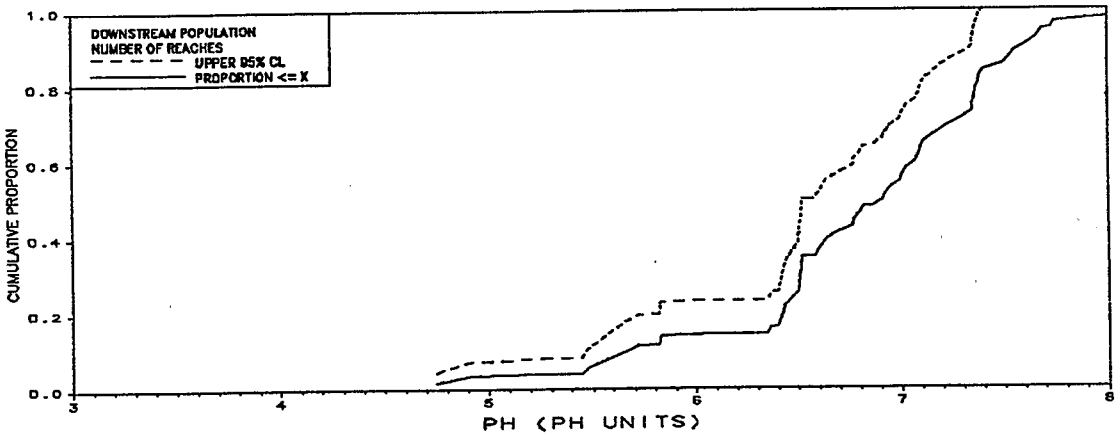
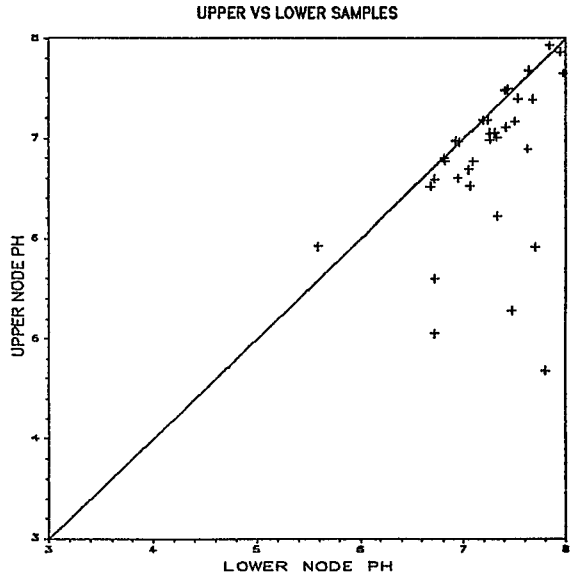


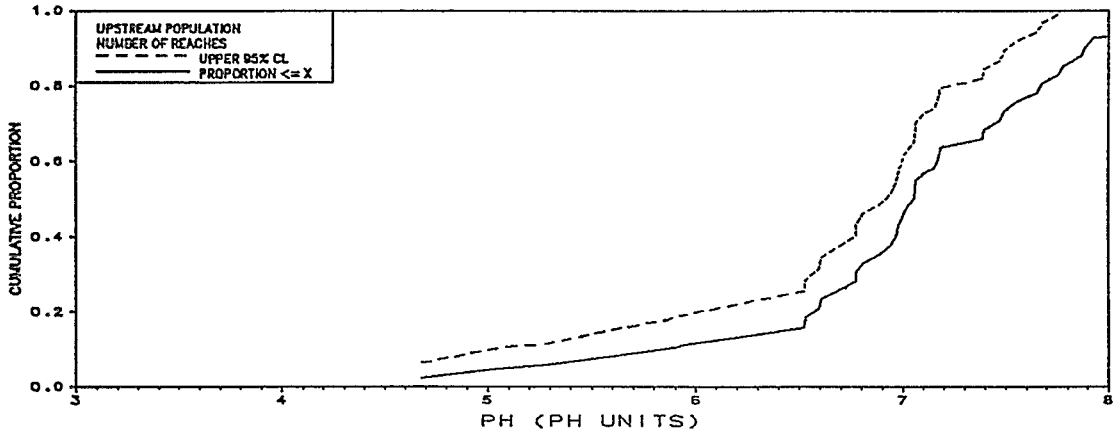
Figure 6-3b. Population distributions and comparison of index pH at upper and lower reach nodes in NSS-I subregion 2Cn (Northern Appalachians).

PH

VALLEY AND RIDGE

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	4.68	5.59
20%	6.57	6.94
40%	6.96	7.31
MEDIAN	7.05	7.41
60%	7.17	7.52
80%	7.67	7.99
MAX	8.62	8.88
MEAN	6.02	7.17
STD	5.46	6.80
SAMPLE(n)	44	47
POP EST(N)	13038	13992
SE(N)	1249	1213





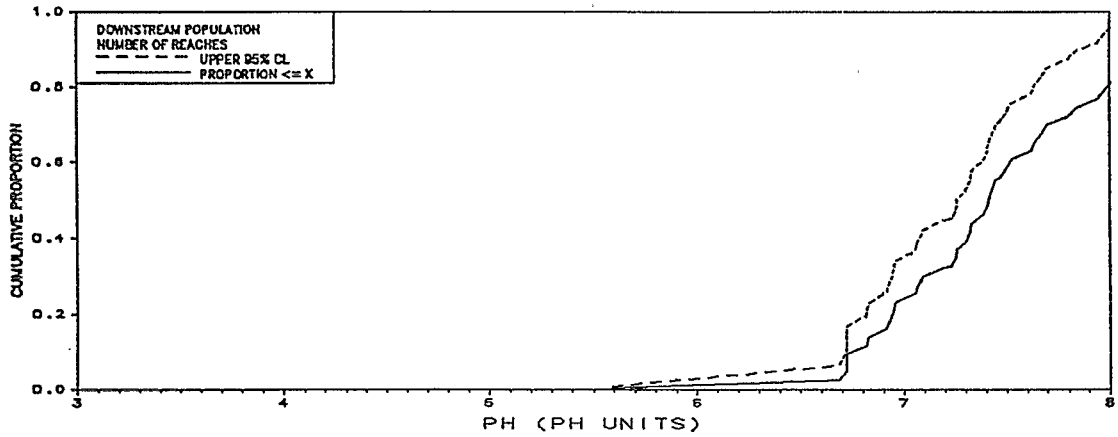
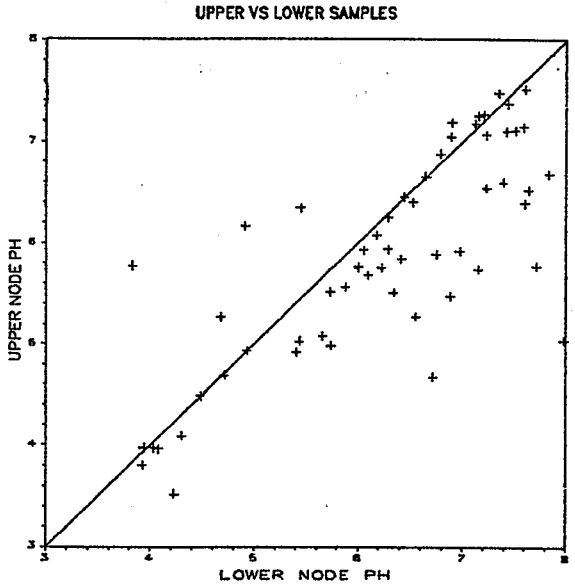


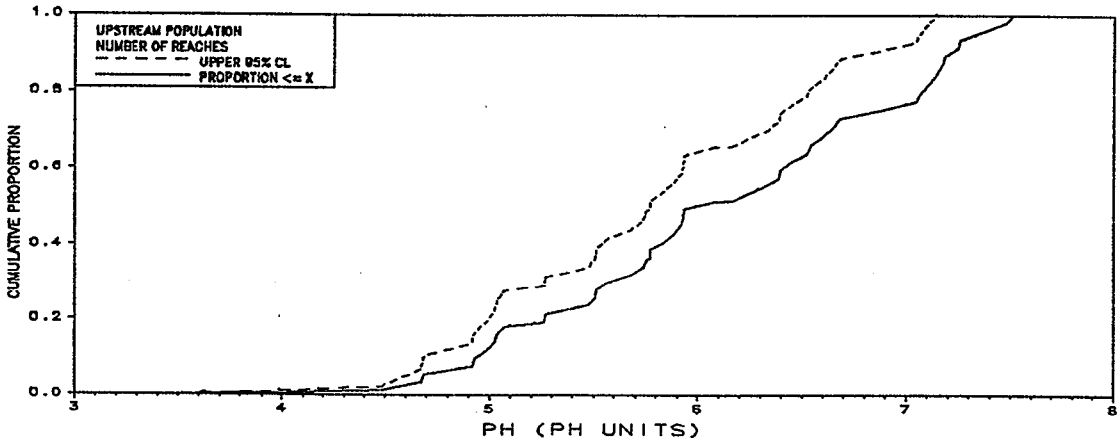
Figure 6-3c. Population distributions and comparison of index pH at upper and lower reach nodes in NSS-I subregion 2Bn (Valley and Ridge).

PH

MID-ATLANTIC COASTAL PLAIN

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	3.51	3.83
20%	5.27	5.77
40%	5.81	6.43
MEDIAN	5.98	6.71
60%	6.40	6.90
80%	7.07	7.38
MAX	7.51	7.98
MEAN	5.38	5.62
STD	4.87	5.00
SAMPLE(n)	57	58
POP EST(N)	11284	11287
SE(N)	1078	1078





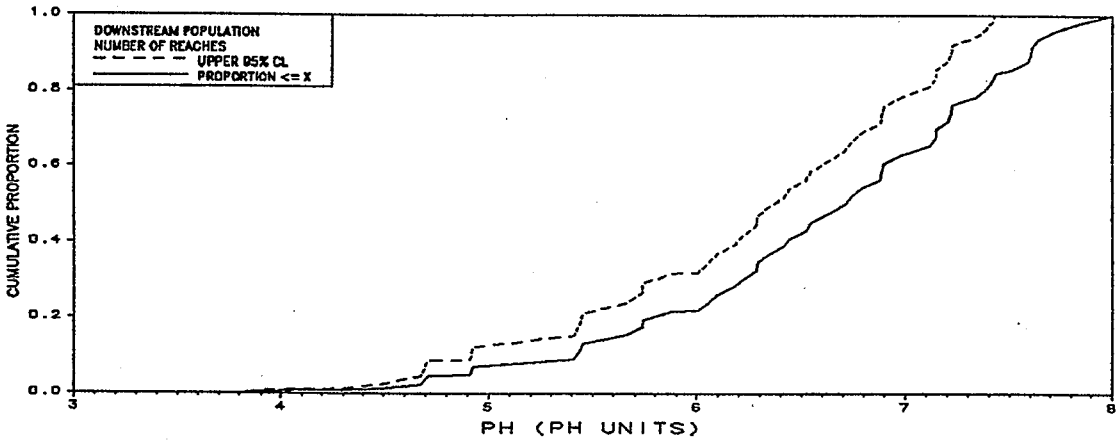
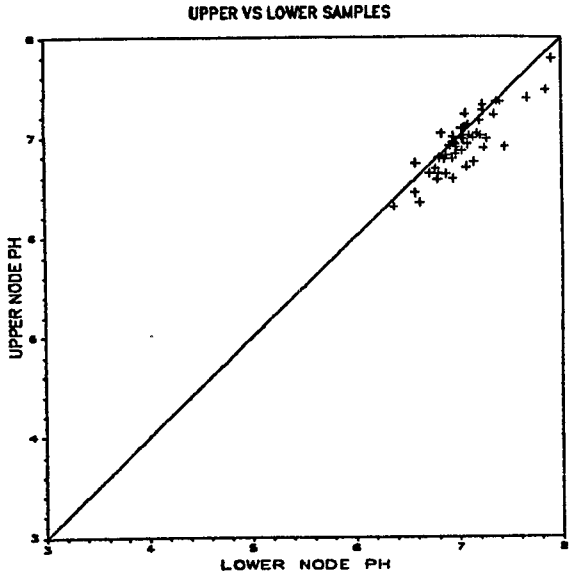


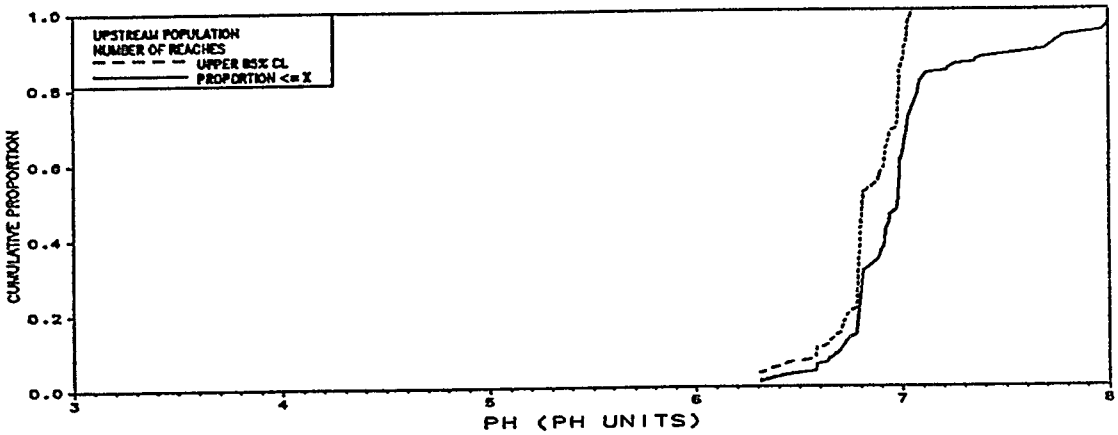
Figure 6-3d. Population distributions and comparison of index pH at upper and lower reach nodes in NSS-I subregion 3B (Mid-Atlantic Coastal Plain).

PH

SOUTHERN BLUE RIDGE

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	6.31	6.38
20%	6.79	6.86
40%	6.92	6.97
MEDIAN	6.99	7.03
60%	6.99	7.07
80%	7.09	7.21
MAX	8.38	8.43
MEAN	6.92	6.99
STD	7.10	7.17
SAMPLE(n)	54	54
POP EST(N)	2031	2031
SE(N)	326	326





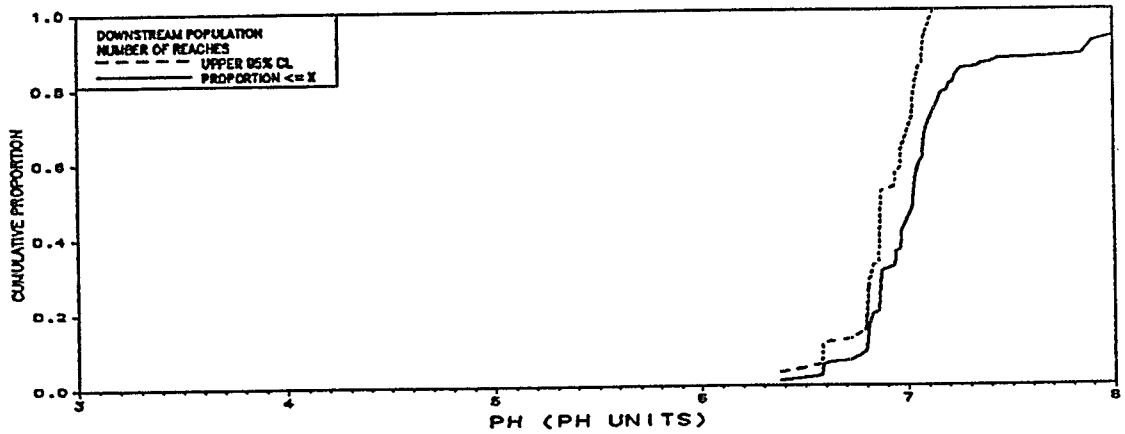
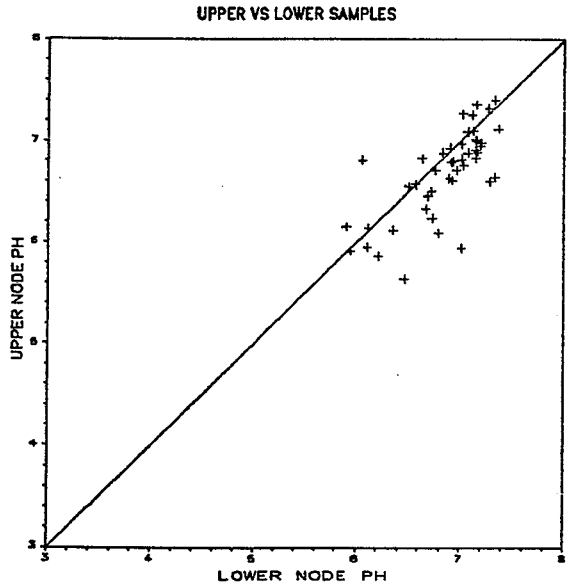


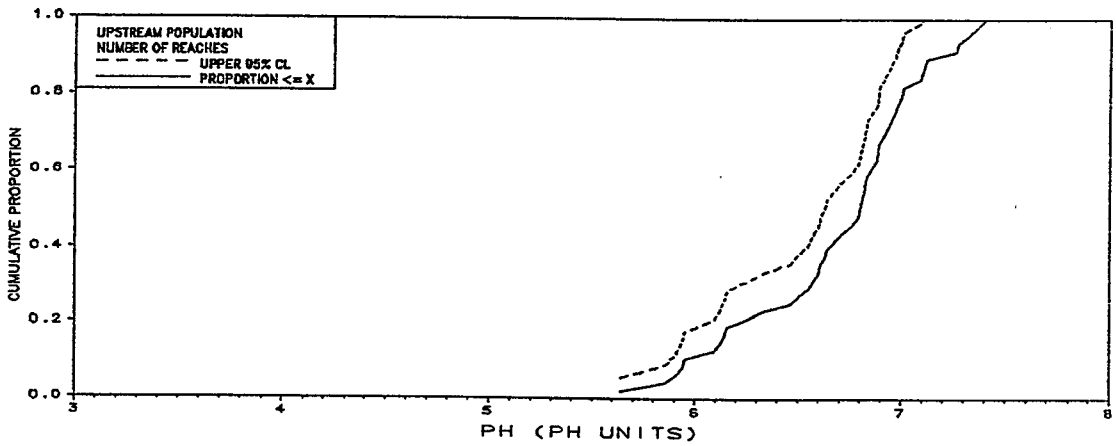
Figure 6-3e. Population distributions and comparison of index pH at upper and lower reach nodes in NSS-I subregion 2As (Southern Blue Ridge).

PH

PIEDMONT

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	5.64	5.90
20%	6.20	6.54
40%	6.64	6.89
MEDIAN	6.80	6.95
60%	6.84	7.03
80%	7.00	7.15
MAX	7.40	7.36
MEAN	6.46	6.64
STD	6.36	6.55
SAMPLE(n)	47	47
POP EST(N)	7515	7515
SE(N)	650	650





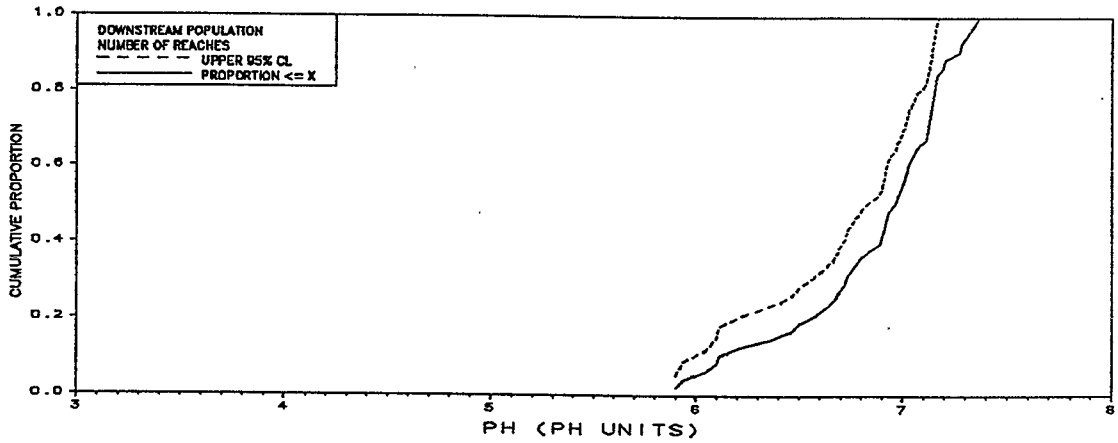
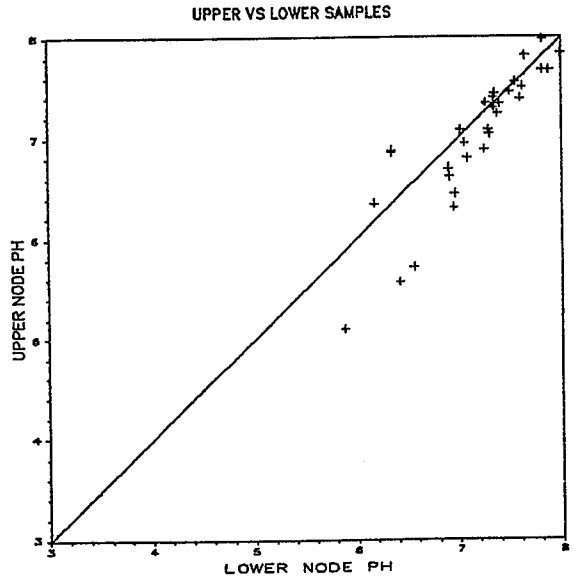


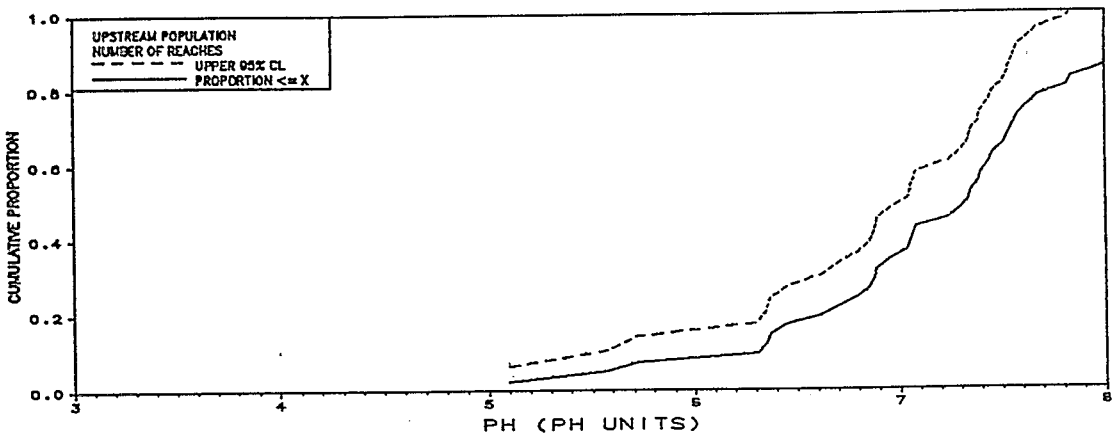
Figure 6-3f. **Population distributions and comparison of index pH at upper and lower reach nodes in NSS-I subregion 3A (Piedmont).**

PH

SOUTHERN APPALACHIANS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	5.10	5.88
20%	6.63	6.92
40%	7.06	7.29
MEDIAN	7.33	7.36
60%	7.44	7.48
80%	7.80	7.82
MAX	8.59	8.40
MEAN	6.40	6.91
STD	5.89	6.63
SAMPLE(n)	39	40
POP EST(N)	4936	5057
SE(N)	529	526





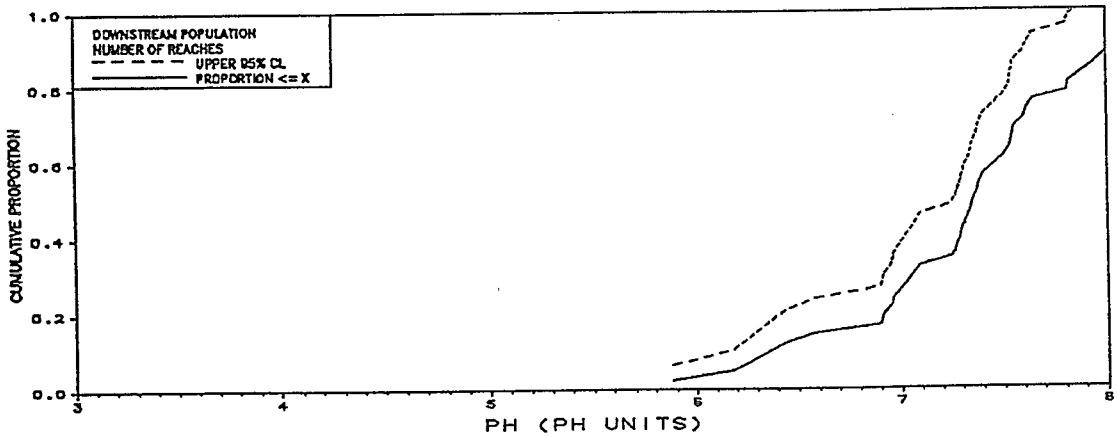
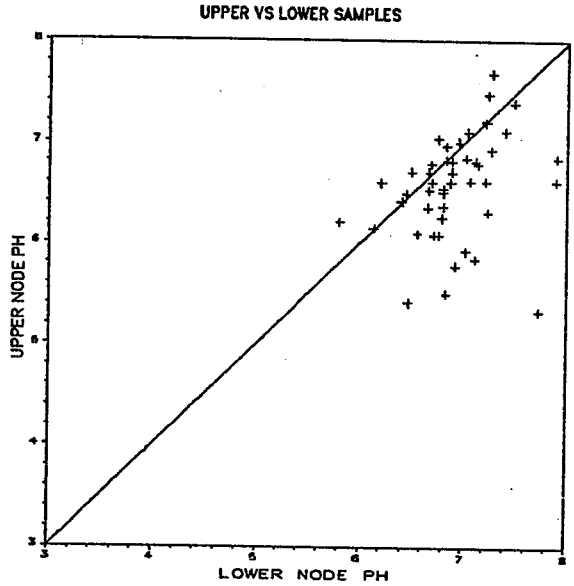


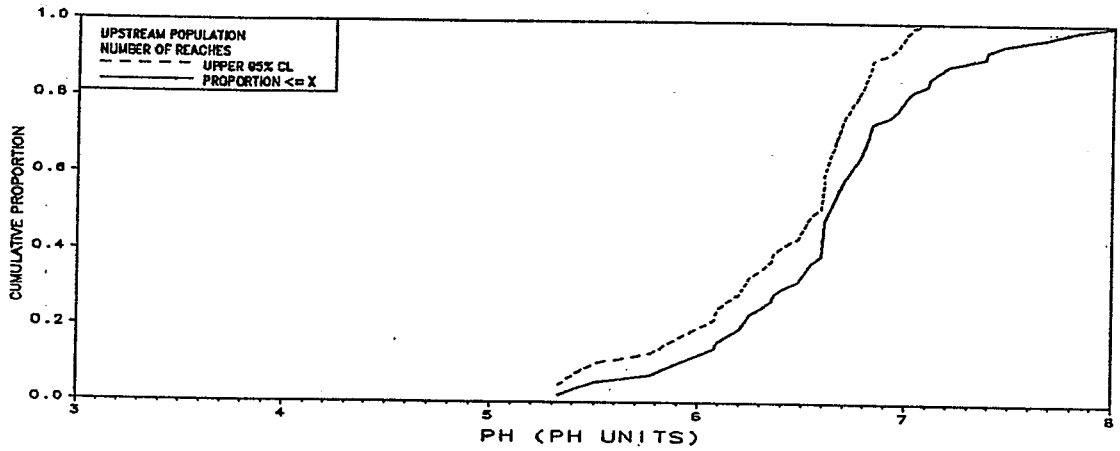
Figure 6-3g. Population distributions and comparison of index pH at upper and lower reach nodes in NSS-I subregion 2X (Southern Appalachians).

PH

OZARKS / OUACHITAS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	5.33	5.80
20%	6.20	6.65
40%	6.59	6.79
MEDIAN	6.62	6.82
60%	6.72	6.93
80%	7.00	7.21
MAX	8.05	8.17
MEAN	6.29	6.73
STD	6.05	6.63
SAMPLE(n)	49	48
POP EST(N)	4204	4116
SE(N)	406	410





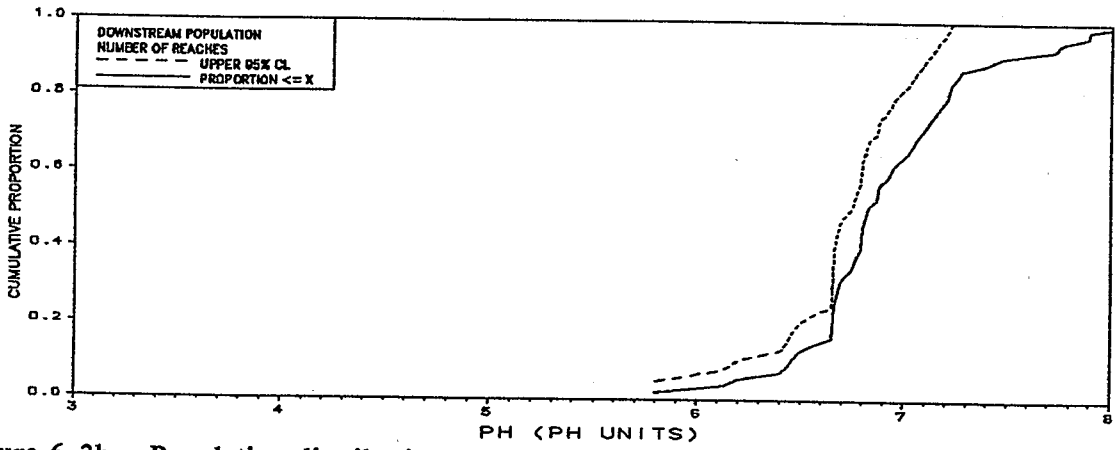
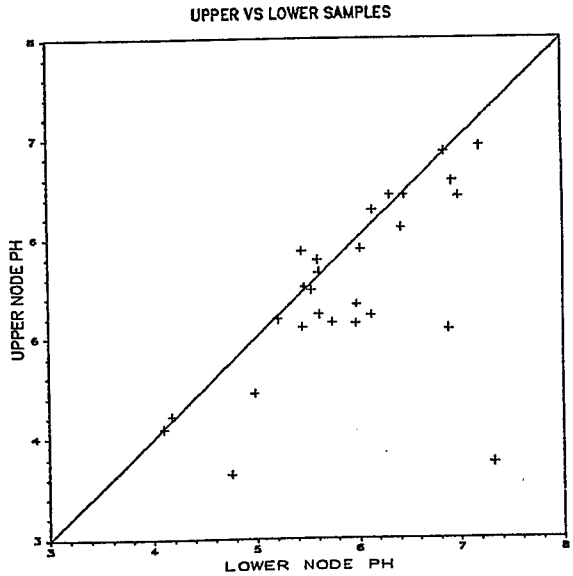


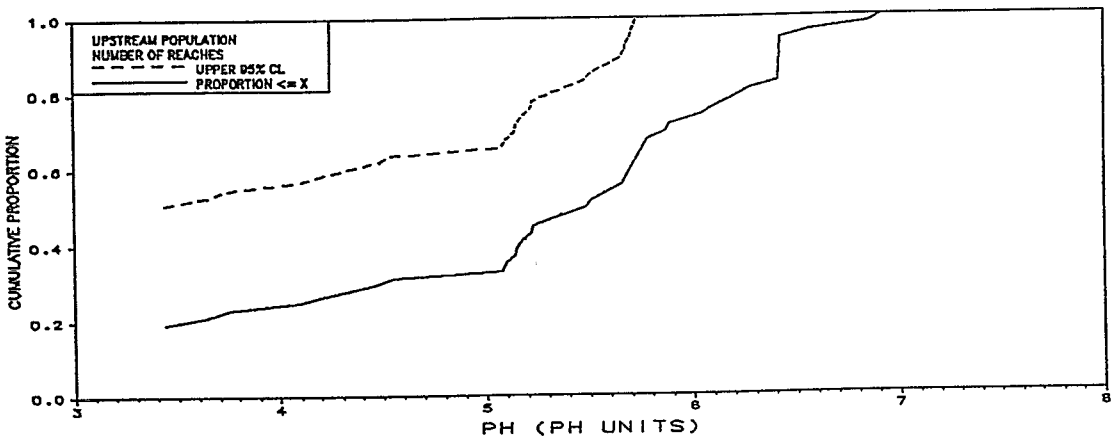
Figure 6-3h. Population distributions and comparison of index pH at upper and lower reach nodes in NSS-I subregion 2D (Ozarks/Ouachitas).

PH

FLORIDA

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	3.44	4.10
20%	3.52	5.37
40%	5.16	5.60
MEDIAN	5.48	5.62
60%	5.70	5.98
80%	6.25	6.30
MAX	6.92	7.57
MEAN	4.08	5.16
STD	3.85	4.80
SAMPLE(n)	31	34
POP EST(N)	1727	1555
SE(N)	437	306





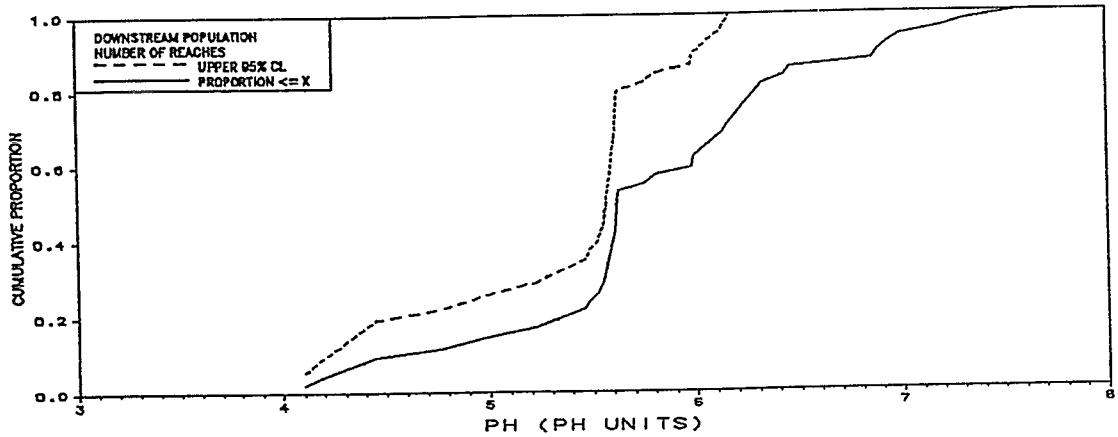


Figure 6-3i. Population distributions and comparison of index pH at upper and lower reach nodes in NSS-I subregion 3C (Florida).

Table 6-1. Population Median ANC, pH, and Sulfate Concentration at Lower (L) and Upper (U) Reach Nodes of NSS-I Subregions

Subregion	ANC (μeq L^{-1})		pH		SO_4^{2-} (μeq L^{-1})	
	L	U	L	U	L	U
1D (Poconos/Catskills)	257	207	7.3	7.0	238	214
2Cn (N. Appalachians)	128	110	6.9	6.6	220	209
2Bn (Valley and Ridge)	396	223	7.4	7.1	185	182
3B (MA Coastal Plain)	309	151	6.7	6.0	151	125
2As (S. Blue Ridge)	122	100*	7.0	7.0*	23.2	20.7*
3A (Piedmont)	259	201	7.0	6.8	38.2	37.5
2X (S. Appalachians)	383	320	7.4	7.3	70.6	61.0
2D (Ozarks/Ouachitas)	162	123	6.8	6.6	64.5	69.9
3C (Florida)$	33	8	5.6	5.5	16.1	10.0

* See text: many S. Blue Ridge upper node chemistry values were calculated (Appendix B).

$ See text: Florida medians are based on a more restricted sample of low ANC streams. Do not compare directly with other subregions.

contact with watershed soil, rock, and vegetation. These upstream-downstream differences were generally overshadowed by the more pronounced differences that occurred among different streams within a subregion, or among subregions, as is perhaps more clearly illustrated in Figure 6-4 (a and b). The lowest subregional median ANC was observed in Florida (3C), with upstream and downstream median ANC of 7.6 and 33 μeq L^{-1}, respectively. Florida was also the only subregion with median pH < 6.0. Of the remaining subregions, only upstream ends of target reaches in the Mid-Atlantic Coastal Plain subregion (3B) had median pH < 6.5. Population median values for spring index ANC at the downstream ends of target reaches in the Mid-Atlantic subregions ranged from 128 μeq L^{-1} in the Northern Applachians (2Cn) to 396 μeq L^{-1} in the Valley and Ridge (2Bn) subregion. Subregion median ANC at the upstream reach ends in the Mid-Atlantic were lower, ranging from 110 μeq L^{-1} in subregion 2Cn to 223 μeq L^{-1} in subregion 2Bn. Population median ANC values < 200 μeq L^{-1} (upstream or downstream) were observed in the Florida (3C), Southern Blue Ridge (2As), Northern Appalachian (2Cn), Mid-Atlantic Coastal Plain (3B), and Ozark/Ouachita (2D) subregions.

6.2.2 Mid-Atlantic Region

Population distributions for ANC and pH in the Mid-Atlantic subregions (3B, 1D, 2Bn, and 2Cn) are illustrated in Figures 6-2 (a - d) and 6-3 (a - d). Among the subregions of the Mid-Atlantic, the NSS-I revealed the greatest number of acidic stream reaches in the Mid-Atlantic Coastal Plain (3B), where 12% of the target reaches (1334) were acidic (ANC $\leq$ 0 μeq L^{-1}) or had pH $\leq$ 5.0 at their upper ends (Tables 6-2 and 6-3; standard errors tabulated in Appendix C). Another 12% of these upper reach ends had pH between 5.0 and 5.5. After flowing typically 2 to 3 km to their downstream ends, 7% (772 reaches) remained acidic (ANC $\leq$ 0) and had pH $\leq$ 5.5. Of particular interest in subregion 3B, because of the presence of sensitive warm water fisheries (subsection 6.2.1), is the relatively large percentage of target reaches that have spring baseflow pH < 6.0 (49% at the upstream node, 22% at the downstream node). This pattern is in marked contrast with the other Mid-Atlantic and Southeast subregions, excluding Florida, where an estimated 0 to 23% of upstream nodes and 0 to 14% of downstream nodes had pH < 6.0. The general pattern of increasing ANC downstream in subregion 3B (scatter plot in Figure 6-2d) is reflected in the comparatively large difference between upstream and downstream population medians in this subregion (151 and 309 μeq L^{-1}).

Among the other Mid-Atlantic subregions--the Poconos/Catskills (1D), the Valley and Ridge (2Bn), and the Northern Appalachians (2Cn)--relatively few of the reaches observed were acidic at their downstream ends. (Acid mine drainage effects are not included, but are discussed in Section 9). Of these three subregions, only 2Cn is estimated to contain reaches acidic at their downstream nodes that were unaffected by acid mine drainage (4% or 326 reaches). However, at the upstream ends, between 5% and 6% (209, 636, and 499 reaches, respectively) were acidic in subregions 1D, 2Bn, and 2Cn. The generally higher downstream ANC in streams of these subregions is again evident in the scatter plots, as well as in the separate upstream and downstream population distributions of ANC (Figures 6-2 [a, b, and c]). The more frequent occurrence of lowland drainages, often with limestone geology, in subregions 1D and 2Bn is reflected in their relatively high median ANC values (Table 6-1) and by the large percentage (70%) of reaches in these subregions with downstream ANC greater than 200 μeq L^{-1}, compared to 38% for subregion 2Cn.

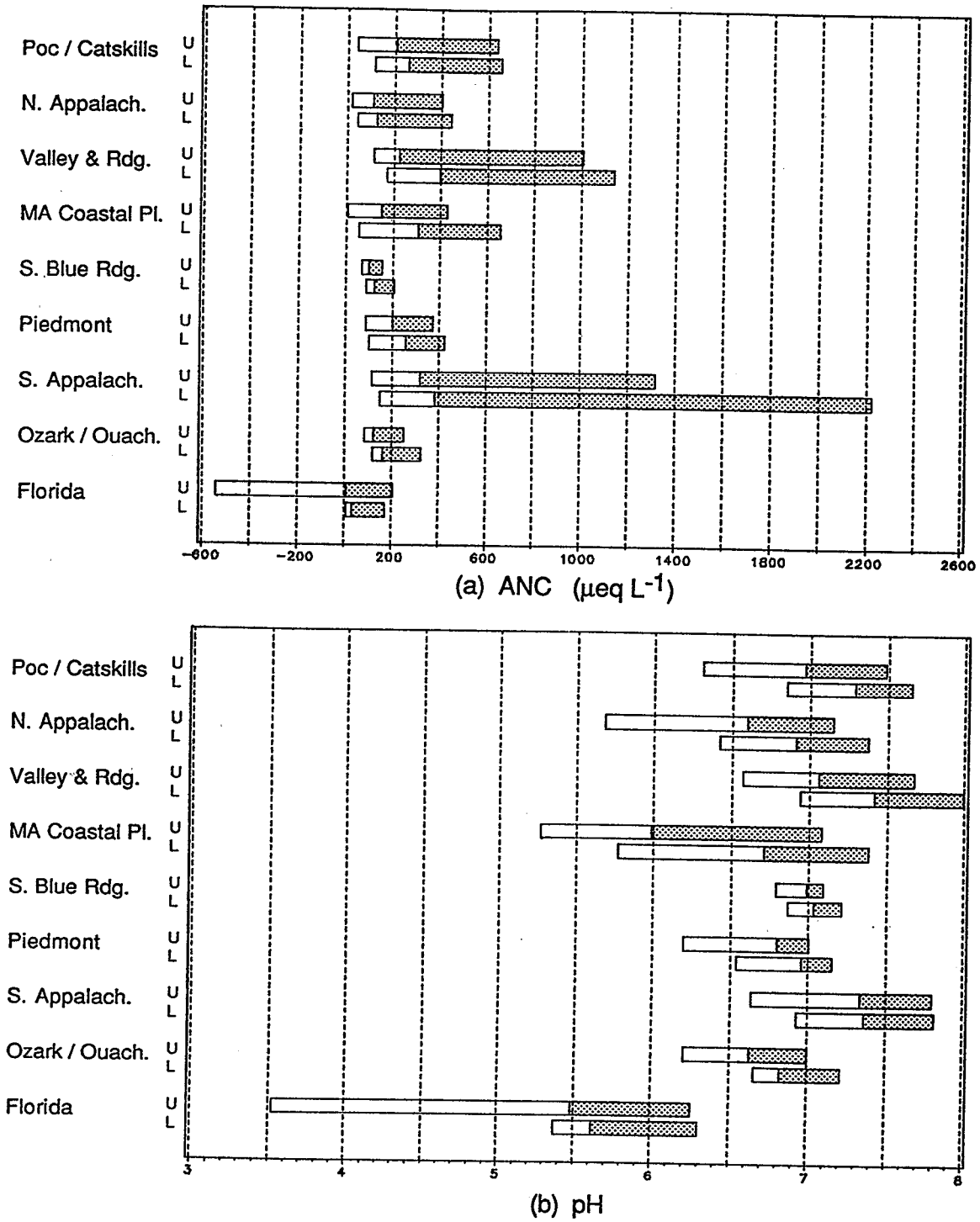


Figure 6-4. Population frequency distribution (Q_{20}, median, and Q_{80}) of index (a) ANC and (b) pH, at upper and lower reach nodes in the NSS-I subregions.

Table 6-2. Population Estimates of the Percentage of Target Stream Lower (L) and Upper (U) Reach Nodes with Spring Index ANC ($\mu eq\ L^{-1}$) in Reference Ranges

	ANC RANGE ($\mu eq\ L^{-1}$)											
	≤ 0		> 0 to ≤ 50		> 50 to ≤ 200		> 200		Totals (No. of Reaches)		Sample Size (No. of Reaches)	
SUBREGION	L	U	L	U	L	U	L	U	L	U	L	U
1D (Poconos/Catskills	*	6	5	16	25	26	70	52	3,235	3,244	(56)	(58)
2Cn (N. Appalachians)	4	6	20	28	38	32	38	34	8,488	8,663	(61)	(67)
2Bn (Valley and Ridge)	*	5	*	6	30	27	70	62	13,992	13,038	(47)	(44)
3B (MA Coastal Plain)	7	12	13	18	21	26	59	44	11,287	11,284	(58)	(57)
2As (S. Blue Ridge)#	*	*	5	6	74	78	22	16	2,031	2,031	(54)	(54)
3A (Piedmont)	*	*	8	8	32	40	60	52	7,515	7,515	(47)	(47)
2X (S. Appalachians)	*	2	7	7	20	20	72	70	5,057	4,936	(40)	(39)
2D (Ozarks/Ouachitas)	*	*	*	4	66	64	34	32	4,117	4,204	(48)	(49)
3C (Florida)$	14	39	43	31	24	8	19	22	1,555	1,727	(34)	(31)
Subtotals:												
Interior Mid-Atlantic (1D, 2Cn, 2Bn)	1	5	7	15	32	29	59	51	25,715	24,945	(164)	(169)
Interior Southeast (2As, 3A, 2X, 2D)	*	1	6	7	41	44	54	48	18,720	18,686	(189)	(189)
Mid-Atlantic Region (1D, 2Cn, 2Bn, 3B)	3	7	9	16	29	28	59	49	37,002	36,229	(222)	(226)
Southeast Region (2As, 3A, 2X, 2D, 3C)	1	4	9	9	39	41	51	46	20,275	20,413	(223)	(220)
Total NSS-I MA + SE	2	6	9	13	33	33	56	48	57,277	56,642	(445)	(446)

*Less than 1%.

#See text: Many S. Blue Ridge upper node spring baseflow index chemistry values were calculated (Appendix B).

$See text: Florida percentages are based on a more restricted sample of low ANC streams. They are not directly comparable to those in the other subregions.

Table 6-3. Population Estimates of the Percentage of Target Stream Lower (L) and Upper (U) Reach Nodes with Spring Index pH in Reference Ranges

SUBREGION		pH RANGE ≤ 5.0		> 5.0 to ≤ 5.5		> 5.5 to ≤ 6.0		> 6.0		Total No. of Reaches		Sample Size (No. of Reaches)	
		L	U	L	U	L	U	L	U	L	U	L	U
1D	(Poconos/Catskills)	*	5	*	2	3	6	97	87	3,235	3,244	(56)	(58)
2Cn	(N. Appalachians)	3	6	2	7	8	10	86	77	8,488	8,663	(61)	(67)
2Bn	(Valley and Ridge)	*	2	*	3	*	5	>99	89	13,992	13,038	(47)	(44)
3B	(MA Coastal Plain)	7	12	6	12	8	26	78	51	11,287	11,284	(58)	(57)
2As	(S. Blue Ridge)#	*	*	*	*	*	*	>99	>99	2,031	2,031	(54)	(54)
3A	(Piedmont)	*	*	*	*	4	11	96	89	7,515	7,515	(47)	(47)
2X	(S. Appalachians)	*	*	*	2	2	5	98	93	5,057	4,936	(40)	(39)
2D	(Ozarks/Ouachitas)	*	*	*	5	2	5	98	89	4,117	4,204	(48)	(49)
3C	(Florida)$	14	31	9	19	38	22	38	28	1,555	1,727	(34)	(31)
Subtotals:													
Interior Mid-Atlantic (1D, 2Cn, 2Bn)		1	4	1	5	3	7	95	85	25,715	24,945	(164)	(169)
Interior Southeast (2As, 3A, 2X, 2D)		*	*	*	2	3	7	97	91	18,720	18,686	(189)	(189)
Mid-Atlantic Region (1D, 2Cn, 2Bn, 3B)		3	6	3	7	5	13	90	74	37,002	36,229	(222)	(226)
Southeast Region (2As, 3A, 2X, 2D, 3C)		1	3	1	3	5	8	93	86	20,275	20,413	(223)	(220)
Total NSS-I	MA + SE	2	5	2	6	5	11	91	78	57,277	56,642	(445)	(446)

*Less than 1%.

#See text: Many S. Blue Ridge upper node spring baseflow index chemistry values were calculated (Appendix B).

$See text: Florida percentages are based on a more restricted sample of low ANC streams. They are not directly comparable to those in the other subregions.

Population distributions of pH (Figures 6-3 [a, b, c, and d] and Table 6-2) showed a pattern similar to that of ANC with 6% of reaches (494) in the Northern Appalachians (2Cn) with pH ≤ 5.5 at the lower end. Less than 1% of target reaches had downstream pH ≤ 5.5 in the Poconos/Catskills (1D) and Valley and Ridge (2Bn). Considering the upper reach ends, however, 6% to 7% of reaches in subregions 1D and 2Bn had pH ≤ 5.5. In 2Cn, 13% of the reaches (1,133) had pH of 5.5 or less.

The geographic distributions of ANC and pH in NSS-I Mid-Atlantic sample sites are shown in Figures 6-5 through 6-8. Acidic stream reaches were concentrated in parts of the Mid-Atlantic Coastal Plain (3B), Northern Appalachian (2Cn), and Pocono/Catskill (1D) subregions. Upper nodes were more commonly acidic than were lower nodes. Because various stream reaches had different statistical sampling inclusion probabilities, and therefore different sample weightings, caution should be used in interpreting these and other maps presented in this report. For example, spatial sampling density was increased in areas such as the New Jersey Pine Barrens, where a large number of acidic or low ANC sites was expected. Sample sites in such areas have relatively lower weightings for calculating statistical population distributions. Displaying all these sites on maps does allow greater resolution of spatial patterns in the distribution of these low ANC streams, however, and such low ANC sites are of greatest interest in the assessment of acidic deposition effects.

Within subregion 3B, stream reaches with ANC < 0 μeq L^{-1} were found primarily in the New Jersey Pine Barrens and the coastal plain west of Chesapeake Bay. The Pine Barrens is a geographic area underlain by quartz sands and gravels (Forman, 1979; Lewis and Kummel, 1950). Of 12 sample reaches visited in the Pine Barrens, 11 were acidic at one or both ends. Although some of these streams can be classified as clearwater acidic streams (Section 9), many of them had colored waters high in dissolved organic carbon (DOC > 4 mg L^{-1}), suggesting that some of their acidity may result from organic acids. About half of the acidic streams in subregion 3B, plus many others with ANC between 0 and 15 μeq L^{-1} (and pH ≤ 5.5), were found along the coastal plain west of Chesapeake Bay, a relatively swampy area underlain with noncalcareous sands and clays (Cleaves et al., 1968). Most acidic sample streams in this part of subregion 3B had high DOC (> 4 mg L^{-1}); the potential sources of acidity in these streams are discussed in Section 9. The highest ANC in the Mid-Atlantic Coastal Plain (3B) was found in reaches draining agricultural basins of the Piedmont lowlands in Maryland and Virginia--areas with highly weathered soils derived from limestone, schist, and gneiss (USDA, 1979; Commonwealth of Virginia, 1963; Cleaves et al., 1968). ANC in these areas ranged from 200 to as high as 2,200 μeq L^{-1} in drainages where limestone was mapped.

In NSS-I subregions 1D, 2Bn, and 2Cn (Figures 6-5 through 6-8), acidic (ANC ≤ 0 μeq L^{-1} and low ANC (≤ 200 μeq L^{-1}) stream reaches were observed to be primarily upper reach nodes in forested upland areas. In subregion 1D, these included the glaciated plateaus of northern Pennsylvania, the Catskills, the Poconos, and forested ridges of the Valley and Ridge physiographic unit (Fenneman 1946) that extend into central and eastern Pennsylvania. These forested uplands are largely underlain by sandstones, shales, siltstones, and quartz conglomerates (Cline and Marshall, 1976; Commonwealth of Pennsylvania, 1980; Cunningham et al., 1977; New York State Education Department, 1970). Coal is mined in many of these uplands. High ANC reaches in subregion 1D were found on glaciated plateaus with agricultural land use (largely between 200 and 500 μeq L^{-1}) and in lowland agricultural valleys (ANC ranging from 200 to > 4,000 μeq L^{-1}). These valleys are part of the Valley and Ridge physiographic unit (Fenneman, 1946) and are used intensively for both agriculture and urbanization. They contain alluvium and glacial till derived from limestone, calcareous shales, and dolomite.

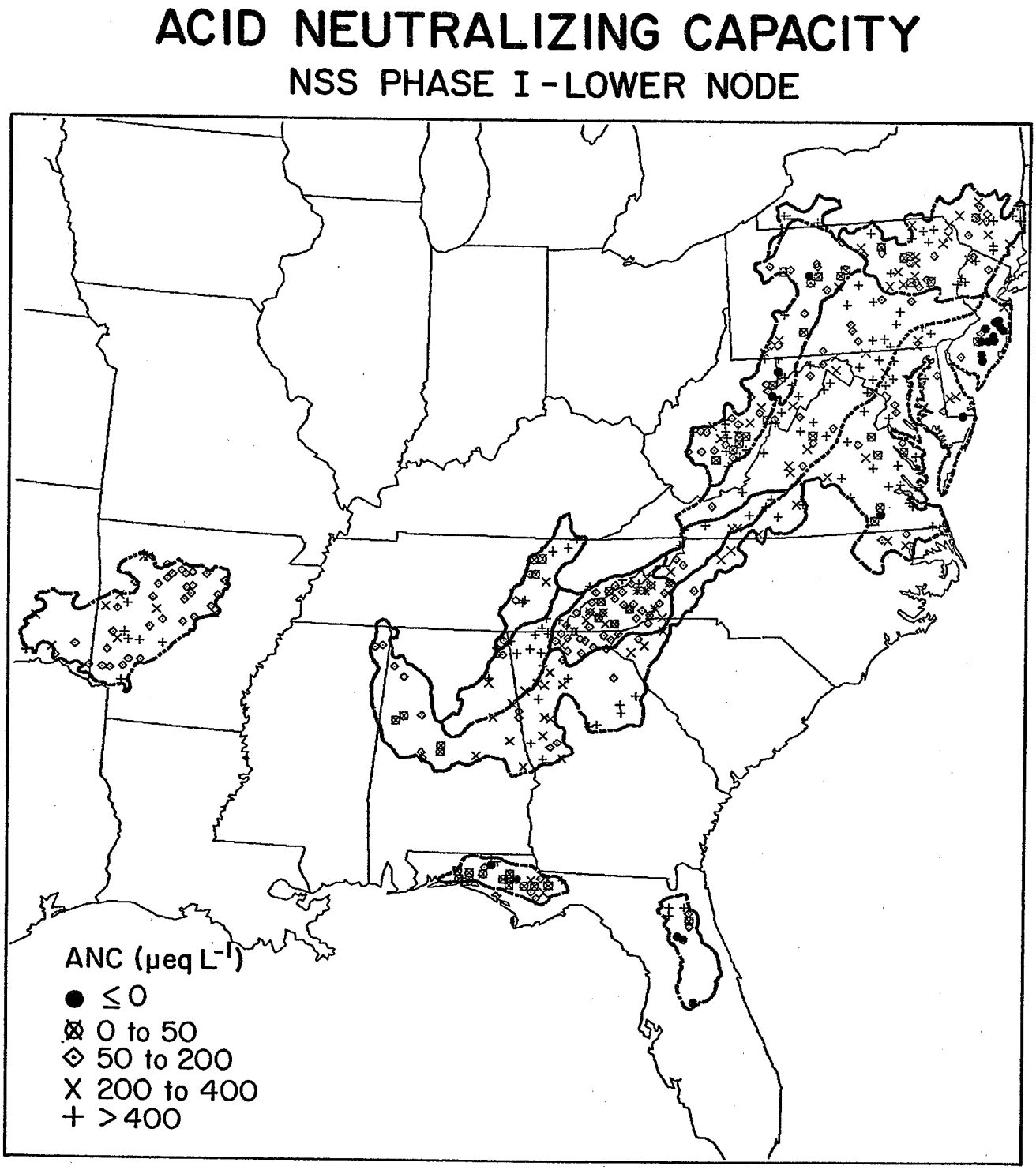


Figure 6-5. Geographic distribution of NSS-I lower node index ANC.

ACID NEUTRALIZING CAPACITY

NSS PHASE I - UPPER NODE

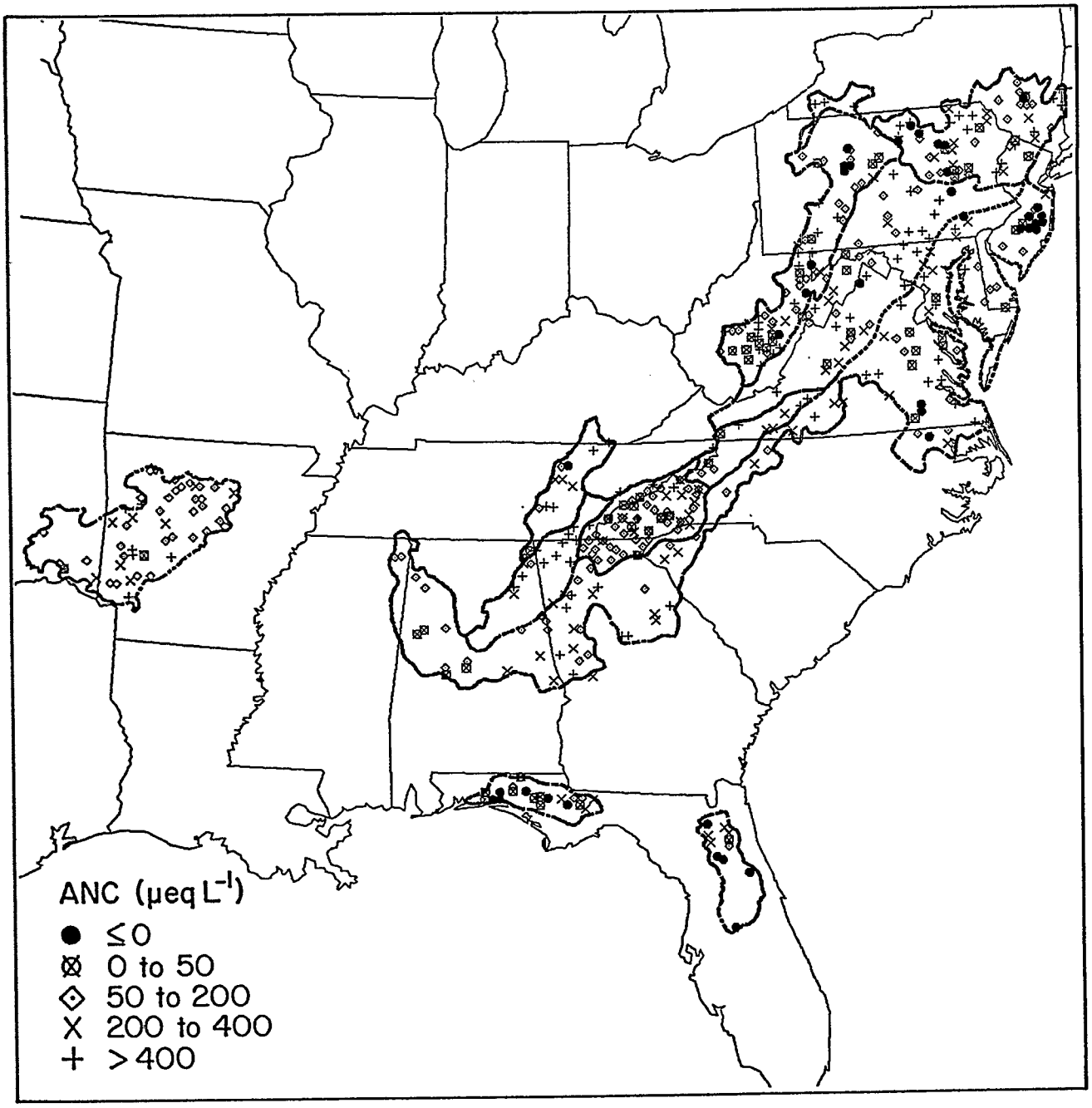


Figure 6-6. Geographic distribution of NSS-I upper node index ANC.

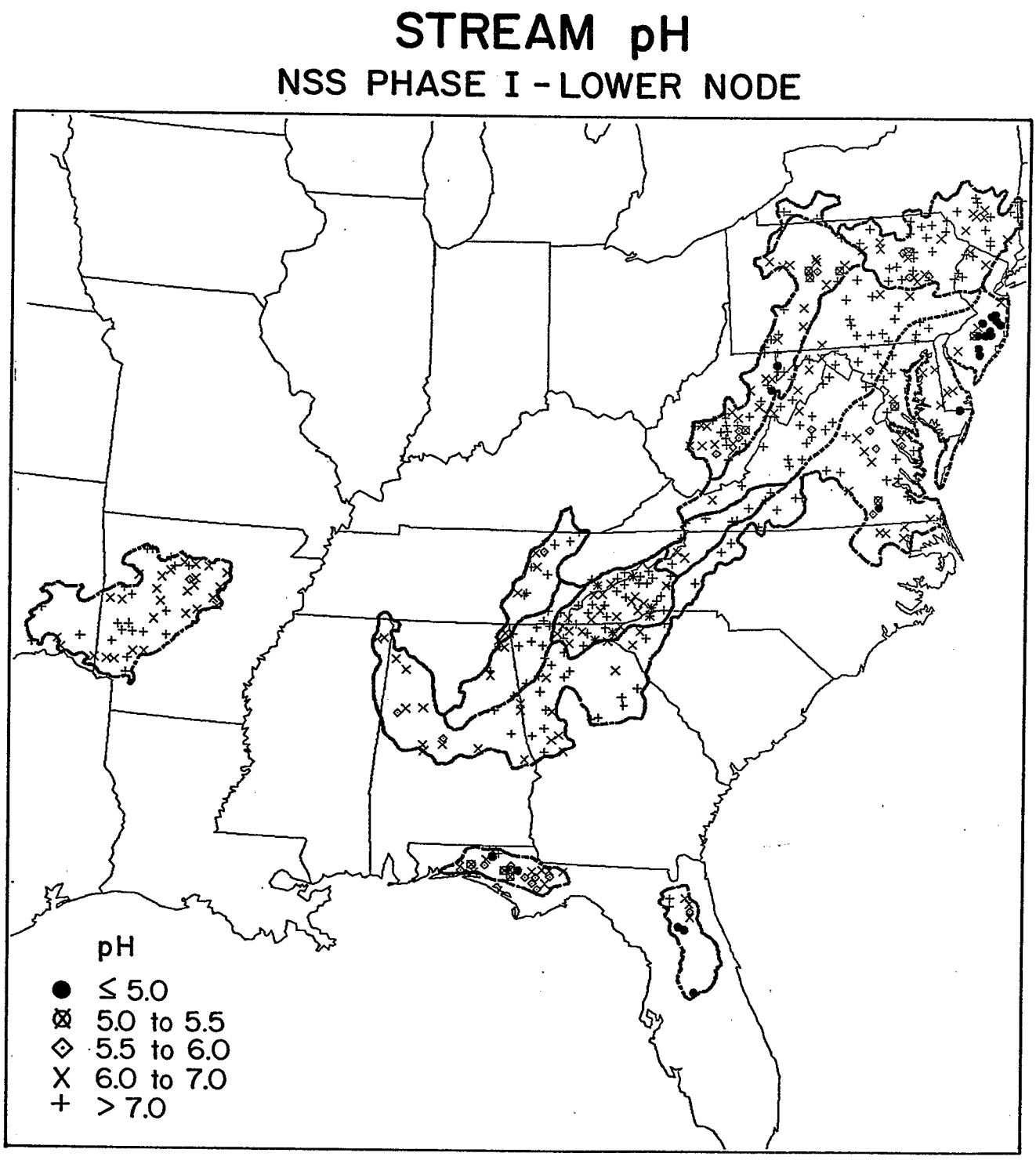


Figure 6-7. Geographic distribution of NSS-I lower node index pH.

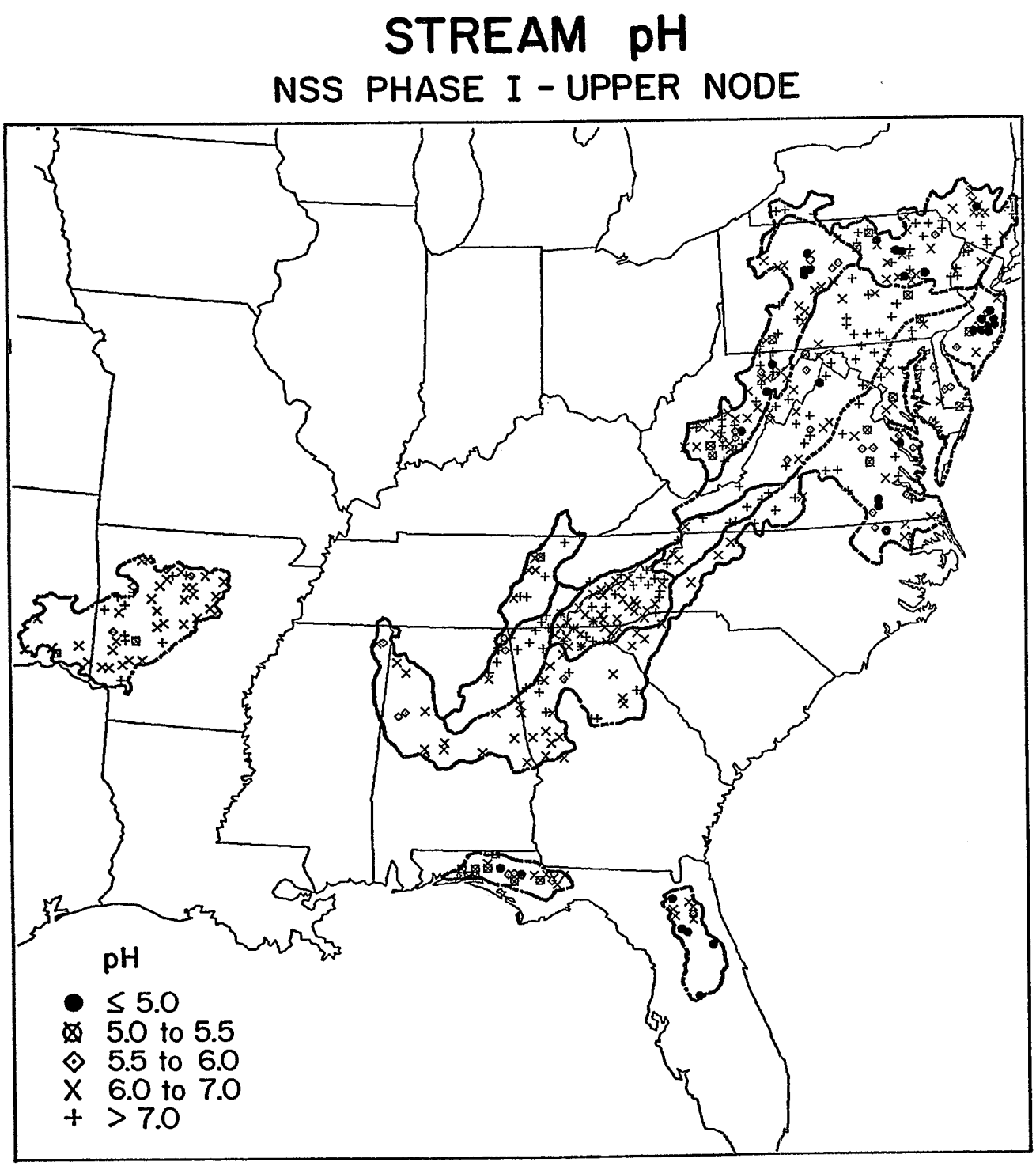


Figure 6-8. Geographic distribution of NSS-I upper node index pH.

In 2Bn, the NSS-I subregion dominated by the Valley and Ridge physiographic province (Fenneman, 1946), few acidic reaches were observed. Those that were found, as well as most of the reaches with ANC < 200 μeq L^{-1}, were located on forested ridges. Underlying geology on these ridges is primarily sandstone, shale, and siltstone. More highly buffered reaches, with ANC up to 6,300 μeq L^{-1}, were found in the valley bottoms alternating between these ridges. These valleys, as discussed in the last paragraph, often contain soils derived from calcareous parent material.

In the Northern Appalachian subregion (2Cn), acidic (ANC $\leq$ 0 μeq L^{-1}) stream reaches and low ANC ($\leq$ 200 μeq L^{-1}) stream reaches were located in forested upland drainages of the Allegheny High Plateau in northwestern Pennsylvania and at higher elevation portions of the Northern Appalachian Plateau, extending from Pennsylvania southward into the eastern half of West Virginia. These upland drainages have deep, well-drained soils derived from sandstones, shales, and siltstones. Many of these drainages have been strip-mined for coal (see maps and discussion in Section 9). Those receiving acid mine drainage have been removed in calculations of regional population distribution estimates and in maps presented in this section, which deals only with the target population of primary interest for assessment of acid deposition effects. Higher ANC (mostly 300 to 900 μeq L^{-1}) was found in Northern Appalachian Plateau drainages of lesser relief that are able to support agricultural land use.

6.2.3 Interior Southeastern Region

The NSS-I Southeast Screening included sample reaches in the Southern Appalachians (2X), the Piedmont (3A) and the Ozarks/Ouachitas (2D). Results from the NSS-I Pilot Survey in the Southern Blue Ridge (Messer et al., 1986) are included here as results for subregion 2As of the Southeast Region, although sampling took place in 1985, one year earlier than the remainder of NSS-I sampling. The NSS-I included only a portion of the southeastern coastal plain (parts of the Florida panhandle and peninsula) in its Southeast Screening. Results for Florida are discussed in subsection 6.2.4--those from the remainder of the Southeast have been grouped into the Interior Southeast Region discussed in the following paragraphs.

Population distribution estimates for ANC in Interior Southeast subregions 2X, 2As, 3A, and 2D are illustrated in Figure 6-2 (e, f, g, and h) and summarized in Table 6-2. Except for the Southern Appalachians (2X), where an estimated 121 reaches (2%) were acidic (ANC $\leq$ 0 μeq L^{-1}) at their upstream ends, no acidic reaches (not affected by acid mine drainage) were observed in the remaining Interior Southeast subregions. Though acidic stream reaches were rare in the Interior Southeast, two Southeast subregions, the Southern Blue Ridge (2As) and the Ozarks/Ouachitas (2D), had among the highest proportion of streams with relatively low ANC. In subregion 2As, 84% of the reaches (1,703) had ANC $\leq$ 200 μeq L^{-1} at their upper ends; in subregion 2D, the proportion was 68% (2,850 reaches).

Population distribution estimates of pH in the Southeast are illustrated in Figures 6-3 (e, f, g, and h) and summarized in Table 6-3. No sample stream reaches with spring index pH $\leq$ 5.5 at their downstream ends were observed in the Interior Southeast subregions of the NSS-I. Except for the Piedmont (3A) subregion, where an estimated 316 reaches (4%) had pH $\leq$ 6.0 at their downstream ends, 2% or fewer (0 to 121) reaches in subregions 2As, 2D, and 2X had spring index pH that low. In subregion 2D, 5% of the upstream reach ends (225) had pH $\leq$ 5.5. In the remaining Southeast subregions, 2% or fewer (0 to 121 reaches) had upstream pH that low. From 5% to 11% of reaches in the 2D, 2X, and 3A subregions had pH between 5.5 and 6.0. No upstream or downstream sampling points in subregion 2As streams had pH < 6.0 (during spring or summer sampling in 1985).

The geographical distributions of spring index ANC in the Southeast subregions of the NSS-I are mapped in Figures 6-5 (downstream) and 6-6 (upstream). The majority of Interior Southeast sites with upstream or downstream ANC ≤ 50 μeq L^{-1} were sample reaches in the East Gulf Coastal Plain (western end of subregion 3A), upstream ends of sample reaches in the Southern Blue Ridge Mountains (including the Great Smoky Mountains National Park in subregion 2As), and the Cumberland Plateau (a portion of subregion 2X located mostly in Tennessee). The East Gulf Coastal Plain is a generally forested area of lower elevation and relief than the Piedmont or Blue Ridge. Deep to moderately deep, well-drained, loamy soils overlie sandstone, shales, clays, gravels, and lignite in the East Gulf Coastal Plain portion of the NSS-I Piedmont subregion. The Southern Blue Ridge is largely underlain by schists, feldspar, and quartzite, which provide little ANC upon weathering (Velbel, 1985). The Cumberland Plateau is largely underlain by noncalcareous shales and sandstones (Hardeman, 1966a,b; Springer and Elder, 1980). Stream reaches with ANC < 50 μeq L^{-1} at their upstream ends were also observed in the Ozark and Ouachita Mountains of Arkansas and Eastern Oklahoma. Spring index ANC values in the Piedmont and in lowland and agricultural sites of the other Southeast subregions were primarily in the ANC range between 200 and 400 μeq L^{-1}; stream reaches with ANC above this range were not commonly observed. Those with ANC > 400 μeq L^{-1} were observed mainly in agricultural valleys of the Piedmont, Southern Appalachian Plateau, Arkansas River basin, and the southern part of the Valley and Ridge Province contained in subregion 2X.

Figures 6-7 and 6-8 map the geographic distribution of spring index pH at upstream and downstream sampling locations of reaches in the Southeast subregions. Excluding Florida (3C), it is apparent that pH in target stream reaches over most of the region is circumneutral (pH 6.5 to 7.5). Three upstream sites with pH < 5.5 were observed, one on the Cumberland Plateau and two in the Ozark and Ouachita Mountains. Index pH in the range between 5.5 and 6.5 was observed mainly at upstream ends of sample reaches in the Great Smokies, the Cumberland Plateau, the Ozarks and Ouachita Mountains, and the East Gulf Coastal Plain.

6.2.4 The Florida Subregion

The Florida subregion (3C), like parts of the Mid-Atlantic Coastal Plain (3B), stands out as a geographic area with a relatively large percentage of acidic and low ANC streams. Like the New Jersey Pine Barrens of subregion 3B, it also is an area with soils largely derived from quartz sands. Again like the Pine Barrens, Florida contains many highly colored streams with high concentrations of dissolved organic material. The potential sources of acidity in 3B, 3C, and other subregions are discussed in Section 9.

Population percentage estimates for subregion 3C are not strictly comparable with those from other subregions. The Florida sample was drawn from a more restrictive target population focused only on the portion of Florida with expected ANC < 200 μeq L^{-1}, eliminating reaches with expected ANC between 200 and 400 μeq L^{-1} that were sampled in all the other subregions. However, estimates of the number or combined length of stream reaches within the boundaries of the subregion characterized by given index chemistry are comparable. Other problems with the Florida estimates stem from the fact that the index time period, mid-March to mid-May, is well into the dry season in Florida, relative to the other NSS-I subregions. An estimated 30% to 40% of the target population consisted of streams that were dry, too shallow to obtain clean water samples, or too swampy and stagnant to be considered streams in the normal sense. For these reasons, regional extrapolations (population estimates) based on the Florida sample data should be used with caution, though inferences regarding chemical characteristics of the sample streams themselves are not similarly hampered.

Population distribution estimates for ANC in subregion 3C are shown in Figure 6-2i and Table 6-2. At the upstream ends, an estimated 678 (39%) of the Florida reaches were acidic (ANC $\leq$ 0 μeq L^{-1}); another 531 (31%) had ANC between 0 and 50 μeq L^{-1}. A smaller number of reaches were acidic at their downstream ends (225 or 14%), but a large number (670 or 43%) had downstream ANC between 0 and 50 μeq L^{-1}. Only 388 (22%) reaches had ANC > 200 μeq L^{-1} at the upstream ends; 292 (19%) had ANC greater than this value at the downstream ends.

Population distribution estimates for spring index pH in subregion 3C are shown in Figure 6-3i and Table 6-3. At the upstream ends, an estimated 539 reaches (31%) had pH $\leq$ 5.0; another 324 (19%) were between pH 5.0 and 5.5. Index pH was generally higher at the downstream ends of reaches, where an estimated 225 reaches (14%) had pH $\leq$ 5.0 and another 146 (9%) were between pH 5.0 and 5.5.

Figures 6-5 through 6-8 map the distribution of ANC and pH in Florida and other NSS-I subregions. Acidic reaches were observed in both the Florida panhandle and the peninsula. However, highly acidic reaches with ANC between -40 and -500 μeq L^{-1} were primarily highly colored streams on the Florida peninsula. Acidic reaches in the Florida panhandle tended to be of two types (see Section 9). One group contained reaches having high DOC (6 to 24 mg L^{-1}) and color (> 60 PCU); these were similar to the colored-water acidic reaches in the peninsula. The second group was at relatively higher elevation and had less acidity (ANC between 0 and -10 μeq L^{-1}). Water in these reaches was very dilute (conductivity < 40 μS cm^{-1}) and clear to weakly colored (color 10 to 60 PCU), with DOC concentrations < 2 mg L^{-1}.

6.2.5 Interpolated Length Distributions

Subsection 6.1.7 discusses the procedure of linear interpolation by which the combined length of the target stream resource within specified ranges of ANC and pH was estimated (detailed in Sale [1988]). For some applications and interpretations, it is more useful to know the distribution of chemistry on the basis of length, rather than the number of reaches. Estimates based on length could also be calculated using only one or the other reach node--or they could be calculated by averaging the upper and lower node chemistries. Distributions based upon the average reach chemistry tend to mask or underestimate the extremes of the distributions. Because the low end of the ANC and pH distributions have considerable importance in this assessment, it would be misleading to present length estimates based on the average of reach nodes. In contrast, length estimates based on one or the other node of sample reaches, as presented in the data compendium to this report (Volume II), tend to exaggerate the extremes of the chemical distribution if there is (as has been observed) a consistent pattern of increasing ANC or pH in the downstream direction. The interpolated length estimates presented in this section were based upon linear interpolation of ANC and hydrogen ion (for pH). In Figure 6-9, the shaded fractions of each stacked bar in the diagram show the proportion of the total length in the population of target stream reaches that is estimated to fall into specified classes of ANC and pH. The interpolated length estimates provided (Figure 6-9, Tables 6-4 and 6-5) are not a perfect representation of the chemical distribution, but without detailed knowledge of the patterns of chemical change between the upstream and downstream sampling points, they are the most reasonable estimates that can be made with the NSS-I data. The standard errors of these interpolated length estimates (Appendix C) are approximate and were calculated from the variance of length-based ($\hat{L}_{(x)}$) distributions.

Population distribution estimates based on interpolated length (Figure 6-9 [a and b]) followed regional patterns similar to those described based on numbers of upper or lower reach nodes. Because many lower and upper sampling locations could not be sampled in Florida (see

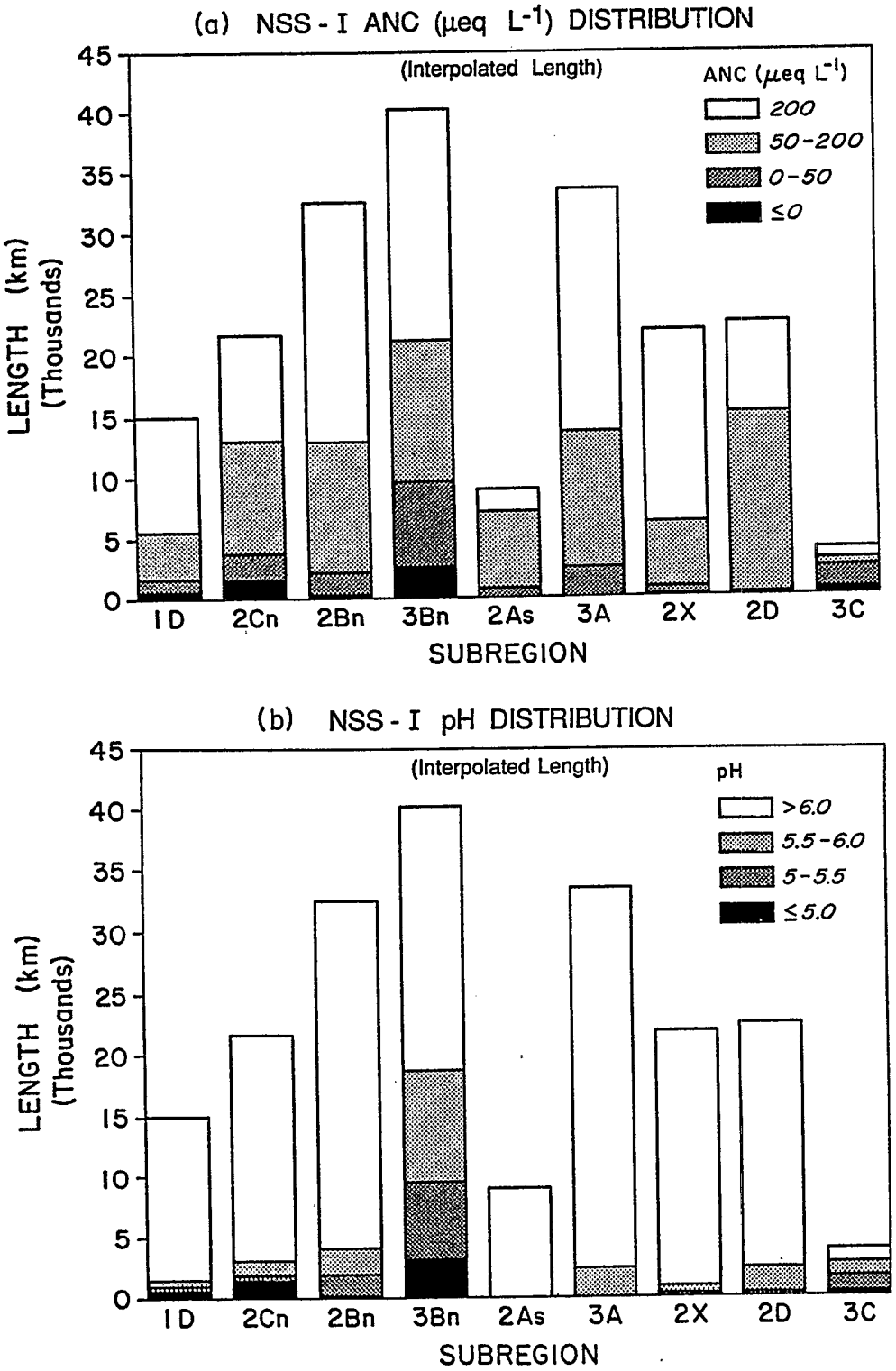


Figure 6-9. Combined length of NSS-I target stream resources within specified categories of (a) ANC, and (b) pH, as estimated by linear interpolation of index concentrations between upper and lower reach node sampling locations.

Table 6-4. Interpolated Length (km) and Percentage Distribution for ANC (μeq L^{-1}) in Specified Concentration Ranges in NSS-I Subregions

Subregion	ANC Ranges (μeq L^{-1})				
	≤ 0	> 0 to ≤ 50	> 50 to ≤ 200	> 200	Total (km)
1D (Poconos/Catskills)	543 (3.6)	1,062 (7.0)	3,883 (25.6)	9,655 (63.8)	15,144
2Cn (N. Appalachians)	1,524 (7.0)	2,189 (10.1)	9,222 (42.4)	8,803 (40.5)	21,738
2Bn (Valley and Ridge)	257 (0.8)	1,854 (5.7)	10,700 (32.7)	19,876 (60.8)	32,687
3B (MA Coastal Plain)	2,527 (6.3)	7,109 (17.6)	11,455 (28.4)	19,205 (47.7)	40,296
2As (S. Blue Ridge#)	* (*)	706 (7.8)	6,378 (70.6)	1,952 (21.6)	9,036
3A (Piedmont)	* (*)	2,390 (7.1)	11,163 (33.3)	19,977 (59.6)	33,531
2X (S. Appalachians)	117 (0.5)	646 (2.9)	5,367 (24.5)	15,762 (72.1)	21,892
2D (Ozarks/Ouachitas)	* (*)	205 (0.9)	14,887 (66.2)	7,388 (32.9)	22,480
3C (Florida$)	461 (12.0)	1,895 (49.2)	584 (15.2)	909 (23.6)	3,848
Subtotals					
Interior Mid-Atlantic (IMA)	2,324 (3.3)	5,107 (7.3)	23,805 (34.2)	38,334 (55.1)	69,569
Interior Southeast (ISE)	117 (0.1)	3,947 (4.5)	37,795 (43.5)	45,079 (51.9)	86,939
Mid-Atlantic (MA)	4,851 (4.4)	12,216 (11.1)	35,260 (32.1)	57,539 (52.4)	109,865
Southeast (SE)	578 (0.6)	5,842 (6.4)	38,379 (42.3)	45,988 (50.7)	90,787
Total	5,429 (2.7)	18,057 (9.0)	73,639 (36.7)	103,527 (51.6)	200,652

*No samples observed in this range; estimated percentage is less than 1%.

#See Text: Many S. Blue Ridge upper node spring baseflow index chemistry values were calculated (Appendix B).

$See Text: Florida estimates are based on a more restricted sample of low ANC streams. They are not strictly comparable to those in other subregions.

Table 6-5. Interpolated Length (km) and Percentage Distribution for pH in Specified Ranges in NSS-I Subregions

Subregion		pH Ranges				
		≤ 5.0	> 5.0 to ≤ 5.5	> 5.5 to ≤ 6.0	> 6.0	Total (km)
1D	(Poconos/Catskills)	550 (3.6)	356 (2.3)	448 (3.0)	13,790 (91.1)	15,144
2Cn	(N. Appalachians)	1,424 (6.6)	446 (2.1)	1,174 (5.4)	18,694 (85.9)	21,738
2Bn	(Valley and Ridge)	257 (0.8)	1,680 (5.1)	2,179 (6.7)	28,571 (87.4)	32,687
3B	(MA Coastal Plain)	3,147 (7.8)	6,418 (15.9)	9,142 (22.7)	21,589 (53.6)	40,296
2As	(S. Blue Ridge#)	* (*)	* (*)	* (*)	9,036 (> 99)	9,036
3A	(Piedmont)	* (*)	* (*)	2,390 (7.1)	31,141 (92.9)	33,531
2X	(S. Appalachians)	* (*)	313 (1.4)	607 (2.8)	20,972 (95.8)	21,892
2D	(Ozarks/Ouachitas)	* (*)	410 (1.8)	2,027 (9.0)	20,043 (89.2)	22,480
3C	(Florida$)	522 (13.6)	1,186 (30.8)	1,120 (29.1)	1,020 (26.5)	3,848
Subtotals						
Interior Mid-Atlantic (IMA)		2,231 (3.2)	2,481 (3.6)	3,801 (5.5)	61,055 (87.8)	69,569
Interior Southeast (ISE)		* (*)	723 (0.8)	5,024 (5.8)	81,192 (93.4)	86,939
Mid-Atlantic (MA)		5,378 (4.9)	8,899 (8.1)	12,944 (11.8)	82,644 (75.2)	109,865
Southeast (SE)		522 (0.6)	1,910 (2.1)	6,145 (6.8)	82,211 (90.6)	90,787
Total		5,900 (2.9)	10,809 (5.4)	19,088 (9.5)	164,855 (82.2)	200,652

*No samples observed in this range; estimated percentage is less than 1.
#See Text: S. Blue Ridge upper node spring baseflow index chemistry values were calculated (Appendix B).
$See Text: Florida estimates are based on a more restricted sample of low ANC streams. They are not strictly comparable to those in other subregions.

Section 5.2), an accurate estimate of the length of acidic streams in subregion 3C cannot be provided. However, an incomplete estimate based on a reduced sample of matched upstream-downstream reach node pairs indicates that approximately 12% to 14% of the combined length of such reaches may be acidic (ANC < 0 μeq L^{-1}) or may have pH $\leq$ 5.0. Another 49% may have ANC between 0 and 50 μeq L^{-1}. It should be kept in mind that the length of the total resource represented by the matched pairs in this analysis is only about three-fourths of that in the initial target population identified on maps in subregion 3C.

The greatest combined length of target stream resources with ANC $\leq$ 0 μeq L^{-1} was estimated for the Mid-Atlantic Coastal Plain (3B) (2,527 km or 6.3%) and the Northern Appalachians (2Cn) (1,524 km or 7.0%), as summarized in Table 6-4. Respectively, 7.8% and 6.6% of the total target stream length in these two subregions had pH $\leq$ 5.0 (Table 6-5). The total stream length with ANC between 0 and 50 μeq L^{-1} was considerable in these two subregions, with 7,109 km (18%) in subregion 3B and 2,189 km (10%) in subregion 2Cn.

Of the remaining subregions, only in the Poconos/Catskills (1D) did more than 1% (543 to 550 km or approximately 3.6%) of the target stream length have ANC $\leq$ 0 μeq L^{-1} or pH $\leq$ 5.0. Acidic (and pH $\leq$ 5.0) water was estimated in less than 1% of the combined length of target stream resources in the Valley and Ridge (2Bn), Southern Blue Ridge (2As), Southern Appalachian (2X), Piedmont (3A), and Ozark/Ouachita (2D) subregions. Between 6% and 8% (706 to 2,390 km) of the combined length of target reaches in subregions 1D, 2Bn, 2As, and 3A had ANC between 0 and 50 μeq L^{-1}, whereas smaller proportions of the combined reach length in subregions 2X (2.9%) and 2D (0.9%) were in this very low ANC category.

The highest percentages of stream length in the 50 to 200 μeq L^{-1} ANC category were estimated in two subregions where no acidic stream reaches were observed, the Southern Blue Ridge (2As) (71% or 6,378 km) and the Ozarks/Ouachitas (2D) (66% or 14,887 km). Florida had the least stream length in this ANC range (15% or 584 km), although the estimates do not apply to the entire state. Considering the remaining NSS-I subregions, the percentage of stream length in this ANC category ranged between 25% (5,367 km) in subregion 2X to 42% (9,222 km) in subregion 2Cn, with between 9,000 and 12,000 km in most of the remaining subregions.

6.3 DISTRIBUTIONS OF OTHER CHEMICAL VARIABLES

6.3.1 Base Cations and Conductivity

There were no data quality problems that would affect data interpretation of any of the constituents making up the sum of base cations (SBC). System decision limits (SDL) were all < 1 μeq L^{-1}, indicating no background contamination problems (Table 4-1). Percent accuracy estimates for all base cations were < 4% (Table 4-2). Among-batch precision estimates, the most conservative (largest) measure of this attribute of data quality, were < 5 μeq L^{-1} for all base cations (Table 4-3).

Examination of distributions of base cations and conductivity in the NSS-I subregions suggests that weathering rates in the Mid-Atlantic Region and the Southern Appalachians subregion are substantially higher than those in the remaining subregions of the southeastern United States (Figure 6-10). The SBC is calculated by adding the concentrations of calcium, magnesium, sodium, and potassium (equivalent basis). Conductivity values measured in the analytical laboratories were used to make the population estimations presented in this report. Downstream medians of both variables were higher than upstream medians in all subregions, indicating that water at downstream locations has had more time in contact with watershed rock, soils, and vegetation.

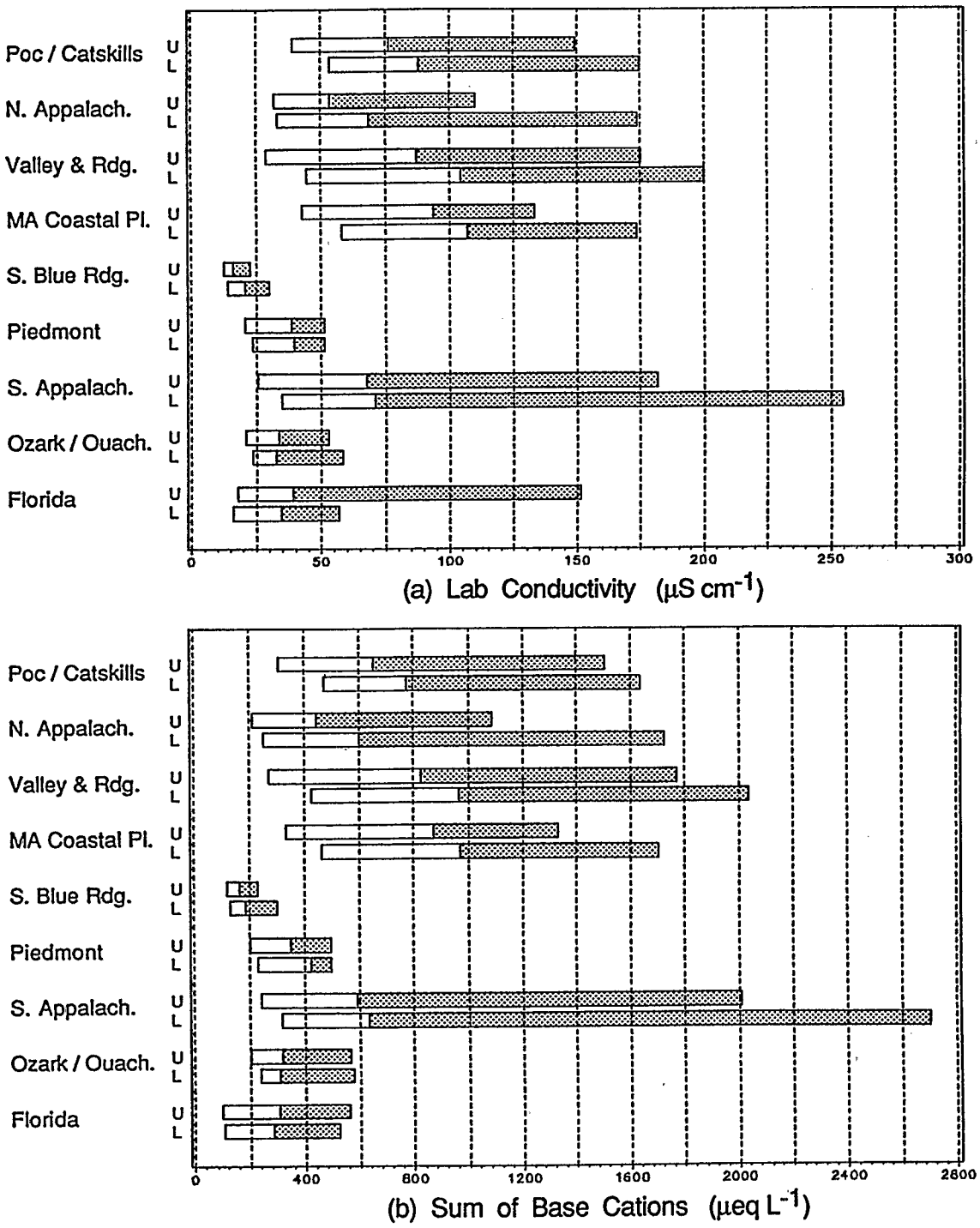


Figure 6-10. Population frequency distribution (Q_{20}, median, and Q_{80}) of index (a) conductivity and (b) base cation sum, at upper and lower reach nodes in the NSS-I subregions.

SBC and conductivity were highly correlated (r = +0.95 to +0.99 in seven subregions), which is not surprising because both are good indicators of total ionic strength. As a result, the two variables also exhibited very similar regional patterns (compare box plots in Figures 6-10 (a and b). High subregional median SBC concentrations (445 to 981 μeq L^{-1}) with large variation (80th percentile - 20th percentile ranges largely > 1000 μeq L^{-1}) were found in all Mid-Atlantic subregions and in the Southern Appalachians (2X) in the southeastern United States. All other Southeast subregions had medians < 425 μeq L^{-1} with lower variation (subregion 80th percentile - 20th percentile ranges largely < 400 μeq L^{-1}). SBC concentrations were generally the lowest in the Southern Blue Ridge (upstream and downstream medians approximately 200 μeq L^{-1}). The Florida (3C) and the Ozark/Ouachita (2D) subregions also had low median SBC concentrations (approximately 300 μeq L^{-1}).

Only the Southern Blue Ridge (2As) had median conductivities < 25 μS cm^{-1}, a value similar to that of rainfall. Subregion medians in the Mid-Atlantic (1D, 2An, 2Cn, and 3B) and the Southern Appalachians (2X) fell between 54 and 107 μS cm^{-1}. Median conductivities in the remainder of Southeast subregions were all < 40 μS cm^{-1}.

6.3.2 Aluminum

The highest median total (unfiltered) aluminum concentrations were found in the Ozark and Ouachita Mountains (11 to 12 μM), Florida (7.3 to 7.7 μM), the Piedmont (6.8 to 7.8 μM), and the upper ends of reaches in the Mid-Atlantic Coastal Plain subregion (3B) (6.7 μM) (Figure 6-11a). All other upstream and downstream medians were < 5 μM. More than 80% of the upstream and downstream ends of reaches in all subregions except the Valley and Ridge (2Bn) had total aluminum concentrations above the system decision limit (SDL) of 0.027 mg L^{-1} (1.00 μM), the value above which field sample concentrations are statistically distinguishable ($p < 0.05$) from blanks. At concentrations less than the SDL, measurements of aluminum variables were very imprecise (%RSD of 50% to 100%), as shown in Table 4-3. Even at concentrations greater than the SDL, precision for the various aluminum components was not good (%RSD of 10% to 30%). This imprecision should be kept in mind when interpreting the NSS-I aluminum data.

The MIBK-extractable component of total aluminum is generally interpreted to be a measure of the sum of organic and inorganic monomeric aluminum (Driscoll, 1984). MIBK-extractable aluminum concentrations were generally low in target reaches of all subregions except Florida (3C) and the Mid-Atlantic Coastal Plain (3B) (Figure 6-11b). In the other seven subregions, roughly 60% of the reaches had concentrations below the SDL of 0.30 μM, meaning the total monomeric aluminum concentration in these samples was statistically indistinguishable from that of deionized water ($p < 0.05$). In the Southern Blue Ridge (2As), more than 80% of the stream reaches were below this concentration. In contrast, more than 90% of the stream reaches in subregion 3C, and 75% of the stream reaches in subregion 3B had extractable aluminum concentrations > 0.30 μM. These concentrations were markedly higher at the upstream reach ends in these two subregions, an exaggeration of the pattern observed in pH and ANC. Subregional median concentrations at the upstream ends of reaches in subregions 3C and 3B were respectively, 2.3 and 1.5 μM, which is 5 to 20 times those observed in the other subregions. Approximately 20% of the reaches in these subregions had extractable aluminum concentrations > 6 μM.

Comparison of total aluminum concentrations with measurements of pH, MIBK-extractable aluminum, DOC, and turbidity suggests a possible interpretation of these results. Total aluminum was positively correlated with turbidity (r = 0.97) and color (r = 0.90), but not with pH or DOC in the Ozark/Ouachita (2D) and Piedmont (3A) subregions. Also, MIBK-extractable aluminum concentrations were low in these subregions. It appears likely that high total aluminum in these

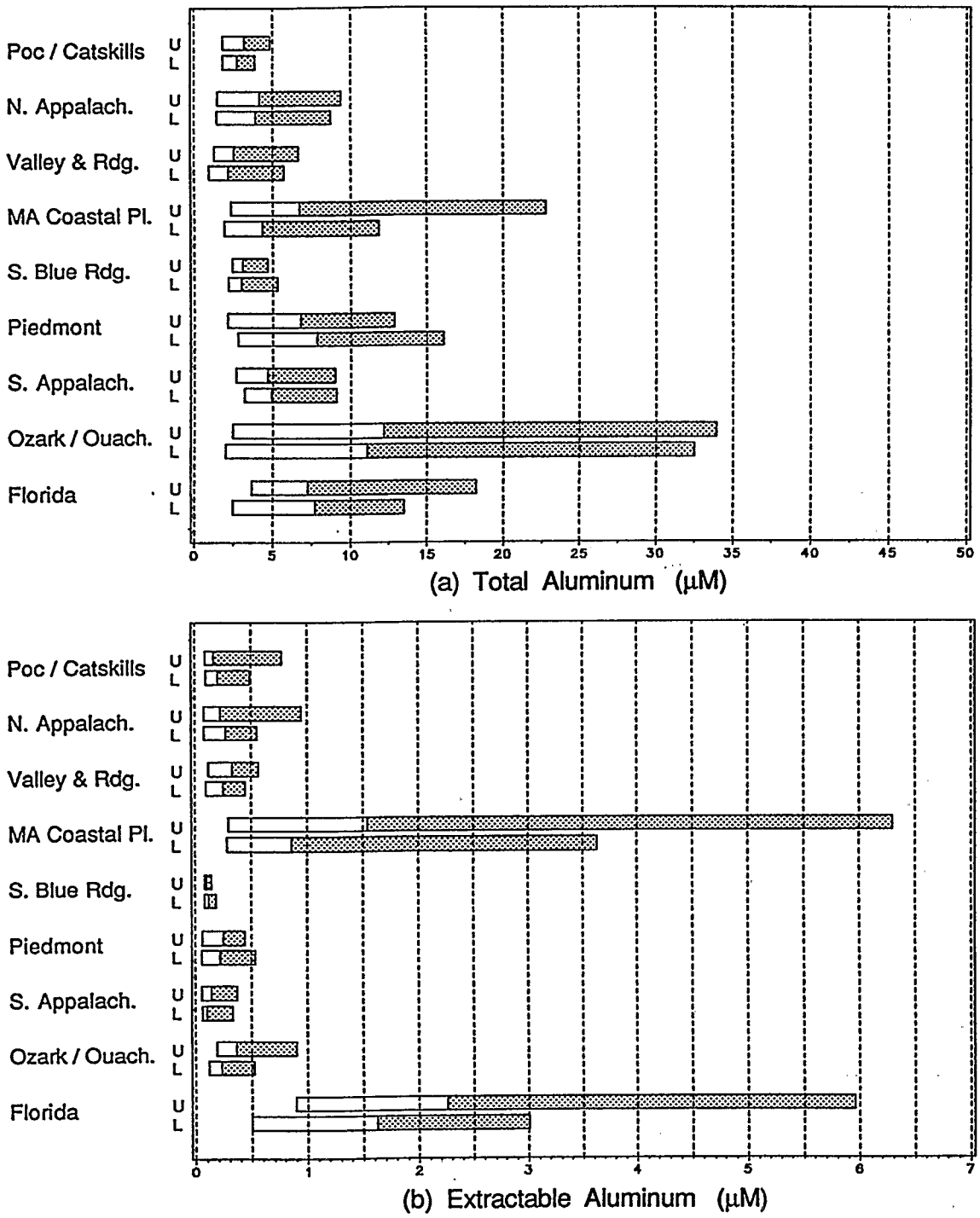


Figure 6-11. Population frequency distributions (Q_{20}, median, and Q_{80}) of index (a) total aluminum and (b) total monomeric aluminum (MIBK-extractable) concentrations at upper and lower reach nodes in the NSS-I subregions.

areas is associated with the suspension of particulate and colloidal aluminum derived from kaolin and other aluminum-rich clays or silts contained in the soils of these regions. In contrast, the MIBK-extractable aluminum concentration was relatively high, and made up a greater fraction of the total aluminum concentration in subregions 3C and 3B. In addition, the total aluminum concentration was positively correlated with DOC and negatively correlated with pH in these two subregions, suggesting that aluminum is largely in the form of dissolved and colloidal inorganic aluminum and organo-aluminum complexes.

Inorganic monomeric aluminum concentration was defined as the difference in aluminum concentration (measured by the pyrocatechol violet technique) before and after passing the sample through a strong cation exchange column. It is this inorganic monomeric component of total aluminum concentration that is of greatest concern because of its toxicity to fish (Driscoll et al., 1980; Baker and Schofield, 1982; Gagen and Sharpe, 1987) and aquatic invertebrates (Witters et al., 1984; Havas, 1985). Free aluminum ions at concentration thresholds between 0.05 and 0.2 mg L^{-1} (1.9 and 7.4 μM) have been demonstrated to reduce growth and survival of various species of fishes (Muniz and Leivestadt, 1980; Baker and Schofield, 1982; Muniz et al., 1987).

Spring index concentrations of inorganic monomeric aluminum ($Al_{(im)}$) > 0.20 mg L^{-1} in the NSS-I were largely restricted to upper reach nodes of the Mid-Atlantic subregions (3B, 2Cn, 2Bn, and 1D) and lower reach nodes in the Florida (3C) subregion, where between 2% and 5% of the reaches had concentrations above this reference value (Table 6-6). Concentrations greater than 0.10 mg L^{-1} were not observed in any of the Southeast subregions except Florida. The Mid-Atlantic Coastal Plain (3B) had the largest percentage of both upper (13%) and lower (6%) reach nodes with $Al_{(im)}$ concentrations above 0.10 mg L^{-1}. Two percent or more of the upper reach nodes in all subregions except the Southern Blue Ridge (2As) and Piedmont (3A) had $Al_{(im)}$ concentrations above the lowest threshold for adverse effects on fisheries (0.05 mg L^{-1}). Mid-Atlantic upper nodes above this concentration ranged from a low of 2% in the Valley and Ridge subregion (2Bn) to a high of 30% in subregion 3B. Subregion 3B also had a high percentage of lower nodes (15%) above the 0.05 mg L^{-1} reference value. Florida had a greater number of lower (18%) than upper nodes (7%) above the 0.05 mg L^{-1} reference value.

6.3.3 Sulfate

There were no data quality problems in the measurement of sulfate that would affect interpretation at the concentration levels observed in the NSS-I. The SDL was 1 μeq L^{-1}, indicating no substantial background or detection problems (Table 4-1). Likewise, precision presented no problem for data interpretation, as all types of precision measurement had %RSD < 6% (Tables 4-2 and 4-3).

Comparing subregional population distributions (Figures 6-12 [a] and 6-13 [a - i]), and medians (Table 6-1), and examining the mapped geographic distribution of sulfate in Figure 6-14, it is readily apparent that the four Mid-Atlantic subregions have substantially higher (and more widely ranging) concentrations than those in the Southeast subregions. Mid-Atlantic subregion medians ranged from a high of 238 μeq L^{-1} for the downstream ends of reaches in subregion 1D, the Poconos/Catskills, to a low of 125 μeq L^{-1} at the upstream ends of target reaches in the Mid-Atlantic Coastal Plain (3B). Medians in the Southeast ranged from 10 μeq L^{-1} at the upstream ends of Florida (3C) reaches to 71 μeq L^{-1} at the downstream ends of Southern Appalachian (2X) reaches.

Table 6-6. Population Estimates of the Percentage of Target Stream Lower (L) and Upper (U) Reach Nodes with Spring Index Inorganic Monomeric Aluminum Above Reference Concentrations

	INORGANIC MONOMERIC ALUMINUM CONCENTRATIONS#					
	> 0.05 mg L^{-1} (> 1.85 μM)		> 0.10 mg L^{-1} (> 3.71 μM)		> 0.20 mg L^{-1} (> 7.41 μM)	
SUBREGION	L	U	L	U	L	U
1D (Poconos/Catskills)	*	7	*	3	*	2
2Cn (N. Appalachians)	4	8	4	6	2	4
2Bn (Valley and Ridge)	*	2	*	2	*	2
3B (MA Coastal Plain)	15	30	6	13	*	4
2As (S. Blue Ridge)	*	*	*	*	*	*
3A (Piedmont)	*	*	*	*	*	*
2X (S. Appalachians)	*	2	*	*	*	*
2D (Ozarks/Ouachitas)	2	2	*	*	*	*
3C (Florida)	18	7	5	4	5	*

* Less than 1%.

\# Based on Pyrocatechol violet technique and use of a cation exchange column for all Subregions except 2As, where it was based on the MIBK technique and use of a cation exchange column.

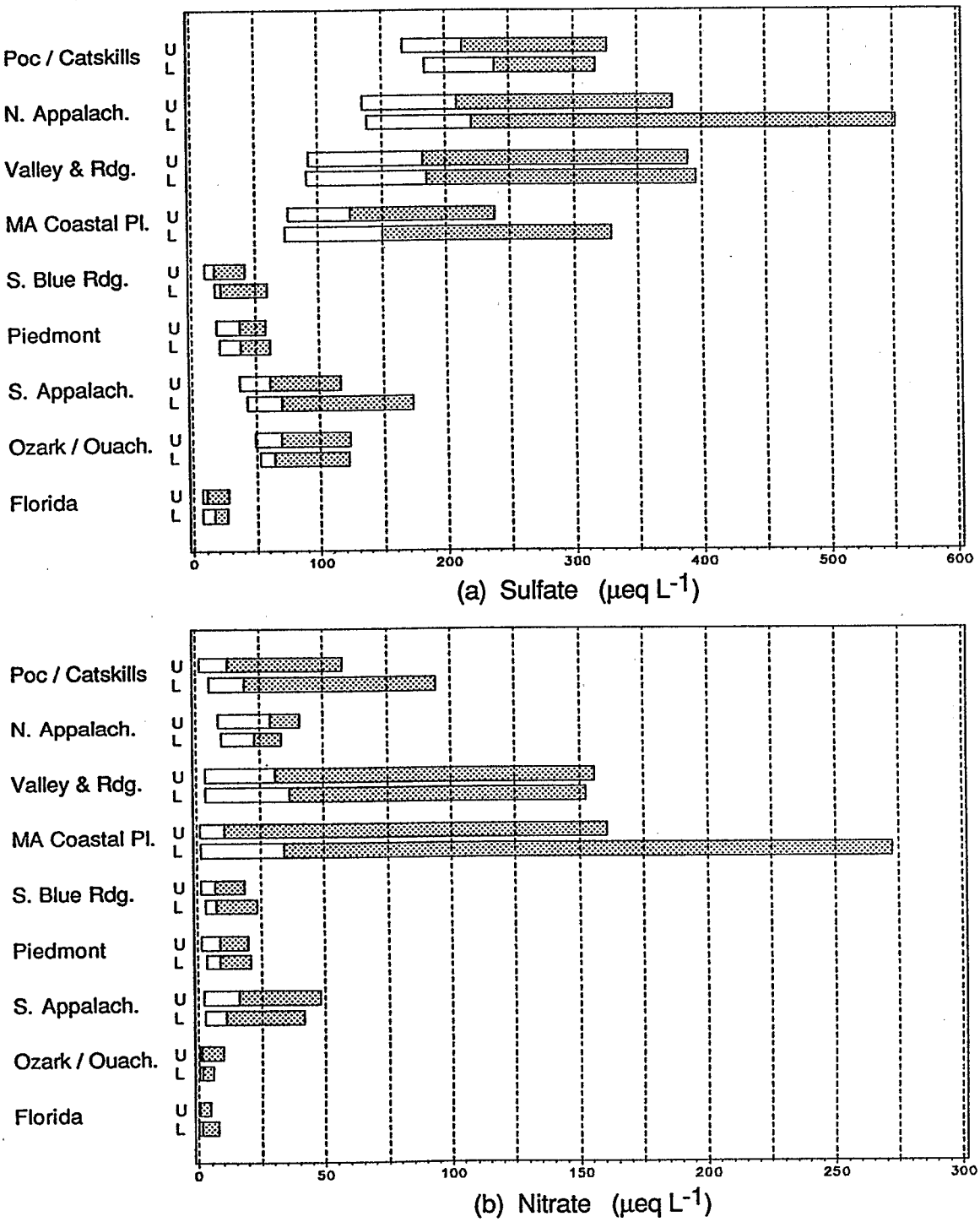
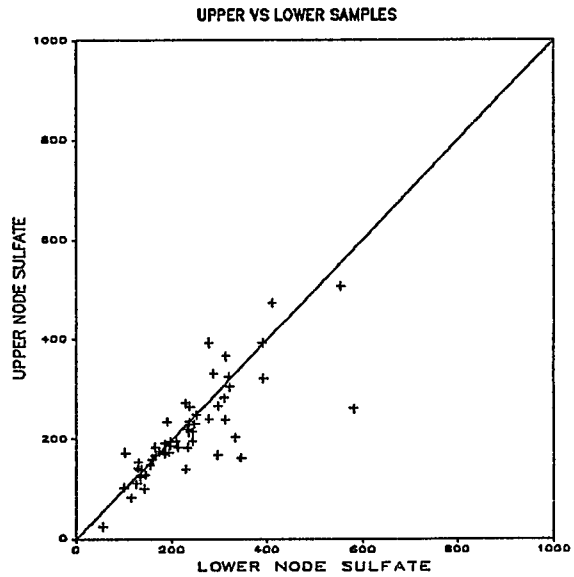


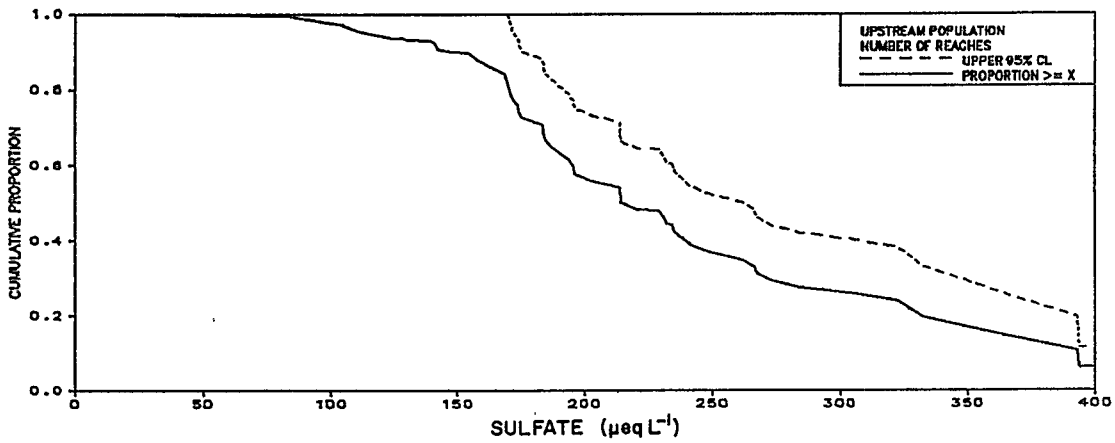
Figure 6-12. **Population frequency distribution (Q_{20}, Median, and Q_{80}) of index (a) sulfate, and (b) nitrate concentrations at upper and lower reach nodes in the NSS-I subregions.**

SULFATE

POCONOS / CATSKILLS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	23.9	54.5
80%	167.1	184.5
60%	193.2	232.1
MEDIAN	213.8	238.2
40%	236.3	278.1
20%	326.2	317.5
MAX	1111.0	1092.4
MEAN	255.0	275.6
STD	154.2	153.3
SAMPLE(n)	58	56
POP EST(N)	3244	3235
SE(N)	347	347





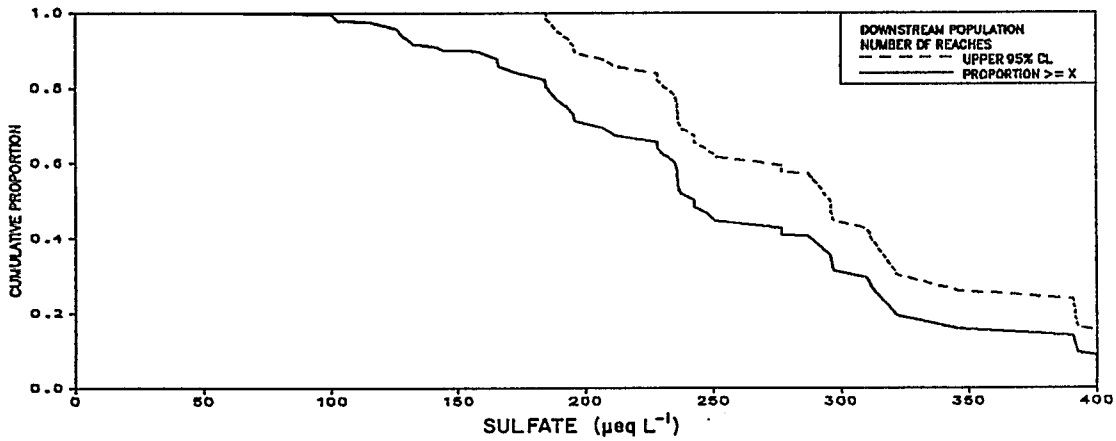
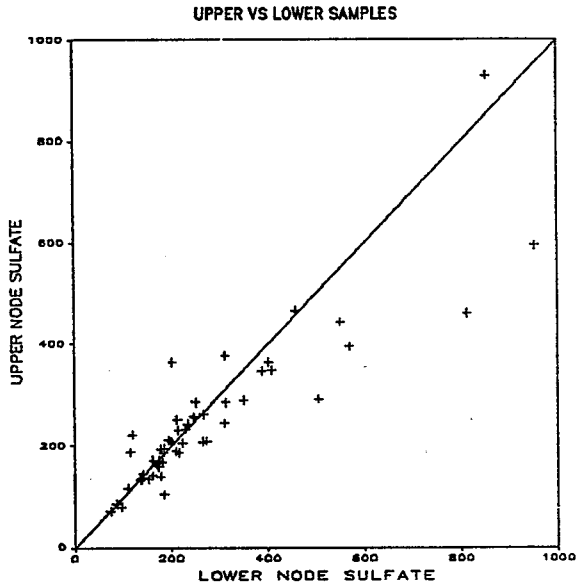


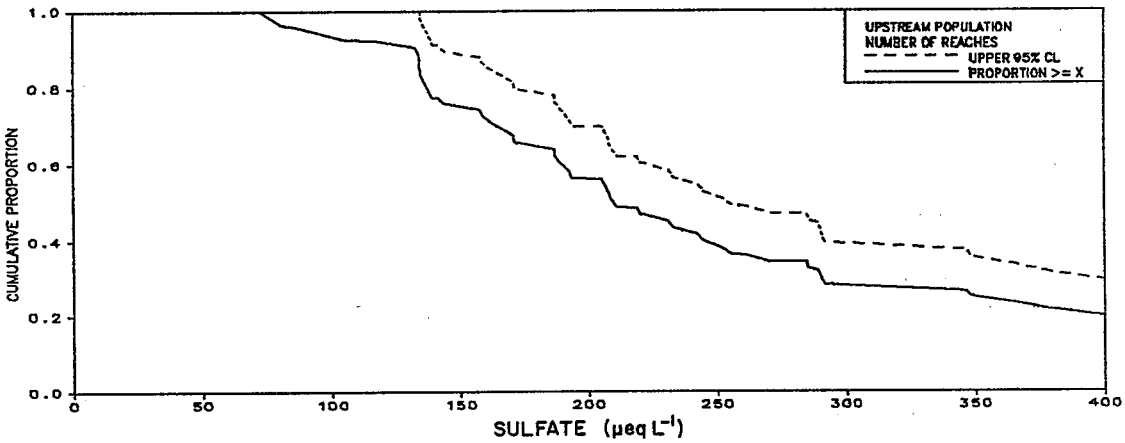
Figure 6-13a. Population distributions and comparison of index sulfate concentrations at upper and lower reach nodes in NSS-I subregion 1D (Poconos/Catskills), presented as inverse cumulative proportions.

SULFATE

NORTHERN APPALACHIANS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	72.6	74.1
80%	135.0	138.8
60%	187.8	181.0
MEDIAN	208.9	220.0
40%	242.4	270.6
20%	377.4	552.2
MAX	2217.3	2383.9
MEAN	404.5	471.6
STD	520.3	572.9
SAMPLE(n)	67	61
POP EST(N)	8663	8488
SE(N)	807	814





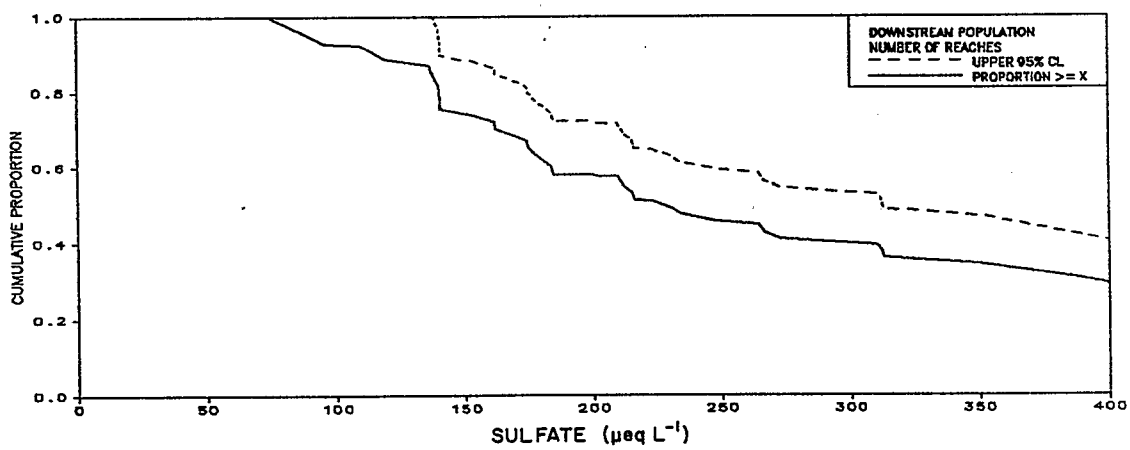
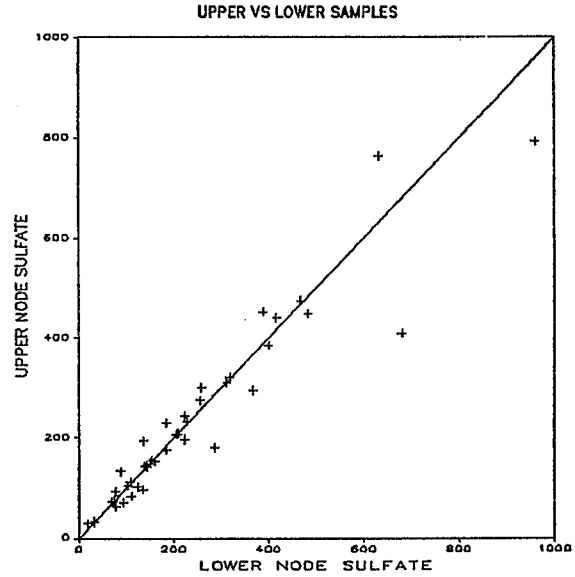


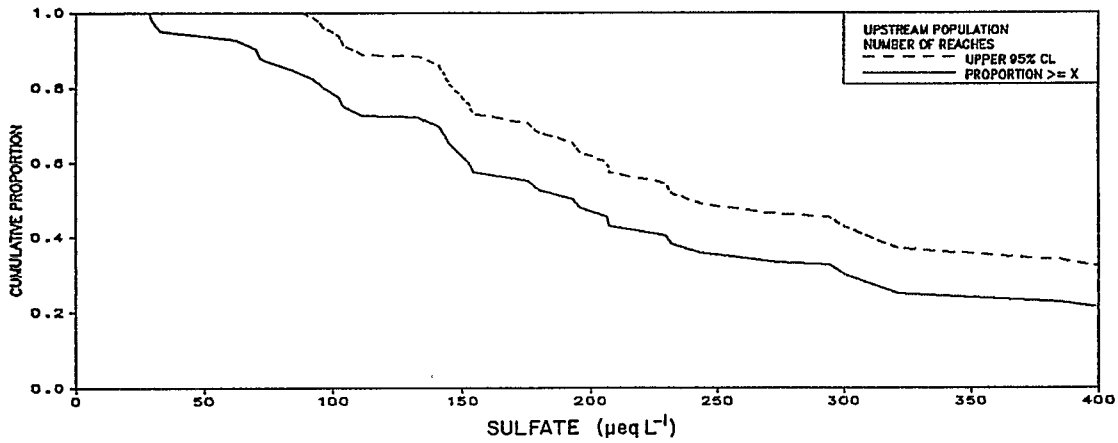
Figure 6-13b. Population distributions and comparison of index sulfate concentrations at upper and lower reach nodes in NSS-I subregion 2Cn (Northern Appalachians), presented as inverse cumulative proportions.

SULFATE

VALLEY AND RIDGE

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	28.6	18.0
80%	92.7	91.4
60%	149.3	145.2
MEDIAN	182.4	185.1
40%	213.7	222.7
20%	389.0	395.4
MAX	809.5	1262.3
MEAN	246.9	278.0
STD	195.6	266.4
SAMPLE(n)	44	47
POP EST(N)	13038	13992
SE(N)	1249	1213





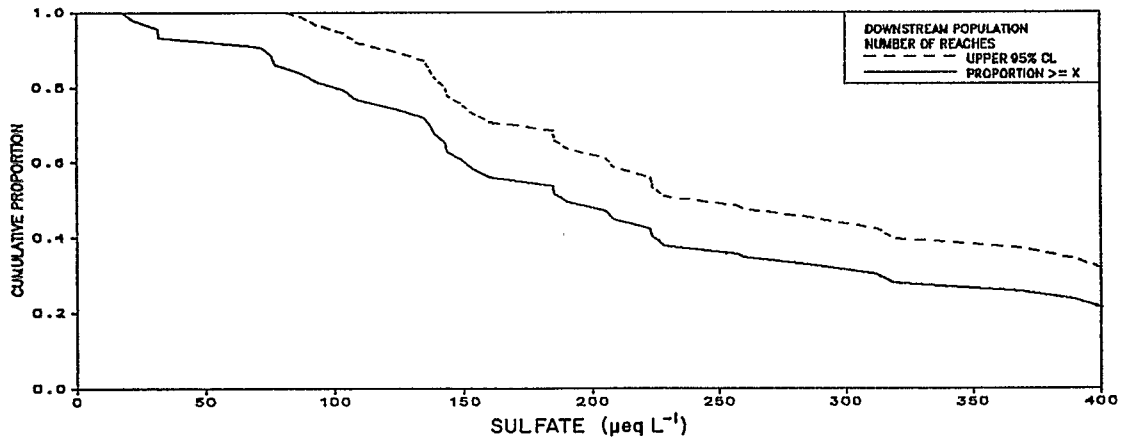
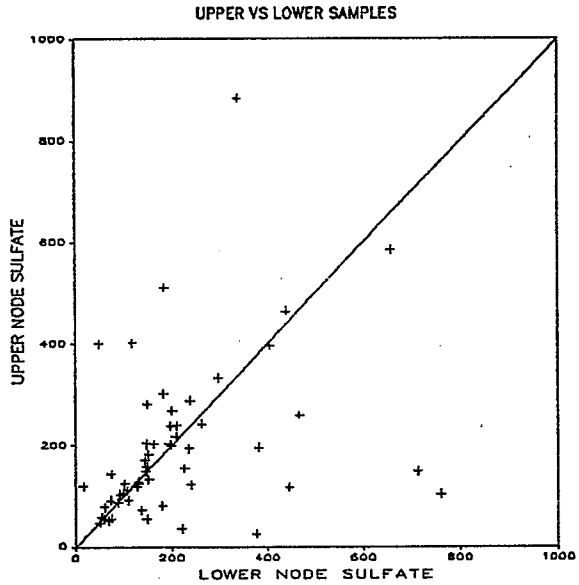


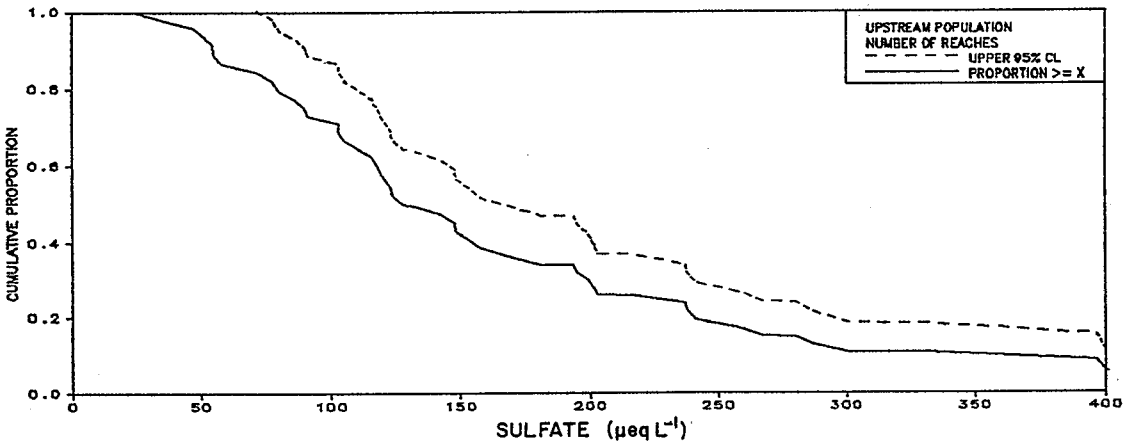
Figure 6-13c. Population distributions and comparison of index sulfate concentrations at upper and lower reach nodes in NSS-I subregion 2Bn (Valley and Ridge), presented as inverse cumulative proportions.

SULFATE

MID–ATLANTIC COASTAL PLAIN

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	24.7	14.8
80%	76.3	74.3
60%	116.3	139.1
MEDIAN	125.1	150.5
40%	150.5	198.1
20%	237.9	328.8
MAX	883.9	760.1
MEAN	173.0	217.0
STD	137.2	171.9
SAMPLE(n)	57	58
POP EST(N)	11284	11287
SE(N)	1078	1078





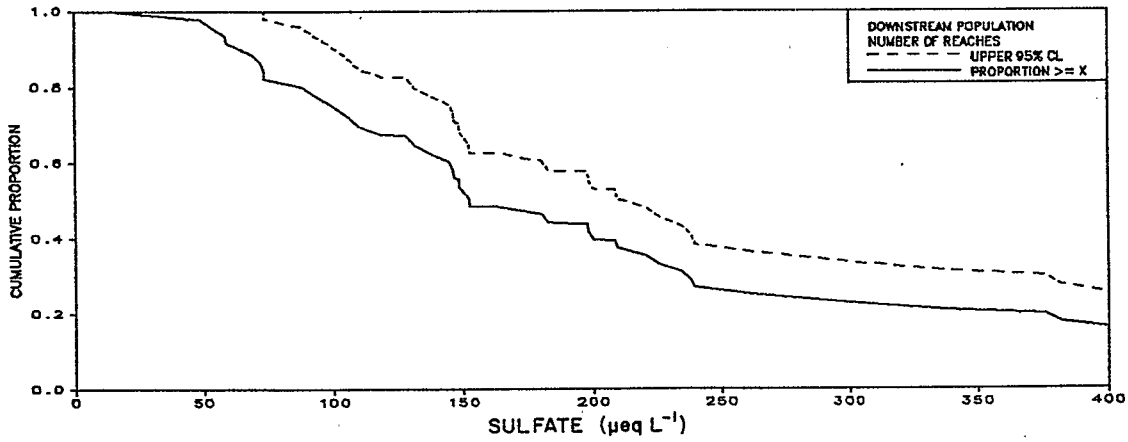
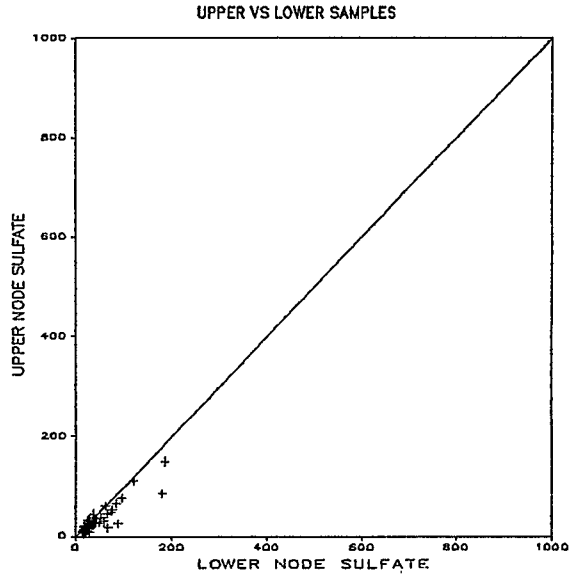


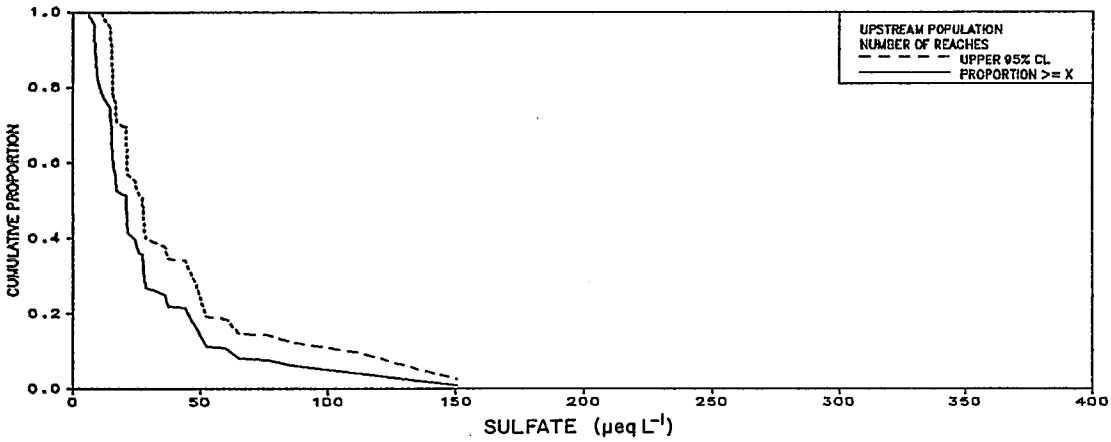
Figure 6-13d. Population distributions and comparison of index sulfate concentrations at upper and lower reach nodes in NSS-I subregion 3B (Mid-Atlantic Coastal Plain), presented as inverse cumulative proportions.

SULFATE

SOUTHERN BLUE RIDGE

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	6.2	12.9
80%	10.2	18.6
60%	15.4	22.4
MEDIAN	20.7	22.9
40%	22.8	27.6
20%	44.3	59.4
MAX	150.3	184.4
MEAN	28.5	39.1
STD	26.1	34.2
SAMPLE(n)	54	54
POP EST(N)	2031	2031
SE(N)	326	326





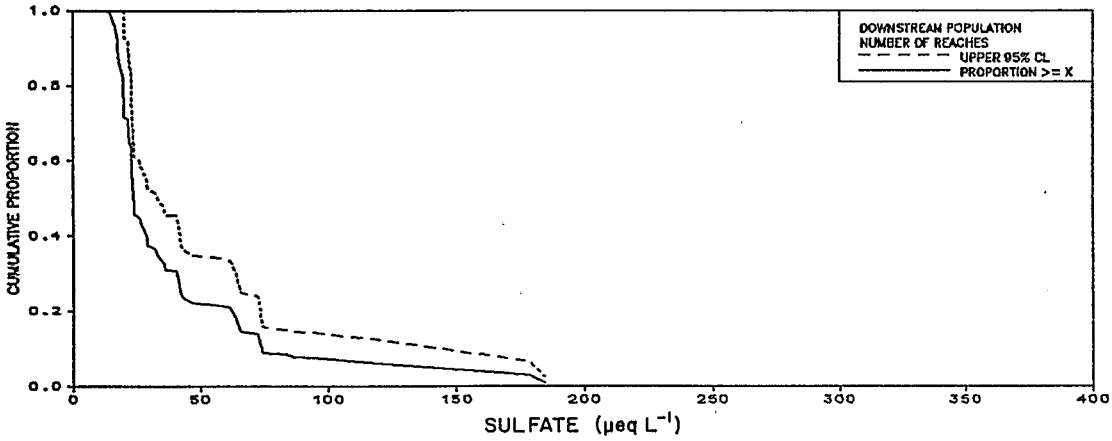
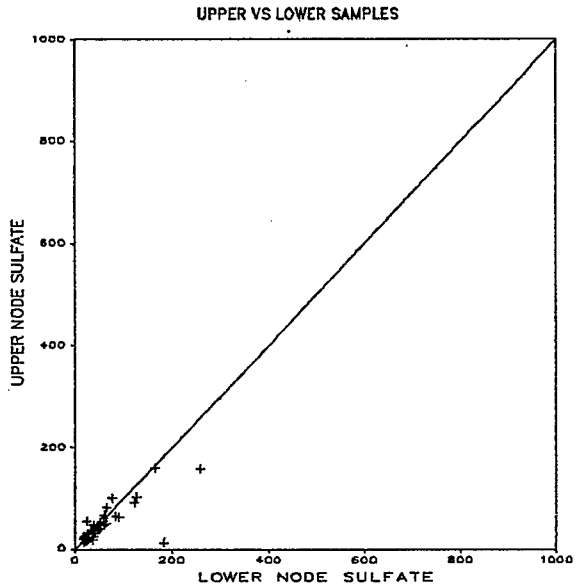


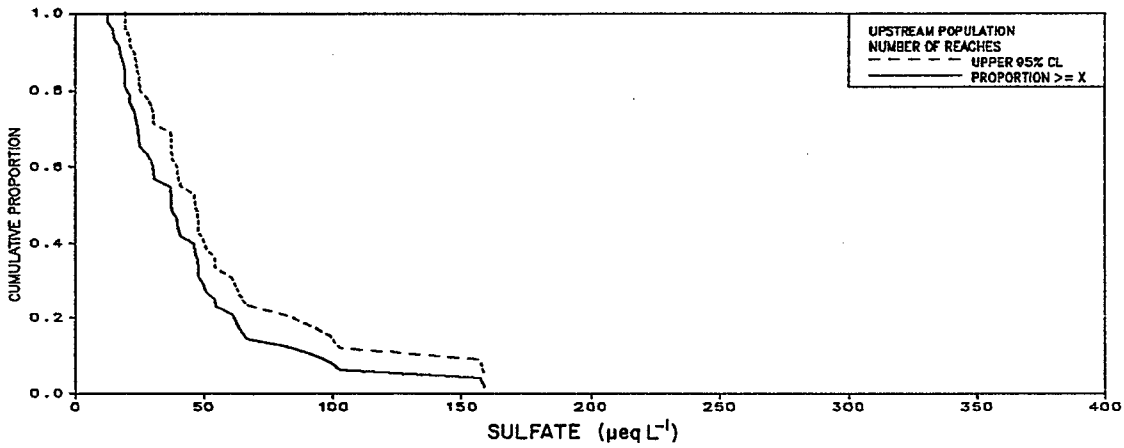
Figure 6.1-13e. Population distributions and comparison of index sulfate concentrations at upper and lower reach nodes in NSS-I subregion 2As (Southern Blue Ridge), presented as inverse cumulative proportions.

SULFATE

PIEDMONT

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	12.5	16.9
80%	19.5	21.9
60%	29.3	34.7
MEDIAN	37.5	38.3
40%	41.1	46.3
20%	57.7	61.7
MAX	158.8	257.5
MEAN	44.7	53.3
STD	32.4	46.8
SAMPLE(n)	47	47
POP EST(N)	7515	7515
SE(N)	650	650





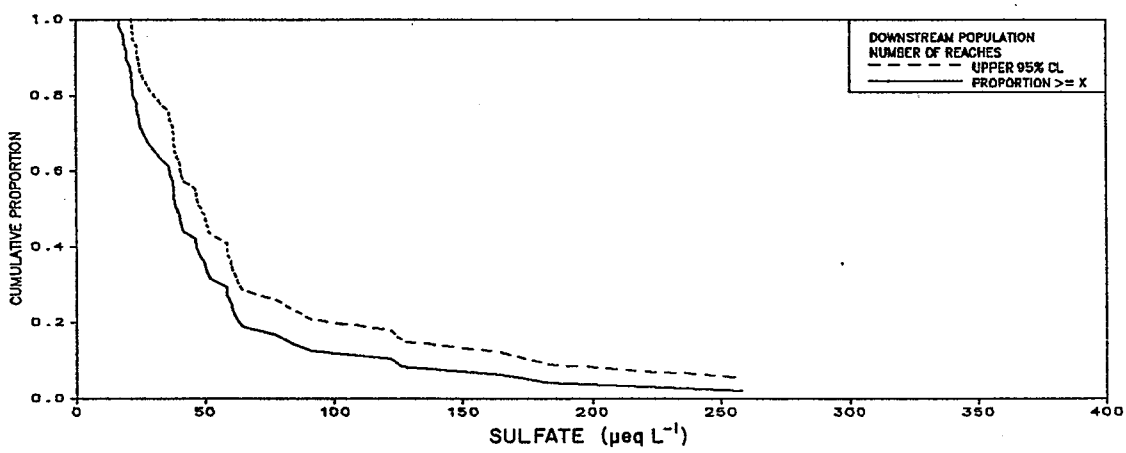
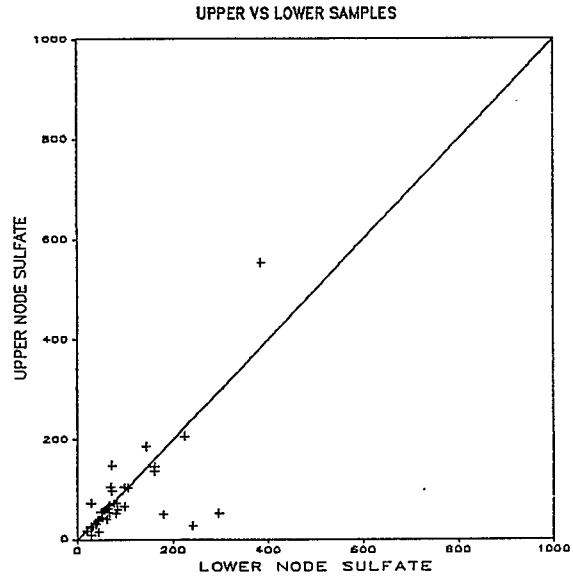


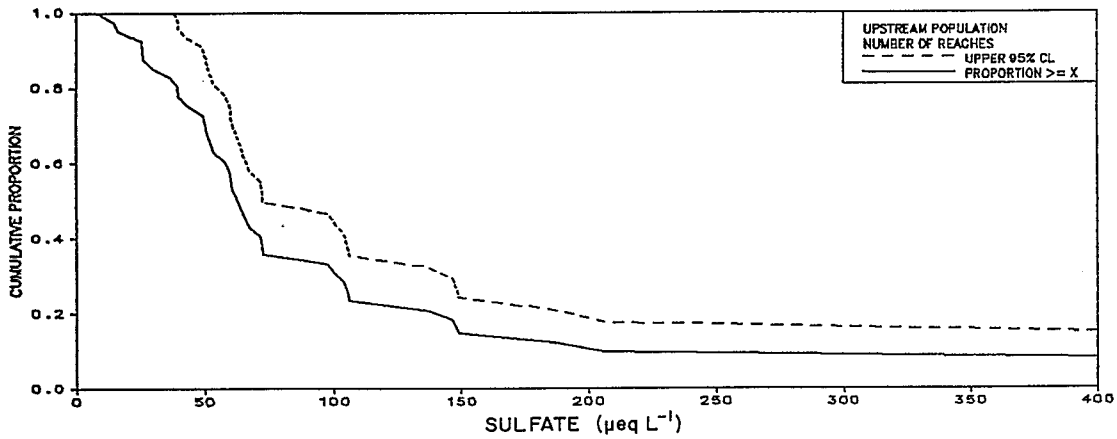
Figure 6-13f. Population distributions and comparison of index sulfate concentrations at upper and lower reach nodes in NSS-I subregion 3A (Piedmont), presented as inverse cumulative proportions.

SULFATE

SOUTHERN APPALACHIANS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	8.5	19.2
80%	37.4	43.6
60%	54.8	63.3
MEDIAN	61.0	70.6
40%	68.3	81.0
20%	116.4	173.4
MAX	2644.1	2852.3
MEAN	155.9	244.0
STD	408.4	519.4
SAMPLE(n)	39	40
POP EST(N)	4936	5057
SE(N)	529	526





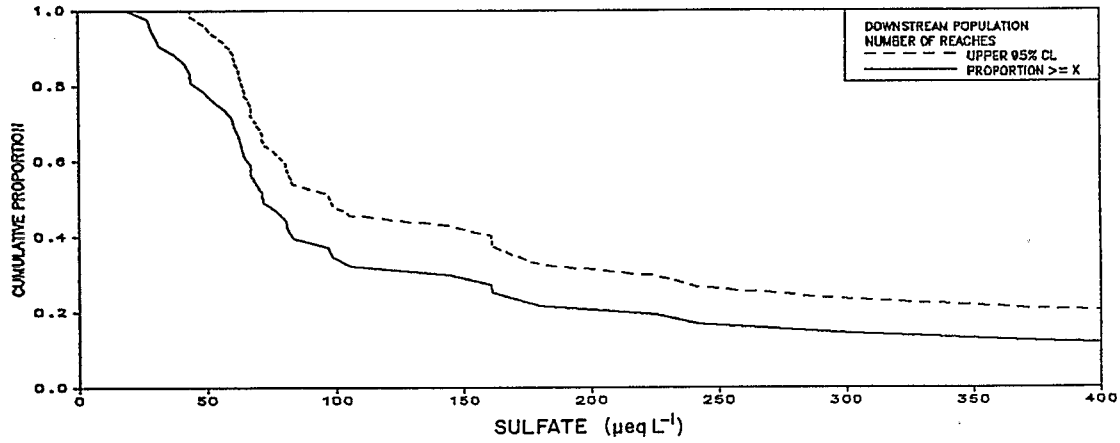
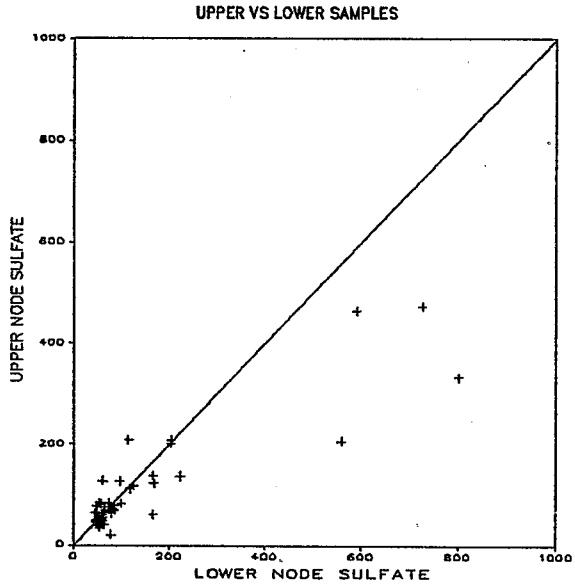


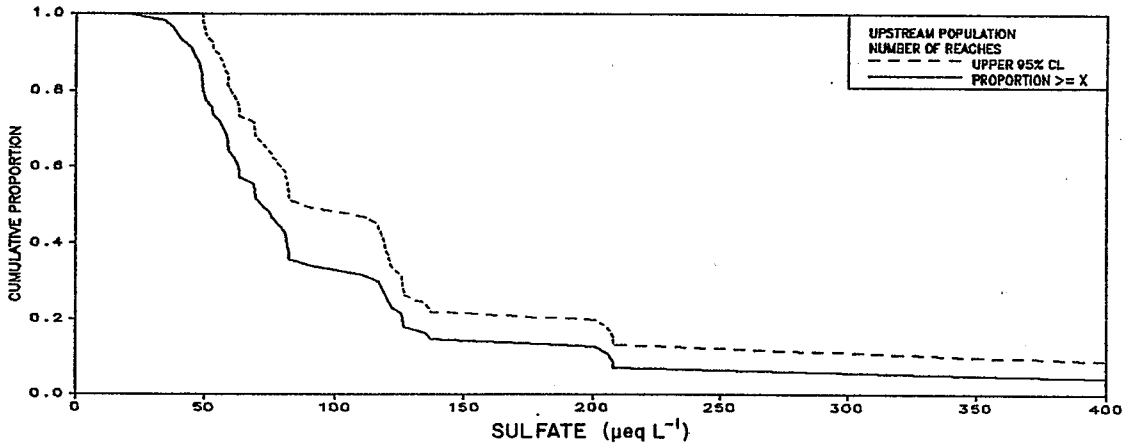
Figure 6-13g. Population distributions and comparison of index sulfate concentrations at upper and lower reach nodes in NSS-I subregion 2X (Southern Appalachians), presented as inverse cumulative proportions.

SULFATE

OZARKS / OUACHITAS

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	20.6	45.0
80%	49.0	52.9
60%	62.2	60.5
MEDIAN	69.9	64.5
40%	81.4	78.1
20%	123.6	122.7
MAX	473.7	801.6
MEAN	102.0	127.1
STD	89.5	160.4
SAMPLE(n)	49	48
POP EST(N)	4204	4116
SE(N)	406	410





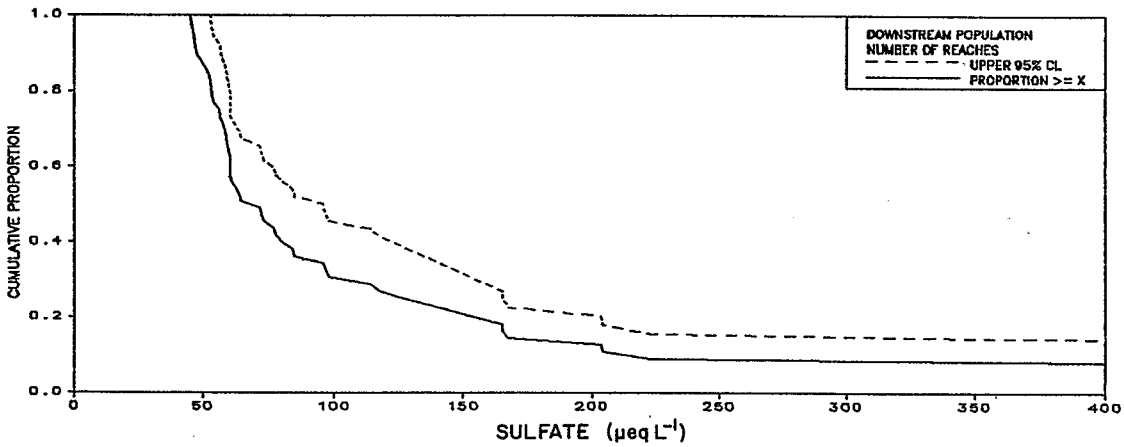
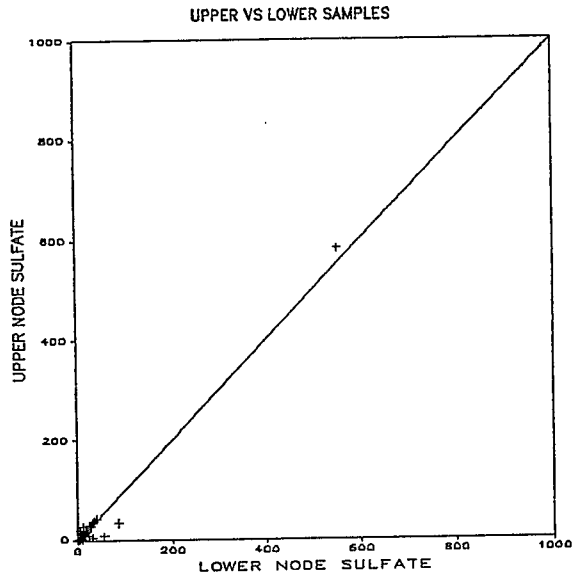


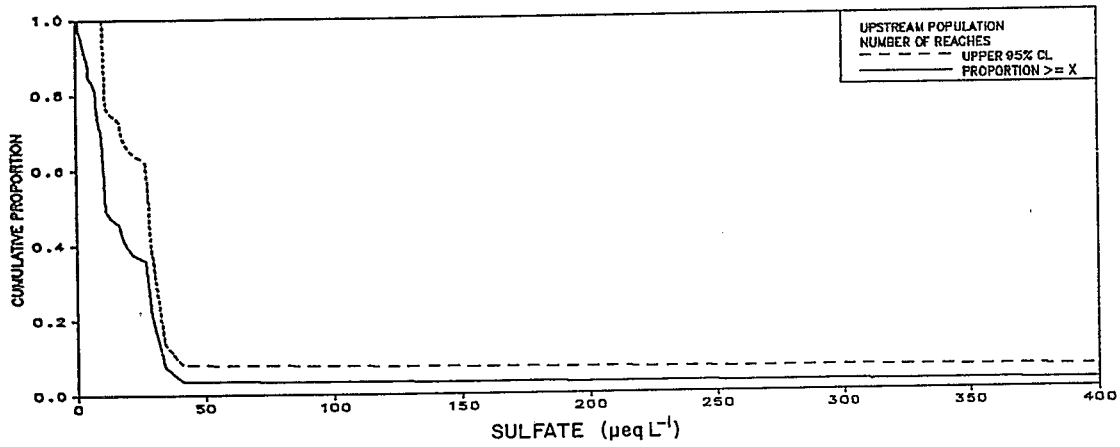
Figure 6-13h. Population distributions and comparison of index sulfate concentrations at upper and lower reach nodes in NSS-I subregion 2D (Ozarks/Ouachitas), presented as inverse cumulative proportions.

SULFATE

FLORIDA

STATISTIC (ESTIMATE)	UPPER NODE	LOWER NODE
MIN	1.0	2.0
80%	7.0	6.7
60%	9.7	11.3
MEDIAN	10.0	16.1
40%	17.8	23.3
20%	27.5	26.5
MAX	583.0	553.8
MEAN	26.9	30.2
STD	77.2	77.3
SAMPLE(n)	31	34
POP EST(N)	1727	1555
SE(N)	437	306





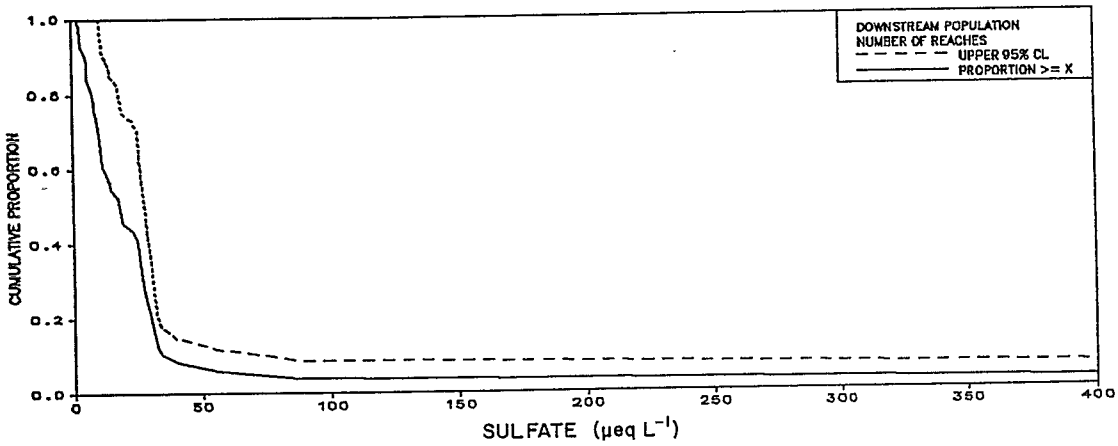


Figure 6-13i. Population distributions and comparison of index sulfate concentrations at upper and lower reach nodes in NSS-I subregion 3C (Florida), presented as inverse cumulative proportions.

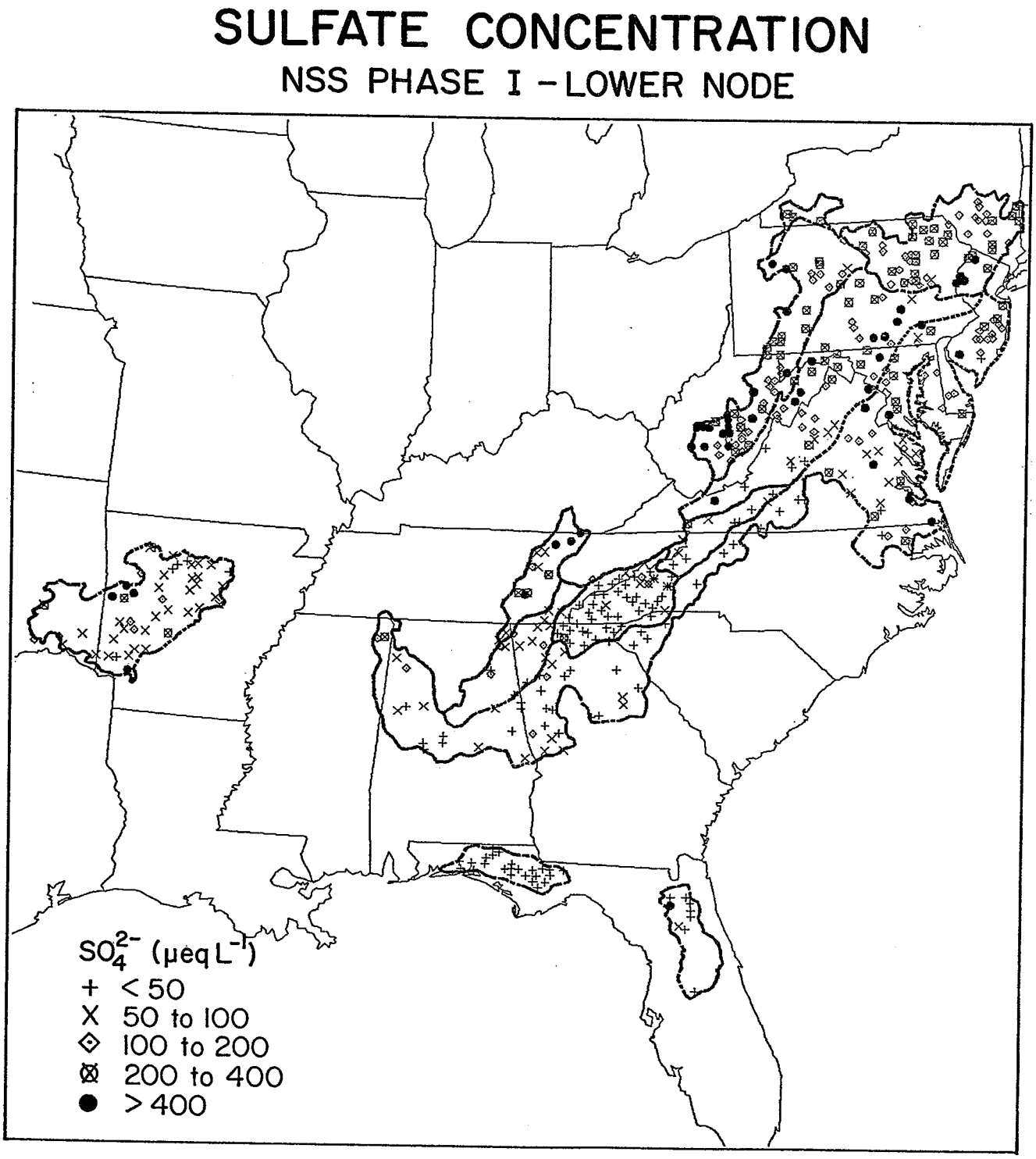


Figure 6-14. Geographic distribution of NSS-I lower node index sulfate concentrations.

The potential sources of sulfate in stream water are wet and dry atmospheric deposition (natural and anthropogenic sources), nonatmospheric anthropogenic sources (e.g., agriculture), and the dissolution of sulfur-bearing minerals. Crude approximations of steady state sulfate concentrations for streams with no internal sulfate sources can be calculated using approximate concentrations of sulfate in precipitation within the various subregions and approximate regional values for the ratio of precipitation to runoff to account for evapoconcentration (Table 6-7). The figures in parentheses in column 3 represent a reasonable range of stream sulfate concentrations that could be attributed to atmospheric deposition. They were calculated using the range of available regional precipitation, runoff, and sulfate deposition data. The method of calculation and sources of information are cited in the table. The middle figure is a best estimate of what a typical (perhaps a median) stream water concentration might be for each subregion, assuming no internal sources or sinks (i.e., sulfate is acting conservatively; mass input equals output and sulfate is simply concentrated by evapotranspiration). Streams with index sulfate concentrations less than the lower end of the predicted sulfate range almost certainly have substantial sinks for sulfate. Those with sulfate greater than the high end of this range almost certainly have substantial internal sources of sulfate. If the median in a subregion is above the best estimate, it does not imply that 50% of the stream reaches have substantial internal sulfate sources. An elevated median sulfate concentration does suggest, however, that internal sources are likely in some streams, particularly if the distribution of measured stream water sulfate includes concentrations above the high value estimate for predicted stream water sulfate.

The most striking result to be gleaned from comparing Table 6-7 with the cumulative frequency distributions of stream water sulfate in the nine NSS-I subregions is the large difference between most Mid-Atlantic and most Southeast subregions with regard to apparent retention or export of sulfate. The overall pattern appears to be that of sulfate retention in watersheds of some Southeast subregions (Southern Blue Ridge, Piedmont, and Florida) and concentrations near steady state in many streams within the Interior Mid-Atlantic subregions. These results, except for Florida, support the hypothesis advanced by Rochelle and Church (1987) that the deeper, more highly weathered soils in unglaciated areas of the southeastern United States are more highly retentive of sulfate from atmospheric deposition than are those in the mid-Atlantic and northeast, many of which are generally younger and shallower, and most of which have been subjected to high rates of atmospheric sulfate deposition for longer periods of time.

The relatively wide range of sulfate concentrations found in many subregions reflects the heterogeneity of watershed characteristics controlling watershed sulfate dynamics (hydrology, sources, and sinks), as well as local differences in sulfate deposition and precipitation. This heterogeneity is particularly evident in the four Mid-Atlantic subregions plus the Southern Appalachians (2X) and the Ozarks/Ouachitas (2D). Even though many streams in the Mid-Atlantic subregions appear to have sulfate concentrations roughly approximating steady-state concentrations (mass input equals output, as very crudely approximated by comparing spring baseflow with annual average precipitation sulfate concentrations), there is evidence for both sulfate retention and internal sources of sulfate in many other streams within these same subregions. Substantial sinks for sulfate are apparent in about 1% to 2% of the Poconos/Catskills (1D) streams, 8% to 11% of the streams in the Northern Appalachians (2Cn), and about 20% of the streams in the Valley and Ridge (2Bn) subregions. Similarly, substantial amounts of sulfate appear to be retained by approximately 30% of the stream reaches in the Ozarks/Ouachitas (2D) and by 40% to 57% of the streams in the Southern Appalachians (2X) and the Mid-Atlantic Coastal Plain (3B).

Table 6-7. Sulfate Concentration in Deposition and Best Estimates and Range of Precipitation/ Runoff Ratios and Predicted Stream Water Sulfate Concentrations (Assuming Only Atmospheric Sulfate Sources) in NSS-I Subregions

Subregion	1986 Volume# Wgt. Wet Deposition $[SO_4^{2-}]$ ($\mu eq\ L^{-1}$)	Precipitation@ /Runoff Ratio	Predicted$ Streamwater $[SO_4^{2-}]$ ($\mu eq\ L^{-1}$)	Percent of Reach Nodes Above High Estimate Upper	Lower
1D (Poconos/Catskills)	57-67	1.70 (1.03-3.46)	158 (88-348)	14%	14%
2Cn (N. Appalachians)	62-73	1.84 (1.24-2.89)	186 (115-316)	27%	34%
2Bn (Valley and Ridge)	62-73	2.11 (1.10-3.77)	214 (102-413)	18%	19%
3B (MA Coastal Plain)	52-62	2.56 (1.90-3.85)	219 (148-358)	9%	20%
2As (S. Blue Ridge)	36-46	2.30 (1.00-6.38)	141 (54-440)	<1%	<1%
3A (Piedmont)	31-41	2.71 (1.08-5.33)	146 (50-328)	<1%	<1%
2X (S. Appalachians)	36-46	2.36 (1.19-4.07)	145 (64-281)	7%	14%
2D (Ozarks/Ouachitas)	21-31	2.45 (1.79-4.08)	96 (56-190)	13%	13%
3C (Florida)	16-26	3.18 (1.56-7.00)	100 (37-273)	2%	2%

Range in precipitation volume weighted sulfate concentration in each subregion. Data taken from the Eastern United States sulfate concentration isopleth map in the 1986 NADP/NTN annual data summary (National Atmospheric Deposition Program, 1987).

@ Estimates of the precipitation/runoff ratio in each subregion, from Geragnty et al. (1973).

$ Predicted stream water sulfate concentration, assuming only atmospheric sulfate sources; calculated by multiplying the midpoint of the subregional range in precipitation sulfate concentration by 1.5 (to account for dry deposition) and then multiplying by the precipitation/runoff ratio (to account for evaporation). Low range estimate was calculated using the low estimate of precipitation sulfate concentration and precipitation/runoff ratio. High range estimate was calculated using the high estimates.

Substantial sulfate sinks are apparent in several of the Southeast subregions (Southern Blue Ridge, Piedmont, and Florida). A large majority of target stream reach upper and lower nodes (80% to 95%) in the Southern Blue Ridge (2As) and Florida (3C) were estimated to have concentrations less than the low stream water sulfate predictions for each subregion. In the Piedmont (3A), more than 60% had sulfate lower than this value. Sulfate retention by adsorption in the deep, highly weathered iron- and aluminum-rich soils of the Southern Blue Ridge and in other areas of the Southeast has been hypothesized by Galloway et al. (1983a) and by Rochelle and Church (1987) on the basis of sulfate input-output modelling incorporating deposition, stream water, and soil chemistry data. The low sulfate concentrations in Florida streams are somewhat anomolous. Several plausible speculations are: (1) precipitation sulfate concentrations for this area are overestimated, or perhaps more likely, the use of annual average precipitation data obscures the actual relationship between stream and precipitation sulfate concentrations (e.g., spring 1986 runoff and sulfate deposition were substantially different from annual averages), (2) sulfate reduction in soils or sediments of slow moving, organic-rich streams results in a net loss of sulfur, or (3) sulfate adsorption may be occurring in watershed soils (though these sandy soils are likely to have low sulfate adsorption capacity, they probably have not been subjected to a long history of high sulfate deposition rates, so present rates of adsorption may be high in clay layers within the soil mantle).

Substantial watershed contributions of sulfate appear likely at 9% to 27% of the upper nodes and 14% to 34% of the lower nodes of target stream reaches in the four Mid-Atlantic subregions. In the Southeast Region, 7% to 14% of Southern Applachian and Ozark/Ouachita reaches had sulfate concentrations high enough to necessitate considering substantial sources in addition to atmospheric deposition. Section 9 discusses the chemical characteristics and probable sources of acidity in the subpopulation of target streams with ANC $\leq$ 200 μeq L^{-1}. An important point discussed in Section 9 is the finding that, after excluding reaches affected by acid mine drainage, the majority of streams with sulfate concentrations > 250 μeq L^{-1} are streams within the target population that have relatively high ANC (> 200 μeq L^{-1}). These findings suggest that high sulfate in many of these high ANC mid-Atlantic streams does not contribute to acidity, but enters in the form of calcium and magnesium sulfates. On the other hand, in stream reaches with ANC < 200 μeq L^{-1}, sulfate concentrations tend not to be extremely high (most are near or less than the best estimates for predicted stream water sulfate) and correlate highly with ANC deficits (Section 10), suggesting that sulfate is likely to be associated with hydrogen ion as a strong acid. Section 10 contains a more thorough discussion of the potential role of sulfate from various sources in the acidification of NSS-I target streams.

6.3.4 Nitrate

Population distributions of nitrate at the upper and lower ends of NSS-I target reaches are summarized in Figure 6-12b. There were no detectability or accuracy problems in the measurement of nitrate (Section 4). At concentrations above the SDL, all precision estimates were < 9% (Table 4-3). All subregion medians were lower than or about the same as the 1986 annual volume-weighted mean concentrations of nitrate in precipitation (as reported by NADP, 1987). Nitrate in precipitation ranged from 10 to 30 μeq L^{-1} within the region covered by the NSS-I, whereas subregion median values ranged from 0.4 to 37 μeq L^{-1}. There was no consistent pattern of difference between medians for upstream and downstream populations.

The relative differences in nitrate concentrations among NSS-I subregions showed some similarity with those observed for sulfate, but sulfate median concentrations were generally 5 to 15 times as high (compare box plots in Figures 6-12a and b). As observed for sulfate, nitrate

medians were relatively high in the Mid-Atlantic subregions (11 to 37 μeq L^{-1}) and in subregion 2X, the Southern Appalachians (11 to 16 μeq L^{-1}), and relatively low in the remainder of the Southeast (0.4 to 8.7 μeq L^{-1}). As observed for sulfate, Florida (3C) had the lowest median nitrate concentrations (0.4 and 1.2 μeq L^{-1}, respectively, at the upper and lower reach ends). The Ozark/Ouachita subregion (2D) also had very low nitrate; upstream and downstream medians in this subregion were, respectively, 1.0 and 1.5 μeq L^{-1}. Comparison of geographic distributions of nitrate (Figure 6-15) with those of sulfate in NSS-I sample sites (Figure 6-14) again illustrates the similarity in these regional distribution patterns.

Observed nitrate concentrations in all subregions were substantially less than the published drinking water standard of 10 mg L^{-1} nitrate as N, or 714 μeq L^{-1}. Substantial fractions (more than 40%) of the stream reaches in the Northern and Southern Appalachians (2Cn and 2X), the Valley and Ridge (2Bn), and the Mid-Atlantic Coastal Plain (3B) had nitrate concentrations above 21 μeq L^{-1} (0.03 mg L^{-1} nitrate as N), a level reported by Vollenweider (1971), Golterman (1975), and Wetzel (1975) as a threshold concentration for contributing to nuisance algal blooms in lakes and reservoirs, assuming sufficient phosphate is present. These high nitrate concentrations were found primarily in reaches draining agricultural areas, and probably result from fertilizer nitrogen inputs.

6.3.5 Chloride

Population distributions of chloride at the upstream and downstream ends of target reaches in the NSS-I subregions are summarized in Figure 6-16a. There were no detectability or accuracy problems in the measurement of chloride (Section 4). The %RSD for field duplicates was < 5% for all concentration ranges. An obvious pattern is that chloride concentrations were substantially higher in the Mid-Atlantic subregions and Florida (3C) than in all the other NSS-I subregions. In all subregions except 3C, the median concentration at lower reach ends was higher than that for upper ends. Although these comparisons of medians are not conclusive (comparison of medians is only a rough indicator), a trend of increasing chloride with distance downstream suggests either a weathering source or the influence of agriculture, other anthropogenic activities, road salt, or evaporative concentration of chloride from deposition.

Chloride concentrations were generally highest in the Mid-Atlantic Coastal Plain subregion (3B), where the upstream and downstream medians were 264 and 318 μeq L^{-1}, more than ten times those for the Southern Blue Ridge (2As), where chloride concentrations were lowest. Regional variability was also high in subregion 3B, with inter-quintile ranges (80th - 20th percentiles) both approximately 350 μeq L^{-1}, again much higher (more than 10 times) than those observed in subregion 2As. The Poconos/Catskills (1D) and Florida (3C) had upstream and downstream medians ranging between 110 μeq L^{-1} and 173 μeq L^{-1}. The median of downstream reach ends (101 μeq L^{-1}) in the Valley and Ridge subregion was intermediate. All the other subregions, which are primarily upland, inland areas, had medians ranging from 32 to 67 μeq L^{-1}.

A map of chloride concentrations at NSS-I sample sites (Figure 6-17) shows that reaches with chloride concentrations > 200 μeq L^{-1} were found primarily within 200 km of the Atlantic Ocean. On the basis of studies of relatively pristine New England lakes (Sullivan et al., 1988a), we would not expect a significant sea salt contribution from precipitation to New England lakes or streams more than 100 km from the coast. The empirical relationship reported by Sullivan et al. (1988a) predicts sea water contributions of 69 μeq L^{-1} and 38 μeq L^{-1} for distances 20 and 50 km from the coast. The chloride concentrations in excess of 50 μeq L^{-1} observed in the

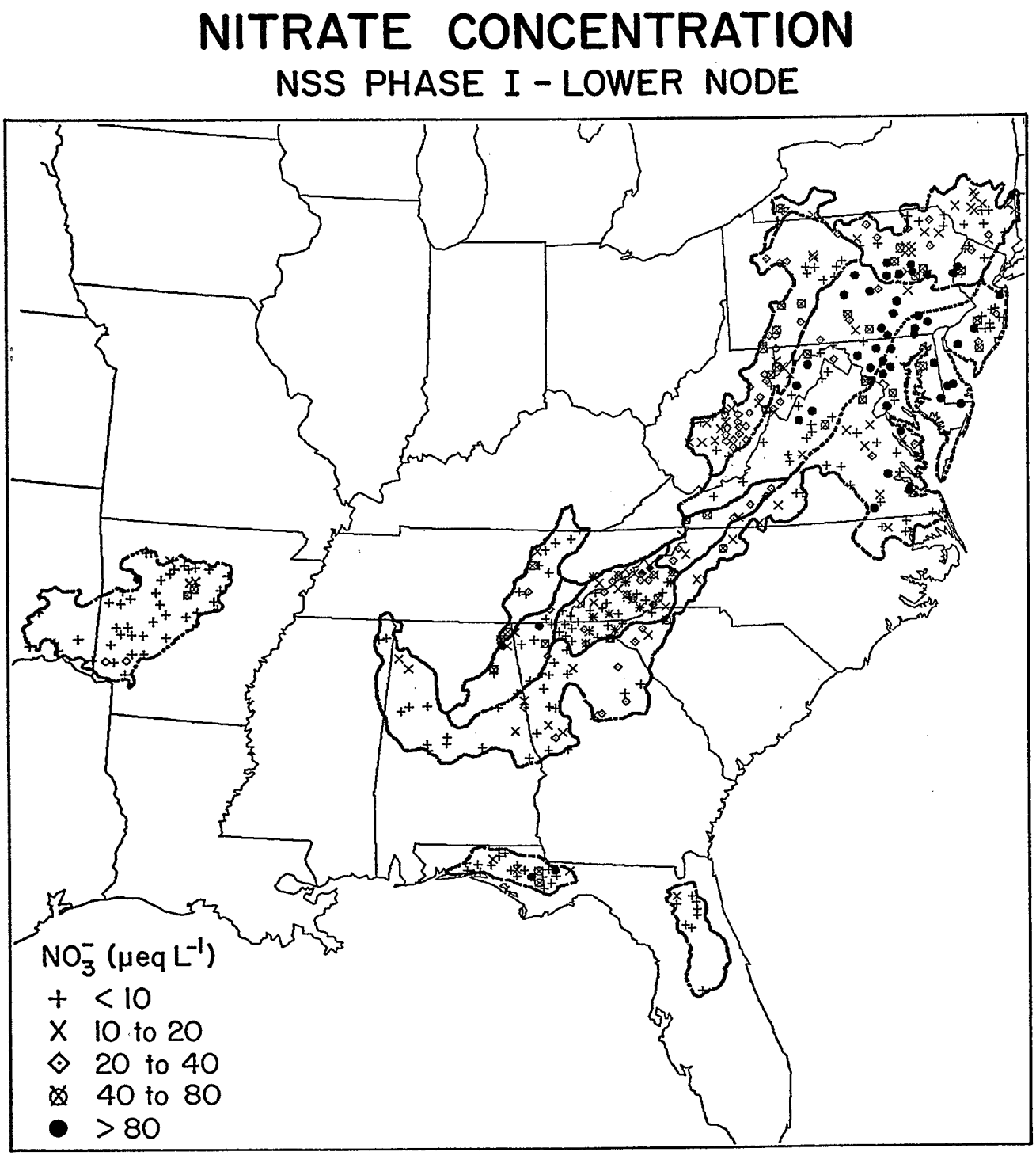


Figure 6-15. Geographic distribution of NSS-I lower node index nitrate concentrations.

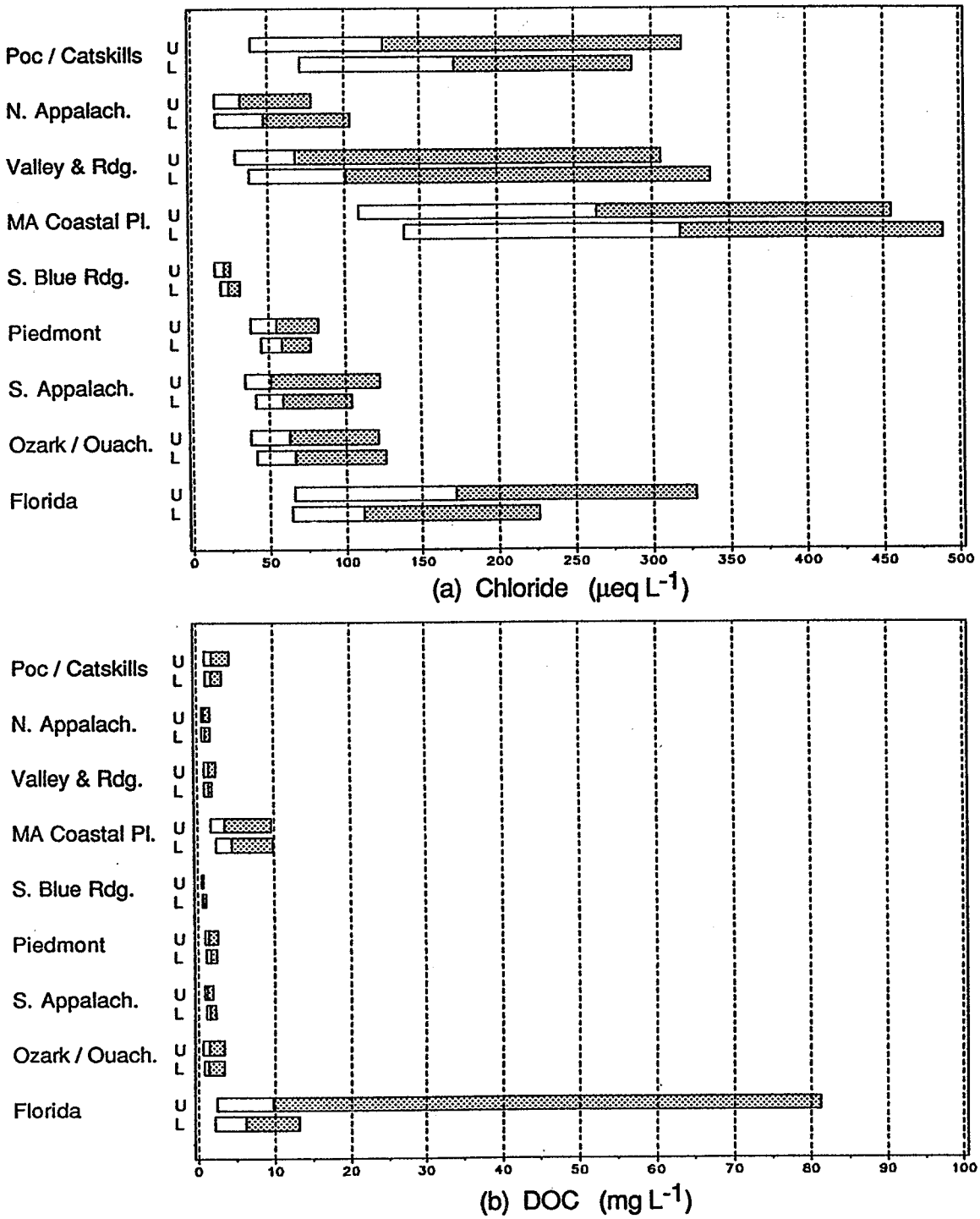


Figure 6-16. **Population frequency distribution (Q_{20}, median, and Q_{80}) of index (a) chloride and (b) DOC concentrations at upper and lower reach nodes in the NSS-I subregions.**

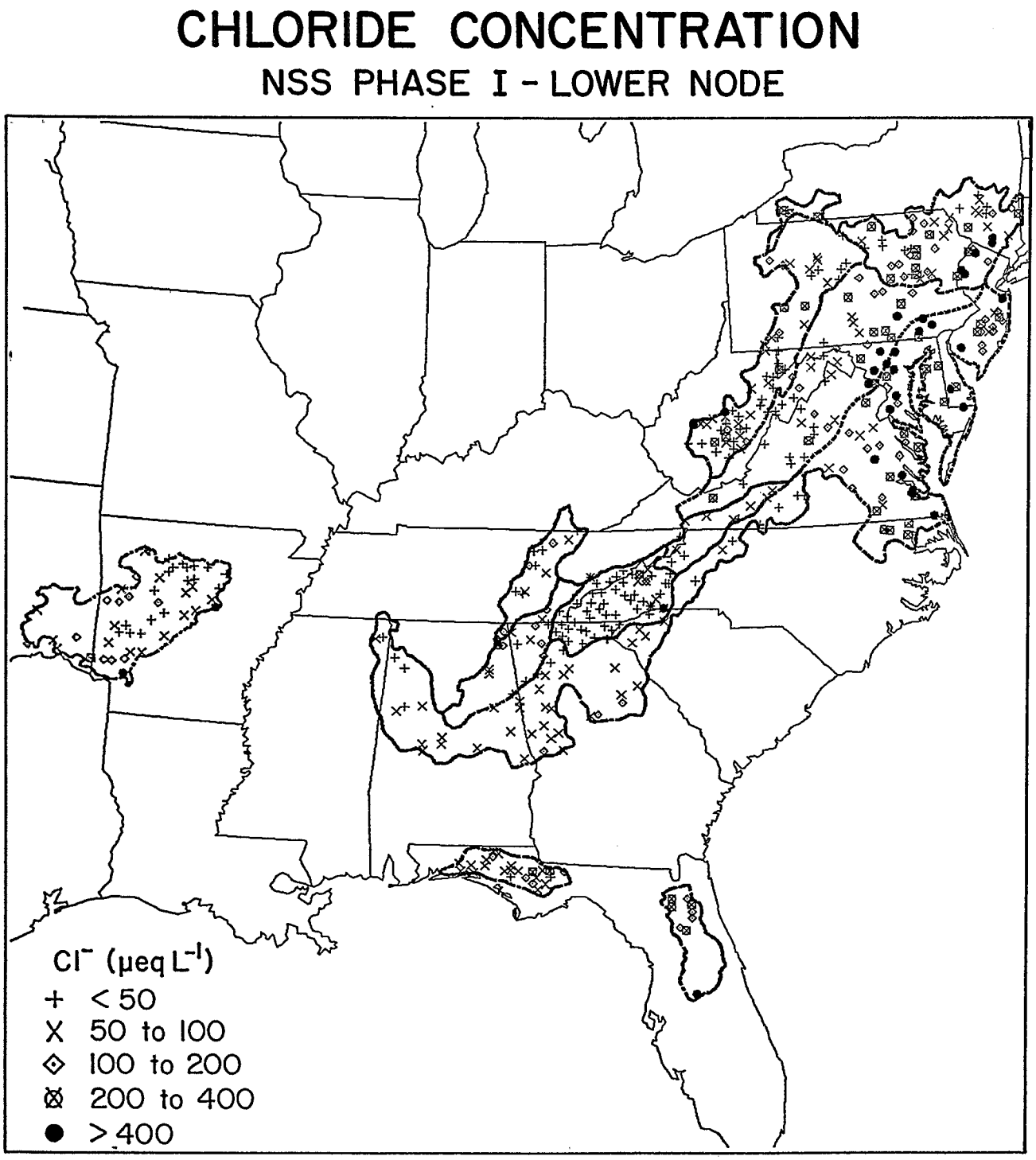


Figure 6-17. Geographic distribution of NSS-I lower node index chloride concentrations.

majority of NSS-I Mid-Atlantic sample streams 60 to 200 km from the Atlantic coast appear, therefore, to be substantially higher than expected. Though in NSS-I sites there was not a close relationship between chloride concentrations and distance from the coast (r = 0.22), the lowest chloride concentrations observed within given ranges of distance decreased logarithmically as distance increased (Figure 6-18). Estimations of sea salt chloride contributions were based upon a curve of concentration versus distance that envelopes these low chloride sites:

$$LOG[Cl] = 3.61 - 1.08(LOG\ Distance\ in\ km)$$

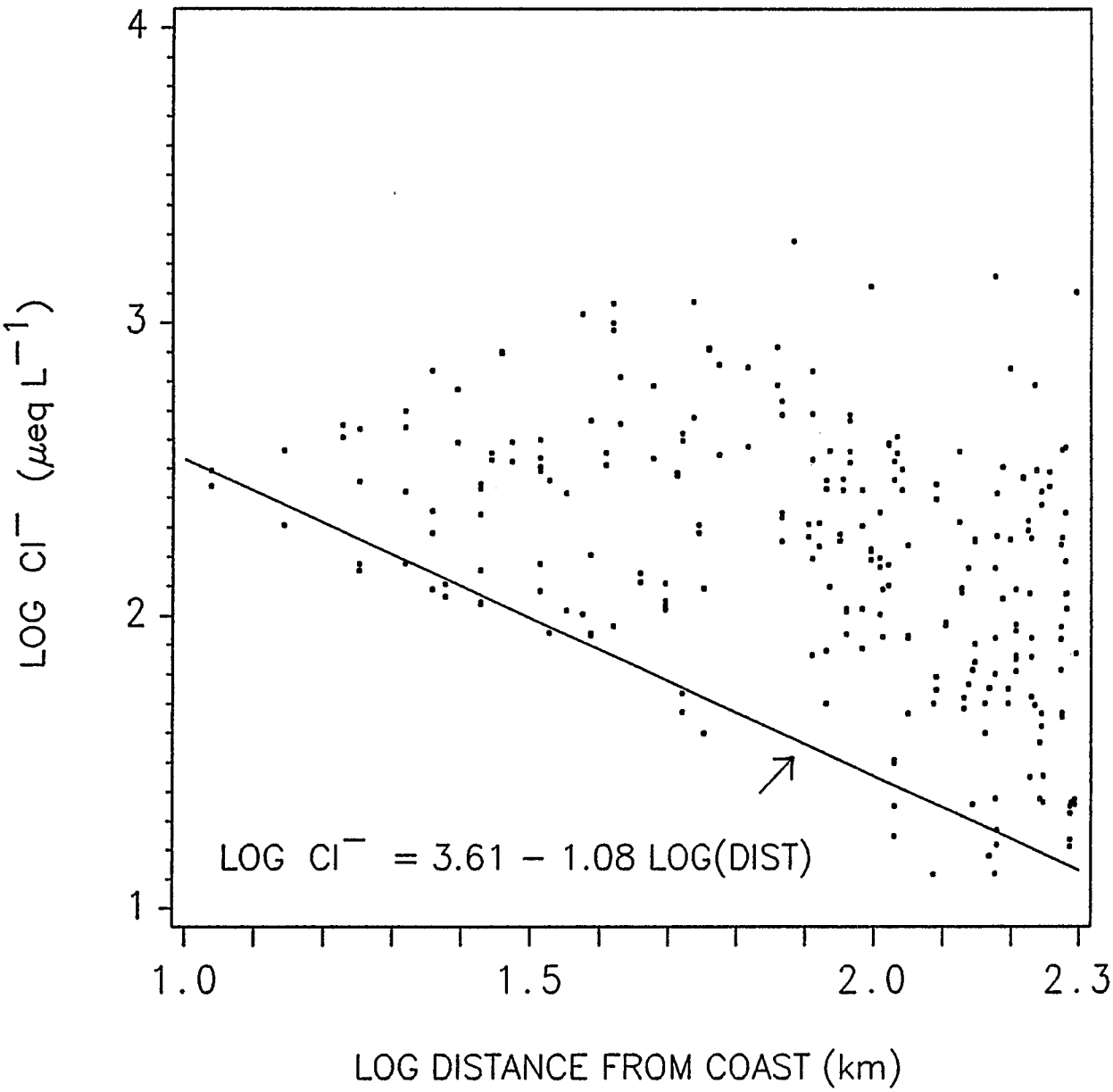
The rationale underlying this approach is that the lowest chloride values along the curve correspond to those streams with the least input of excess chloride from nonmarine sources. This relationship predicts sea water chloride contributions of approximately 160 μeq L^{-1} at 20 km from the coast, decreasing to 60 μeq L^{-1} at 50 km from the coast, 28 μeq L^{-1} at 100 km, and 13 μeq L^{-1} at 200 km. These estimates are about twice those predicted on the basis of the pristine New England lakes relationship of Sullivan et al. (1988a). Though both approaches must be considered crude, higher evapotranspiration rates in the Mid-Atlantic should result in higher stream water chloride concentrations. In addition, it is possible that the more gentle slope of the Mid-Atlantic Coastal Plain presents less impedance to weather systems and sea spray.

The high chloride concentrations observed by the NSS-I in parts of the Mid-Atlantic subregions may be derived from roadsalt, agricultural sources, or groundwater flowing through salt-bearing geologic formations. Some high chloride concentrations (> 100 μeq L^{-1}) were observed in the Ozark/Ouachita subregion (2D); these may be associated with salt-bearing shales of marine origin (Arkansas Geological Survey, 1929) or with agricultural activity in drainages within the Arkansas River Valley.

In Florida (3C), chloride concentrations in peninsula sites were mostly > 100 μeq L^{-1}. Concentrations in panhandle streams, on the other hand, were largely between 50 and 100 μeq L^{-1}. Chloride concentrations in these Florida streams were not highly correlated with distance from the coast, though a reasonable amount of evaporative concentration (3.19; Table 6-7) of precipitation at 12.4 μeq L^{-1} chloride at the Quincy, Florida, NADP site in the panhandle (from NADP, 1987) yields a concentration of 39 μeq L^{-1}. The concentration of chloride in precipitation appears sufficient to account for most of the chloride observed in panhandle streams. The higher chloride concentrations in peninsula streams are probably augmented by another source.

6.3.6 Dissolved Organic Carbon

Population distributions of DOC at the upstream and downstream ends of NSS-I target stream reaches are summarized in Figure 6-16b. The SDL for DOC was 0.45 mg L^{-1} (Table 4-1). Concentrations below this value are not statistically different from field blanks with a concentration of zero. DOC concentrations < 2 mg L^{-1} were not very precise (%RSD = 25%), whereas concentrations > 2 mg L^{-1} had %RSD between 7% and 14%. Population median DOC concentrations exceeded 4 mg L^{-1} only in reaches in the Florida (3C) subregion (6.18 mg L^{-1} at lower, 9.67 mg L^{-1} at upper) and at the lower end of reaches in the Mid-Atlantic Coastal Plain (3B) subregion (4.45 mg L^{-1} at lower, 3.48 mg L^{-1} at upper). All other subregions had medians < 2 mg L^{-1}. Medians in the Southern Blue Ridge (2As) (upstream and downstream ends) and at the upstream ends of the target reaches in the Northern Appalachians (2Cn) were very low (< 1 mg L^{-1}). Twenty percent of the Florida reaches had DOC > 80 mg L^{-1} at their upper nodes. Except for the Poconos/Catskills (1D) (upper and lower 80th percentiles = 3.2 and 4.3 mg L^{-1}),



The NSS-I chloride distance envelope method fits a line through the lowest chloride values (see above figure). The following steps describe the process used to calculate this line.

1. **The X-axis was divided into 10 equal intervals and data were subset to include the 5 lowest values along the Y-axis within each interval.**

2. **A least squares regression line was fit to these points using a modification of trimmed least squares (Ruppert and Carroll, 1980). Values were iteratively removed based on a residual threshold (studentized residual $\geq$ 4). Studentized residual = residual/standard error of residual (SAS, 1985).**

Figure 6-18. NSS-I index chloride concentration versus distance from the ocean in Mid-Atlantic sites within 200 km of the sea coast. The line is an envelope describing the lower bounds of the data.

and the Ozarks/Ouachitas (2D) (upper and lower 80th percentiles = 3.3 mg L^{-1}), all other subregions had 80th percentiles < 2.5 mg L^{-1}. Thus the vast majority of streams in the NSS-I target population had low DOC.

The geographical distribution of DOC at NSS-I sampling sites is mapped in Figure 6-19. High DOC concentrations were observed primarily in subregions 3C and 3B, as illustrated by population distributions in the preceding paragraph. In these two subregions, DOC was positively correlated with color (r = 0.88) and hydrogen ion activity (r = 0.61) and negatively correlated with ANC (r = -0.20). The relationship between DOC and acidity is discussed in Sections 8 and 9, as is the location of acidic streams whose acid-base chemistry is likely to be dominated by organic acids. High DOC stream reaches in subregions 3C and 3B were primarily swampy, lowland coastal streams. These were distributed throughout the Florida (3C) subregion. In the Mid-Atlantic Coastal Plain (3B), however, they were concentrated in the New Jersey Pine Barrens and the lowlands west of Chesapeake Bay.

The elevated DOC concentrations in the Poconos/Catskills subregion (1D) were found in low gradient, headwater reaches flowing through swampy meadows on plateaus subjected to past glaciation. In other inland subregions, high DOC was usually associated with agricultural land use.

6.3.7 Other Chemical Variables

Population medians of other chemical variables at upstream and downstream ends of NSS-I target stream reaches are listed in Table 6-8. Where appropriate, sample concentrations or weighted statistics for these other chemical variables are incorporated into discussions in Sections 8 and 9.

6.4 SMALL STREAMS

ANC tends to decrease with distance upstream within most stream drainages (scatter plots in Figures 6-2 [a - i]), and vulnerability to acid deposition impacts therefore tends to increase. Similarly, pH tends to decrease as one proceeds upstream in a given drainage (scatter plots in Figures 6-3 [a - i]). A plot of ANC versus drainage area for a subset of headwater reaches in the Interior Mid-Atlantic Region (Figure 6-20) shows that acidic (ANC ≤ 0) reaches are largely restricted to drainages of < 20 km^2. (Organic-dominated reaches and reaches impacted by acid mine drainage were excluded from this analysis.) The converse was not true, however, as most reaches with drainages < 20 km^2 were not acidic. The most acidic reaches, nevertheless, were in the smallest drainages. A similar relationship was observed between pH and drainage area (same data set), with all clearwater sample reaches having pH ≤ 5.5 found in drainages < 30 km^2. As with ANC, the lowest index pH values were found in the reaches with the smallest drainage areas. Many reaches with small drainage areas, however, had relatively higher pH, ranging as high as pH 7.

Examination of a subset of small streams sampled by the NSS-I allows some inference about the regional distribution of chemistry in streams smaller than those sampled during the survey. Two-thirds of the stream reaches sampled in the NSS-I were blue-line headwater reaches (Shreve Order = 1) on 1:250,000-scale maps. When taken together, these reaches are representative of a population of streams smaller in watershed area than the total target population. These were almost universally first order (sensu Strahler, 1957, on 1:24,000-scale maps) with subregion median drainage areas of 1.5 to 9.0 km^2 at their downstream nodes and 0.18 to 1.2 km^2 at their upstream nodes. Population distributions of ANC at the upstream sampling nodes of these small headwater streams give some indication of the acid/base status at the downstream ends of a

DISSOLVED ORGANIC CARBON

NSS PHASE I - LOWER NODE

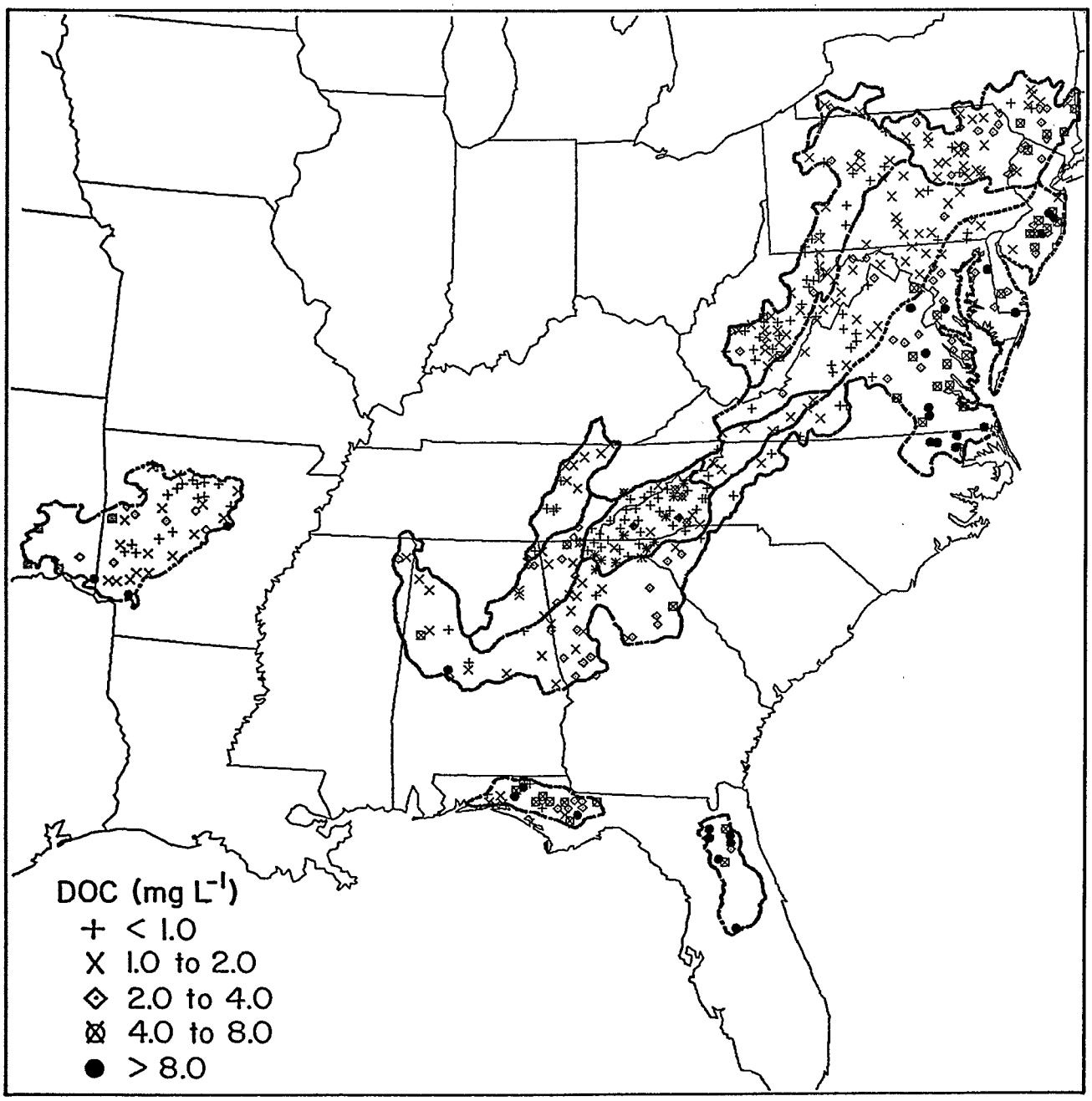


Figure 6-19. Geographic distribution of NSS-I lower node index DOC concentrations.

Table 6-8. Population Medians for Chemical Variables at Upper (U) and Lower (L) Reach Nodes in NSS-I Subregions$

Subregion		NODE	Al-tot (μm)	Al-ext (MIBK) (μm)	Al-ext (PCV) (μm)	Al-org (PCV) (μm)	ANC	BNC	Anion Deficit
1D	(Poconos/Catskills)	L	2.76	0.20	0.60	0.60	257.36	61.91	42.60
		U	3.18	0.17	0.61	0.63	206.94	70.82	38.37
2Cn	(N. Appalachians)	L	3.95	0.27	0.63	0.62	127.58	45.33	31.80
		U	4.14	0.23	0.66	0.58	110.46	49.81	25.02
2Bn	(Valley and Ridge)	L	2.18	0.25	0.52	0.60	395.70	35.73	13.09
		U	2.54	0.33	0.54	0.65	223.39	47.03	10.68
3B	(MA Coastal Plain)	L	4.33	0.86	0.83	0.80	308.72	61.56	33.78
		U	6.72	1.54	1.30	1.08	150.53	92.75	31.67
2As	(S. Blue Ridge)	L	3.01	0.12	#	#	121.62	38.65	31.59
		U	*	0.10	#	#	99.64	*	33.64
3A	(Piedmont)	L	7.82	0.22	0.39	0.40	259.31	45.42	5.55
		U	6.79	0.24	0.37	0.48	201.39	49.10	5.02
2X	(S. Appalachians)	L	4.92	0.11	0.57	0.69	382.63	63.39	45.62
		U	4.66	0.15	0.64	0.65	319.53	65.61	46.65
2D	(Ozarks/Ouachitas)	L	11.12	0.23	0.40	0.49	161.89	40.39	11.46
		U	12.15	0.36	0.40	0.47	122.61	44.72	10.24
3C	(Florida)	L	7.71	1.63	1.95	1.28	33.17	112.15	53.19
		U	7.30	2.26	3.23	1.91	7.65	149.39	77.79

$ All units are in $\mu eq\ L^{-1}$ unless otherwise indicated
* Predicted values for these chemical variables were not calculated for the spring upper nodes in the Southern Blue Ridge.
\# Chemical variable was not measured in the Southern Blue Ridge (Pilot Study).

NOTE: - Many Southern Blue Ridge upper nodes were calculated (see text, Appendix B).
- Florida medians are based on a more restricted sample of low ANC streams and are not directly comparable with other subregions.

Table 6-8. Population Medians for Chemical Variables at Upper (U) and Lower (L) Reach Nodes in NSS-I Subregions$ (Continued)

Subregion		NODE	Ca^{2+}	Cl^-	Color (PCU)	DIC (closed sys.) (mg L^{-1})	DO (mg L^{-1})	DOC (mg L^{-1})	Fe (μm)	F^-
1D	(Poconos/Catskills)	L	450.29	172.56	12.50	3.34	10.67	1.91	0.56	2.47
		U	314.34	125.78	15.00	2.76	10.11	1.96	0.53	2.43
2Cn	(N. Appalachians)	L	311.30	47.31	10.00	1.91	9.97	1.03	0.21	1.87
		U	199.08	32.01	10.00	1.99	9.75	0.88	0.15	1.76
2Bn	(Valley and Ridge)	L	492.10	100.79	12.50	4.95	10.86	1.46	0.34	2.06
		U	298.47	67.92	11.25	3.50	10.55	1.48	0.32	1.91
3B	(MA Coastal Plain)	L	392.37	318.34	42.50	5.33	9.90	4.45	4.33	2.88
		U	302.10	264.43	30.00	5.36	9.34	3.48	3.62	2.65
2As	(S. Blue Ridge)	L	64.72	23.45	13.33	1.61	9.95	0.72	0.49	1.42
		U	44.70	20.66	*	*	*	0.58	0.26	1.36
3A	(Piedmont)	L	131.93	58.55	30.00	3.88	9.20	1.59	1.88	2.15
		U	108.26	55.01	25.00	3.31	9.20	1.36	1.62	1.88
2X	(S. Appalachians)	L	332.21	58.75	15.00	5.03	9.48	1.47	1.14	2.58
		U	312.47	50.91	10.00	4.33	9.43	1.11	1.21	2.07
2D	(Ozarks/Ouachitas)	L	117.84	66.55	20.00	2.41	9.70	1.32	1.51	1.65
		U	91.36	63.05	20.00	3.03	9.26	1.39	1.12	1.57
3C	(Florida)	L	69.95	111.49	83.71	1.84	7.19	6.18	2.96	1.51
		U	37.66	172.13	125.00	3.64	6.66	9.67	4.29	1.00

$ All units are in μeq L^{-1} unless otherwise indicated
* Predicted values for these chemical variables were not calculated for the spring upper nodes in the Southern Blue Ridge.
# Chemical variable was not measured in the Southern Blue Ridge (Pilot Study).

NOTE: - Many Southern Blue Ridge upper nodes were calculated (see text, Appendix B).
- Florida medians are based on a more restricted sample of low ANC streams and are not directly comparable with other subregions.

Table 6-8. Population Medians for Chemical Variables at Upper (U) and Lower (L) Reach Nodes in NSS-I Subregions$ (Continued)

Subregion		NODE	HCO_3^-	K^+	Mg^{2+}	Mn	Na^+	NH_4	NO_3^-
1D	(Poconos/Catskills)	L	199.37	20.99	164.11	0.24	141.72	1.49	19.00
		U	131.54	17.09	137.05	0.49	117.78	1.56	12.30
2Cn	(N. Appalachians)	L	89.21	25.71	157.42	0.42	59.08	1.14	23.07
		U	67.80	21.95	134.43	0.19	42.06	0.99	29.06
2Bn	(Valley and Ridge)	L	366.67	29.75	237.51	0.14	110.56	1.16	36.88
		U	221.28	29.65	184.72	0.19	93.35	1.25	31.19
3B	(MA Coastal Plain)	L	275.86	44.99	223.47	0.90	252.79	1.76	34.45
		U	144.38	35.50	202.22	0.99	203.23	1.47	10.87
2As	(S. Blue Ridge)	L	91.16	14.77	49.39	0.11	59.08	0.86	7.55
		U	74.61	14.23	35.17	0.04	60.51	0.85	6.94
3A	(Piedmont)	L	243.06	28.46	101.49	1.73	126.76	1.37	8.69
		U	183.90	26.36	77.34	1.04	123.26	1.39	8.62
2X	(S. Appalachians)	L	323.73	27.44	146.26	0.50	80.78	2.03	10.97
		U	296.50	22.34	122.90	0.37	71.47	1.33	15.87
2D	(Ozarks/Ouachitas)	L	150.71	19.96	100.64	0.10	95.33	1.06	1.50
		U	126.87	19.28	89.93	0.09	83.29	1.02	1.01
3C	(Florida)	L	17.57	4.72	37.46	0.10	93.53	1.20	1.25
		U	6.08	2.93	51.42	0.11	350.54	1.01	0.42

$ All units are in μeq L^{-1} unless otherwise indicated
* Predicted values for these chemical variables were not calculated for the spring upper nodes in the Southern Blue Ridge.
# Chemical variable was not measured in the Southern Blue Ridge (Pilot Study).

NOTE: - Many Southern Blue Ridge upper nodes were calculated (see text, Appendix B).
- Florida medians are based on a more restricted sample of low ANC streams and are not directly comparable with other subregions.

Table 6-8. Population Medians for Chemical Variables at Upper (U) and Lower (L) Reach Nodes in NSS-I Subregions$ (Continued)

Subregion		NODE	pH	P-tot diss. (μm)	SiO_2 (μm)	Base Cat.	SO_4^{2-}	spec. cond. (μS cm^{-1})	Temp. (°C)	Turb. (NTU)
1D	(Poconos/Catskills)	L	7.30	0.20	66.51	774.63	238.19	88.22	11.56	1.34
		U	6.98	0.17	52.65	654.86	213.79	76.43	12.50	1.39
2Cn	(N. Appalachians)	L	6.91	0.09	68.83	603.72	219.99	68.69	11.78	1.90
		U	6.64	0.09	69.24	445.29	208.86	53.62	11.60	1.65
2Bn	(Valley and Ridge)	L	7.41	0.17	111.02	965.29	185.12	104.22	10.70	1.85
		U	7.06	0.19	99.99	826.74	182.42	87.41	10.59	1.86
3B	(MA Coastal Plain)	L	6.73	0.24	145.73	970.08	150.53	107.00	12.95	3.94
		U	6.01	0.19	130.16	871.70	125.08	93.82	12.75	3.26
2As	(S. Blue Ridge)	L	7.03	#	138.45	188.22	22.92	20.65	12.29	2.41
		U	6.99	#	144.92	164.32	20.69	15.87	*	*
3A	(Piedmont)	L	6.95	0.11	214.23	424.13	38.26	39.47	15.34	11.17
		U	6.80	0.09	200.70	349.46	37.47	38.70	15.02	8.77
2X	(S. Appalachians)	L	7.36	0.16	95.15	634.46	70.57	70.91	15.02	3.32
		U	7.33	0.19	95.15	592.87	61.01	67.50	14.39	2.69
2D	(Ozarks/Ouachitas)	L	6.83	0.10	116.78	308.86	64.53	32.50	14.80	8.23
		U	6.63	0.12	130.62	317.27	69.92	33.57	15.02	9.31
3C	(Florida)	L	5.62	0.27	57.61	283.97	16.12	34.59	20.02	1.62
		U	5.48	0.21	65.35	303.95	10.00	39.10	19.46	2.63

$ All units are in μeq L^{-1} unless otherwise indicated
* Predicted values for these chemical variables were not calculated for the spring upper nodes in the Southern Blue Ridge.
# Chemical variable was not measured in the Southern Blue Ridge (Pilot Study).

NOTE: - Many Southern Blue Ridge upper nodes were calculated (see text, Appendix B).
- Florida medians are based on a more restricted sample of low ANC streams and are not directly comparable with other subregions.

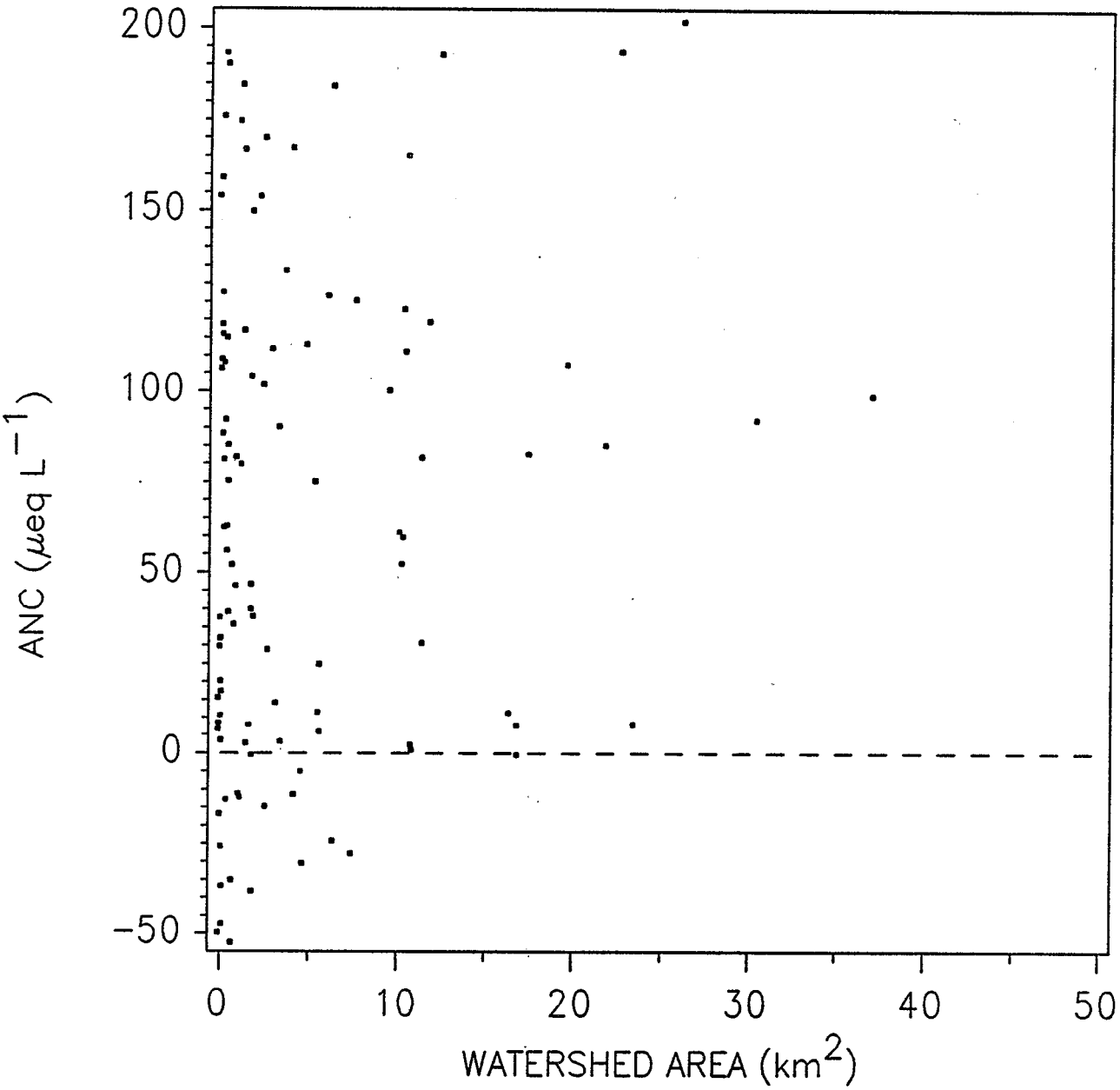


Figure 6-20. NSS-I spring index ANC (μeq L^{-1}) vs. watershed area (km^2) in headwater reaches in the Interior Mid-Atlantic.

population of small streams with substantially smaller watershed areas than those of the NSS-I target population as a whole (Figure 6-21). Distributions of chemistry for this population can be interpreted as a description of water quality measured where stream water enters the blue-line network of streams on 1:250,000-scale maps.

The influence of map scale on the interpretation of headwater distribution estimates warrants consideration. On 1:250,000-scale maps, the mainstem blue lines extend upstream nearly to the limits of perennial flow, whereas lateral tributaries equal in size to the upstream nodes of blue-line headwaters are generally not shown. Thus the upstream nodes of headwater streams very nearly represent the smallest streams that flow perennially, but sample reaches drawn from the 1:250,000-scale maps probably greatly underestimate the total number of these very small streams (on the ground or on 1:24,000-scale maps) within the total population of all streams. However, because mainstem headwaters are likely to be at least as acidic as lateral tributaries, population distribution estimates describing chemical characteristics <u>within</u> this population of smaller streams probably do not underestimate the status and extent of acidic and low ANC conditions on a <u>proportionate</u> basis (e.g., "x percent of these reaches are acidic"). But because of the many equal-sized lateral tributaries that may not be represented as blue lines on 1:250,000-scale maps, the actual <u>number</u> or combined length of these small streams may be underestimated from the sample and may be very large.

For the reasons stated in the preceding paragraph, only percentage distributions for the headwater stream population have been presented. Figures 6-22 and 6-23 compare the population distribution estimates for ANC at the upstream and downstream reach nodes of blue-line headwater stream reaches with the upstream and downstream nodes of the NSS-I target population as a whole. In all NSS-I subregions containing acidic reaches, except the Mid-Atlantic Coastal Plain (3B), the percentages of acidic reaches in the headwater reach subpopulation were greater than those for the NSS-I target population as a whole (Figure 6-23).

Stream reaches upstream of these smallest streams sampled during the NSS-I (i.e., upstream of blue-line representation on 1:250,000-scale maps) probably do not themselves contain significant amounts of economically or recreationally important fish habitat. However, the impact of acidification of these small headwaters on downstream fish habitat, through changes in rates of headwater detritus processing (Allard and Moreau, 1986; Chamier, 1987; Mulholland et al., 1987), nutrient cycling (Elwood and Mulholland, in review) and contribution of drifting aquatic macroinvertebrates has not been extensively studied and is largely unknown. Further study is underway, aimed at quantifying the number and length of the population of lateral tributary reaches not represented as blue lines on 1:250,000-scale maps.

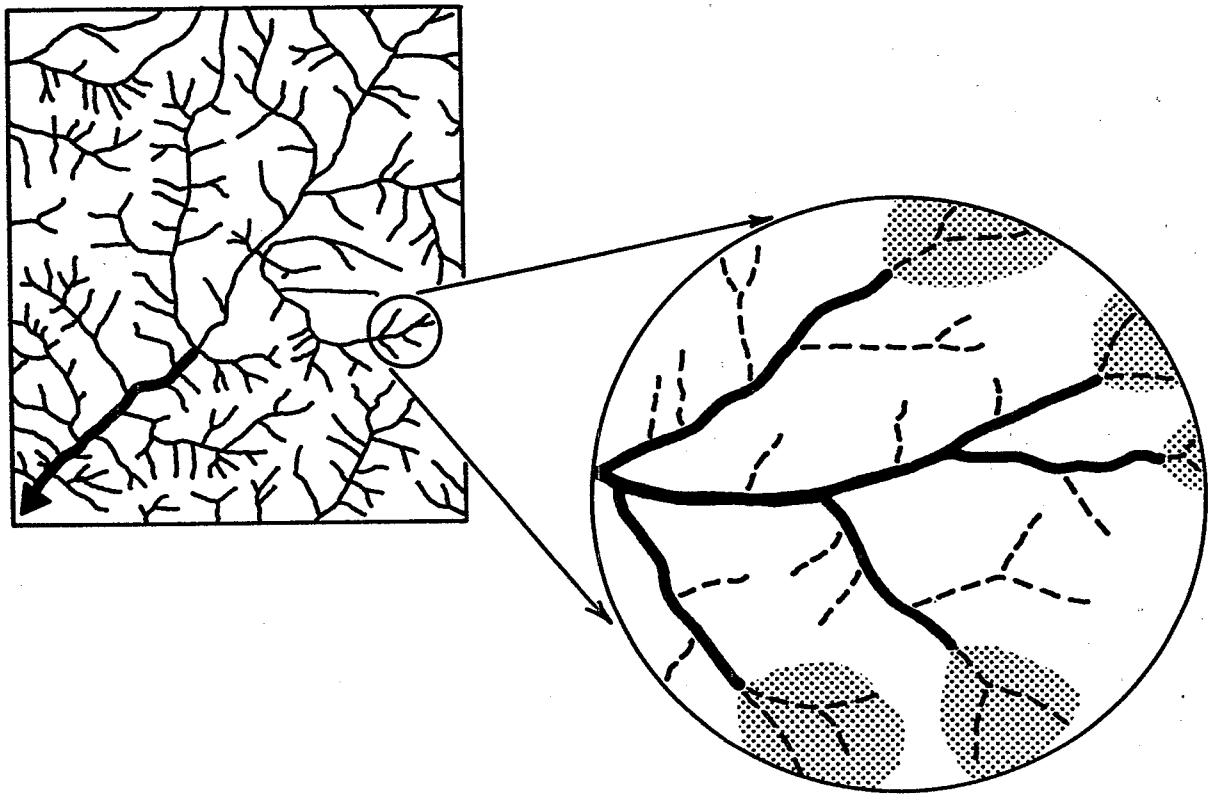
6.5 UNCERTAINTY IN REGIONAL ESTIMATES

Several areas of uncertainty regarding NSS-I population estimates are quantified or explored in this report. The primary areas of uncertainty, along with the report sections where they are addressed, are as follows:

1. The variance resulting from the spatial sampling procedure, including the number of sample reaches. (Section 2.4, confidence bounds on CDF figures, and standard errors in tables in Appendices C and D.)

2. Uncertainty associated with the definition and identification of the target resource. What are the physical characteristics of NSS-I target reaches, and are these streams the appropriate size and type for study? (Sections 2.3, 5.2, 5.4, and 6.4.)

Blue-line network on 1:250,000-scale map. The large stream (heavy line) is excluded from the population of interest because its drainage area exceeds 155 km^2.



Enlargement: Broken lines represent small streams not sampled by NSS-I, but drawn on 1:24,000-scale maps, including a subset flowing into extreme upstream ends of blue-line target streams.

Figure 6-21. The population of small streams upstream of NSS-I blue-line headwater reaches.

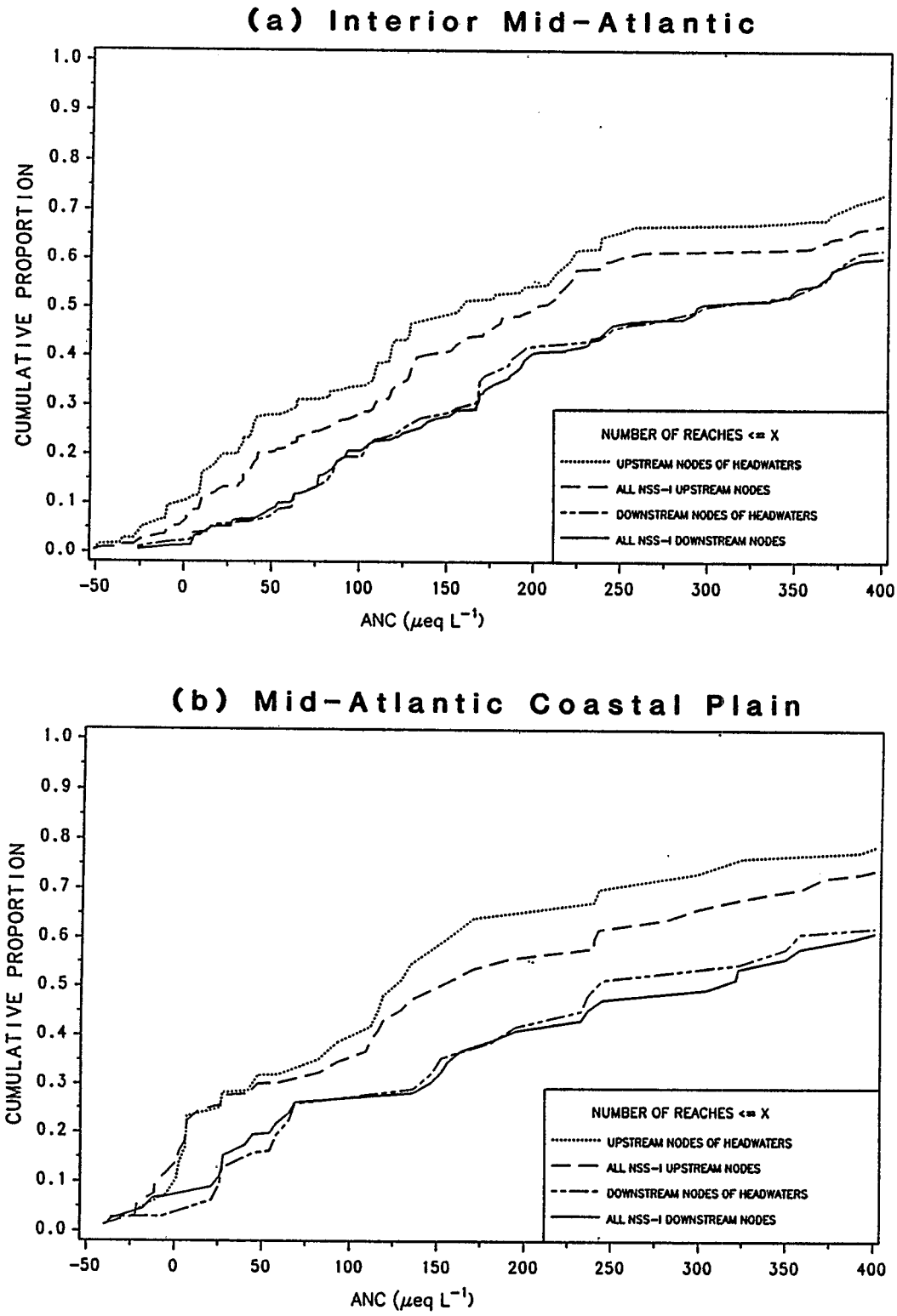


Figure 6-22. Population distributions comparing ANC in the NSS-I target population with ANC in a subpopulation including only headwater reaches: (a) Interior Mid-Atlantic subregions and (b) the Mid-Atlantic Coastal Plain.

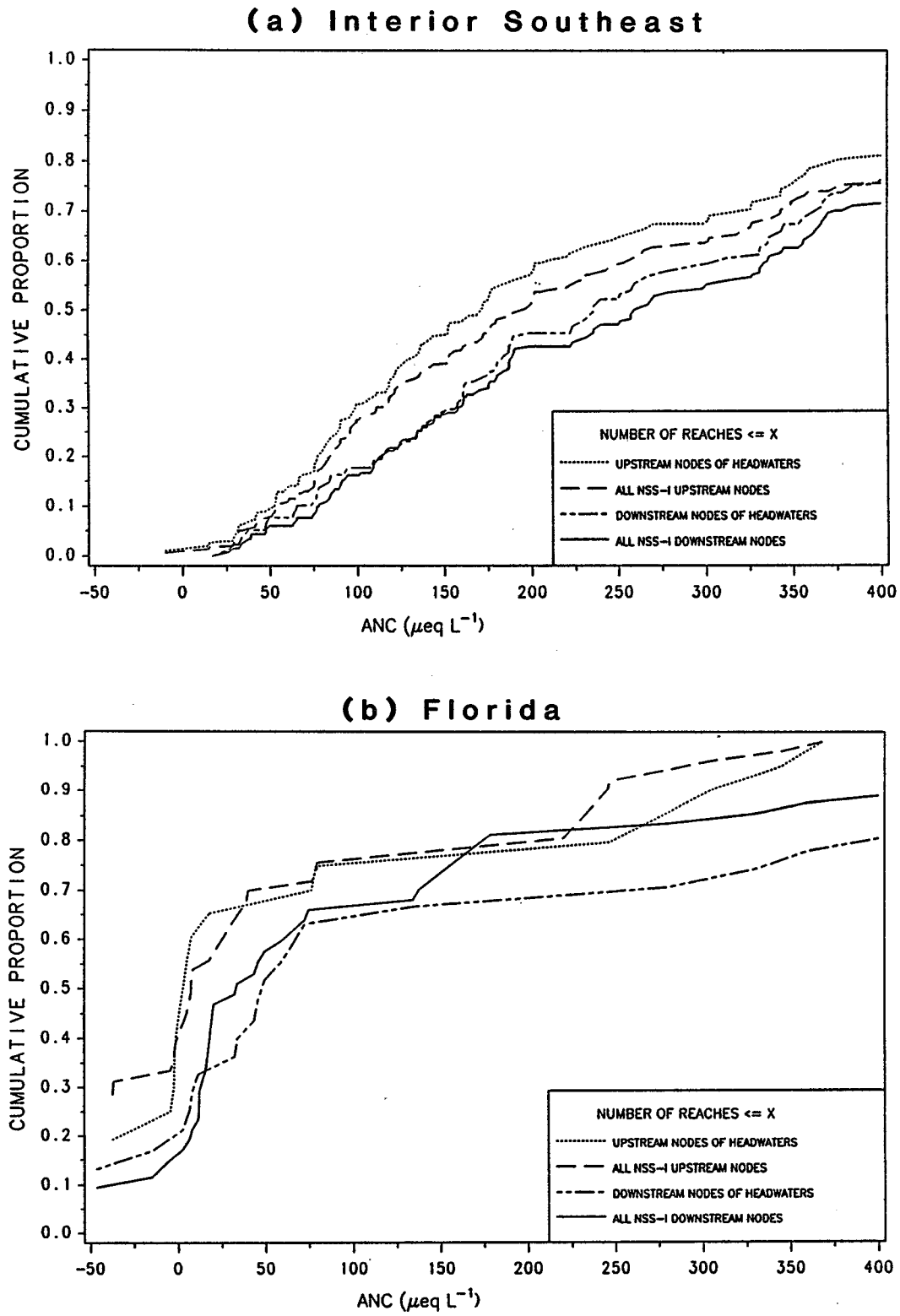


Figure 6-23. Population distributions comparing ANC in the NSS-I target population with ANC in a subpopulation including only headwater reaches: (a) Interior Southeast subregions and (b) Florida subregion.

3. Uncertainty regarding the chemical status of streams smaller than those targetted by the NSS-I. Are reaches upstream of the NSS-I target population more acidic than those of the target population? (Section 6.4.)

4. Uncertainty regarding the factors that control stream chemistry. In particular, what are the probable sources of acidity in target streams? (Section 8 and 9.)

5. Applicability of the Chemical Index for Streams.

   a. The survey year 1986 was a dry year, particularly in the Southeast. Would subregional estimates of the number of reaches that are acidic or have low ANC during spring baseflow change substantially, had they been measured in a more typical water year? (Section 7.2.)

   b. Are there times of the year when non-episodic pH or ANC would be substantially or consistently lower than in the spring baseflow period? (Section 7.3.)

   c. Does the variability of baseflow chemistry within the spring index period preclude calculation of stable population distribution estimates and site classifications. (Section 7.4.)

   d. Do estimates of sampling system detection limit, analytical accuracy, and sampling/analytical precision significantly affect confidence bounds on NSS-I regional population estimates? (Sections 4 and 6.)

SECTION 7
TEMPORAL VARIABILITY IN BASEFLOW CHEMISTRY

7.1 OVERVIEW

The NSS-I population estimates in this report and in its data compendium (Volume II) are based on one or two samples taken during spring baseflow conditions in 1986, except for the Southern Blue Ridge, where baseflow chemistry was indexed by three spring samples in 1985. In order to assess the uncertainty in the population estimates caused by this limited temporal sampling, we need to understand the temporal variability in NSS-I streams. The concept of temporal variability can be broken down into three components in order to answer three major questions about the accuracy and robustness of the NSS-I population estimates:

1. Among-year variability. Was 1986 an atypical year? Would subregional estimates of the number of acidic or low ANC reaches during spring baseflow differ substantially had measurements been made in a more typical year?

2. Among-season variability. Are there times of the year when non-episodic pH or ANC would be substantially or consistently lower than in the spring baseflow period? Was spring the right season in which to conduct the NSS-I?

3. Within-season variability. Does the variability of baseflow chemistry within the spring index period preclude calculation of stable population distribution estimates and site classifications?

These questions are addressed in the next three parts of this section, drawing on NSS-I data (special interest site [Section 2.6] and regular samples) and intensive long-term monitoring data from several of these streams provided by other researchers.

The NSS-I was not designed to quantify temporal variability in streams, but to provide relatively stable index chemical descriptions that can be related to other characteristics of these streams (e.g., basin geochemistry, episodic variability). Studies of seasonal trends and spring seasonal variability in long-term and intensive data sets collected at special interest sites within the NSS-I subregions will be an important aspect of additional research. An eventual goal is to define a stochastic model of seasonal and episodic chemical change in these streams. Using the NSS-I index chemistry, precipitation data, mapped hydrologic data, and classification of synoptic and intensive study sites, researchers hope to be able to predict the temporal patterns in concentrations of important chemical constituents in baseflow (and possibly episodes). For the present, however, it is important to use available information on temporal variability to evaluate potential inaccuracies in the population estimates provided in this report.

7.2 AMONG-YEAR VARIABILITY

The NSS-I was designed to make population estimates of streamwater baseflow chemistry during the spring of 1986 (1985 for the Southern Blue Ridge). It was not designed to predict or examine long-term trends in chemical data. Nevertheless, it is important to know whether stream chemistry during the 1986 spring index period was atypical in comparison to other years,

because nearly all of the estimates in this report are based on 1986 spring index data. Of potentially major concern was the fact that 1986 was a relatively dry year in most of the NSS-I subregions.

In order to address the question of annual variability, NSS-I special interest site data (Section 2.6) were compared to long-term data gathered by other researchers at the same sites. Chemical data from one such site, Fernow Control (Section 2, Figure 2-1 and Table 2-4; Section 9, Table 9-12), a stream in the forested Allegheny Plateau (subregion 2Cn, the Northern Appalachians) of West Virginia, is used to illustrate the annual changes in spring index chemistry. The data from Fernow Control were collected and kindly provided by the USFS Timber and Watershed Laboratory in Parsons, West Virginia (Dr. David Helvey, principal investigator). Annual spring index period chemical statistics (20th percentile, median, and 80th percentile) in Fernow Control were calculated for data collected between April 1 and May 15 (the spring index period in this part of West Virginia) of each year. The data for each year's index period includes from 3 to 12 separate samples. No attempt was made to remove hydrologic episodes from the data.

The spring index values in Fernow Control since 1980 for pH (Figure 7-1), alkalinity (Figure 7-2), sulfate (Figure 7-3), and sum of base cations (Figure 7-4) were plotted, along with the two NSS-I spring index samples collected in 1986. In all four chemical variables, spring index period data in 1986 were similar to spring index period data collected in other years in the 1980s. The data exhibit a cyclical pattern, but the 1986 values do not seem atypical. Using the Timber and Watershed Laboratory data, there was no significant difference between the mean alkalinity during the spring index periods of 1986 and the mean alkalinity during the composite spring index periods of 1980-1985 and 1987 ($t = -1.26$; $p = 0.22$). Similarly, there was no statistically significant difference in mean H^+ concentrations ($t = 0.92$; $p = 0.36$) and in sum of base cations ($t = 1.00$; $p = 0.32$) between 1986 and the other years. There was a significant difference in mean sulfate concentrations between 1986 and the other years ($t = 3.22$; $p = 0.003$). The 1986 mean value was 10 μeq L^{-1} higher than the mean for the other years.

Sulfate, base cation, and pH data collected in the NSS-I were in good agreement with data collected by the Timber and Watershed Laboratory. One of the NSS-I alkalinity data points, however, was approximately 10 μeq L^{-1} higher than 80% of the Fernow Control spring index period alkalinity data. Note, first, that the standard deviation of duplicate ANC measurements by the NSS-I within this ANC range is 7.8 μeq L^{-1} (Section 4, Table 4-3), and second, that two different methods were used (Gran's titrations in NSS-I and double endpoint titrations by the Timber and Watershed Laboratory). While the NSS-I index pH (6.05) was larger than the 1986 Timber and Watershed Laboratory pH measurements (median = 5.99; 80th percentile = 6.01), these pH differences are well within the precision of the method, especially in light of the fact that the measurements were made with different equipment and transport conditions.

In order to estimate between-year chemical changes on a broad regional scale, 1986 NSS-I index data were compared to data collected in an acid streams reconnaissance, conducted by EPA from April to June in 1987 to revisit stream reaches where acidic nodes had been observed in 1986. Longitudinal transects of pH and conductivity were collected for 26 stream reaches in the Mid-Atlantic Region. By comparing the 1986 spring index pH and conductivity to the 1987 pH and conductivity, an estimate of among-year variability on a regional scale can be made. Resampled streams with evidence of acid mine drainage (subsection 9.3.1) were not included in this comparison because chemical concentrations in acid mine drainage streams were highly variable due to a strong dependence on stream discharge. A good relationship for pH ($r^2 = 0.836$) exists between streams sampled in 1987 and 1986 (Figure 7-5). The slope of the regression line was 0.914 (SE = 0.071) indicating a one-to-one correspondence in pH between the two years. The root mean square error of the relationship was 0.47. There was also a strong

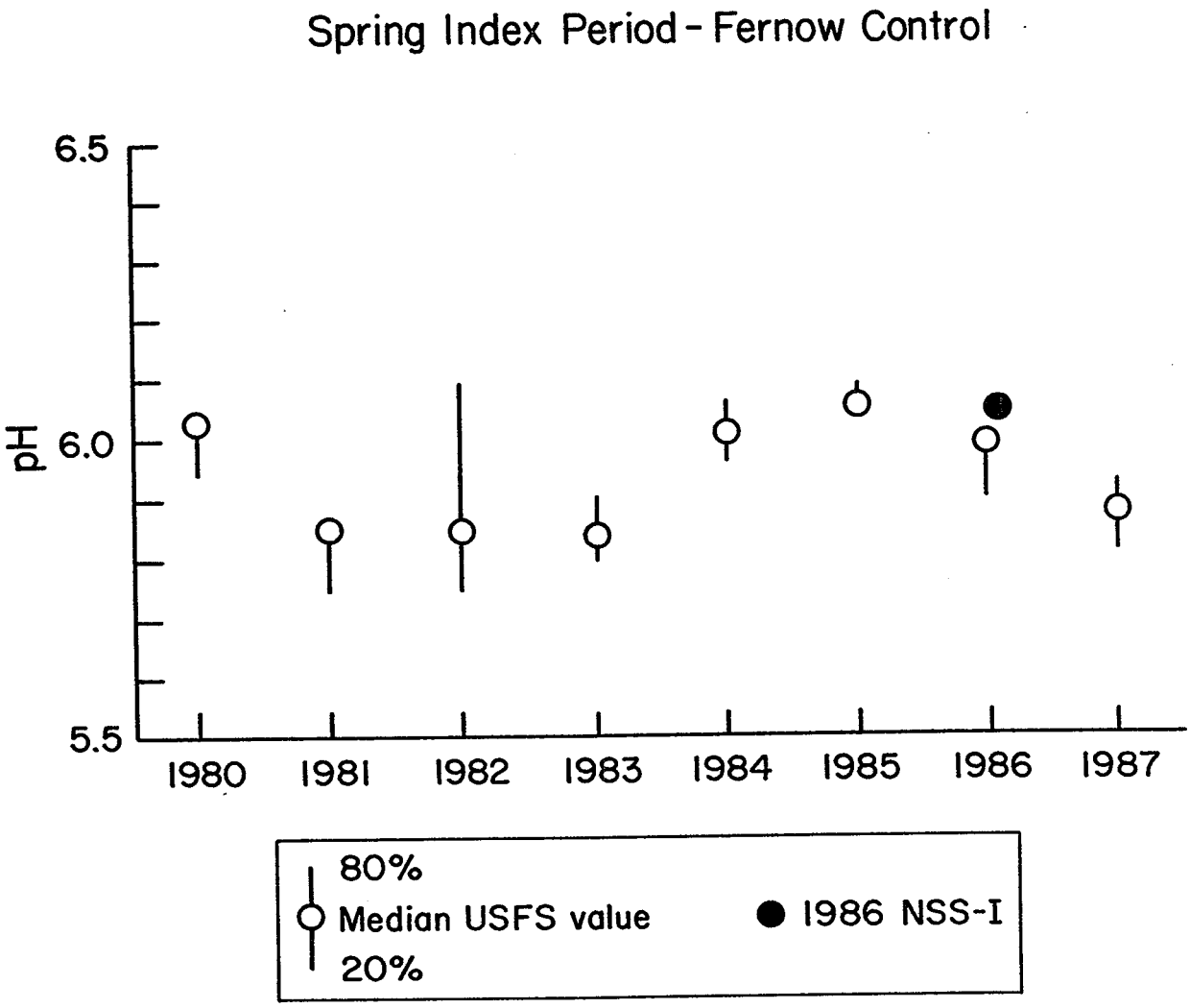


Figure 7-1. pH in Fernow Control during the spring index period from 1980 to 1987. Data were provided by the USFS, Timber and Watershed Laboratory in Parsons, West Virginia. The pH range between the two NSS-I observations was smaller than the data symbol.

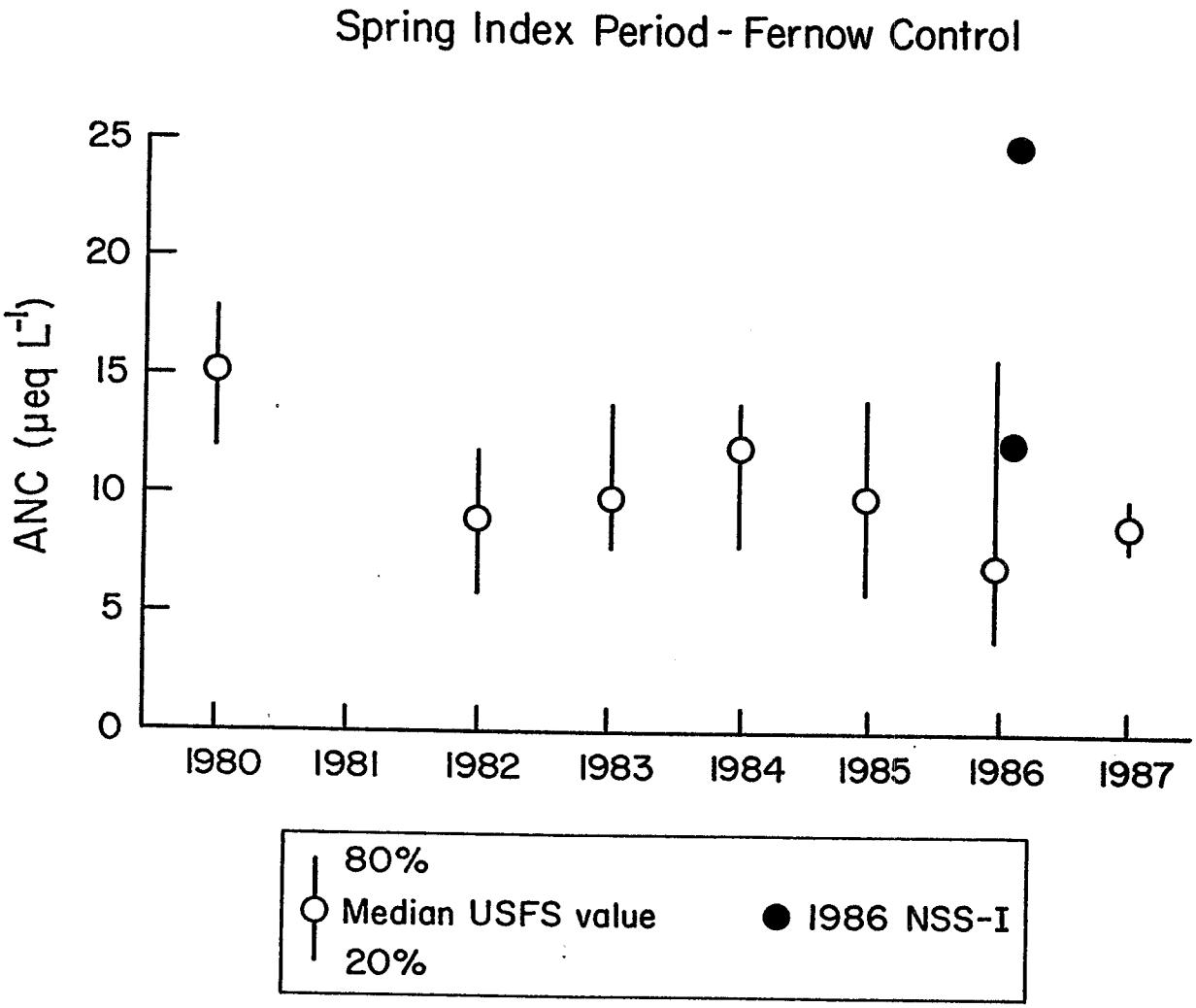


Figure 7-2. ANC (μeq L^{-1}) in Fernow Control during the spring index period from 1980 to 1987. Data were provided by the USFS Timber and Watershed Laboratory in Parsons, West Virginia. ANC was determined using a double endpoint titration by the USFS and a Gran's titration in the NSS-I.

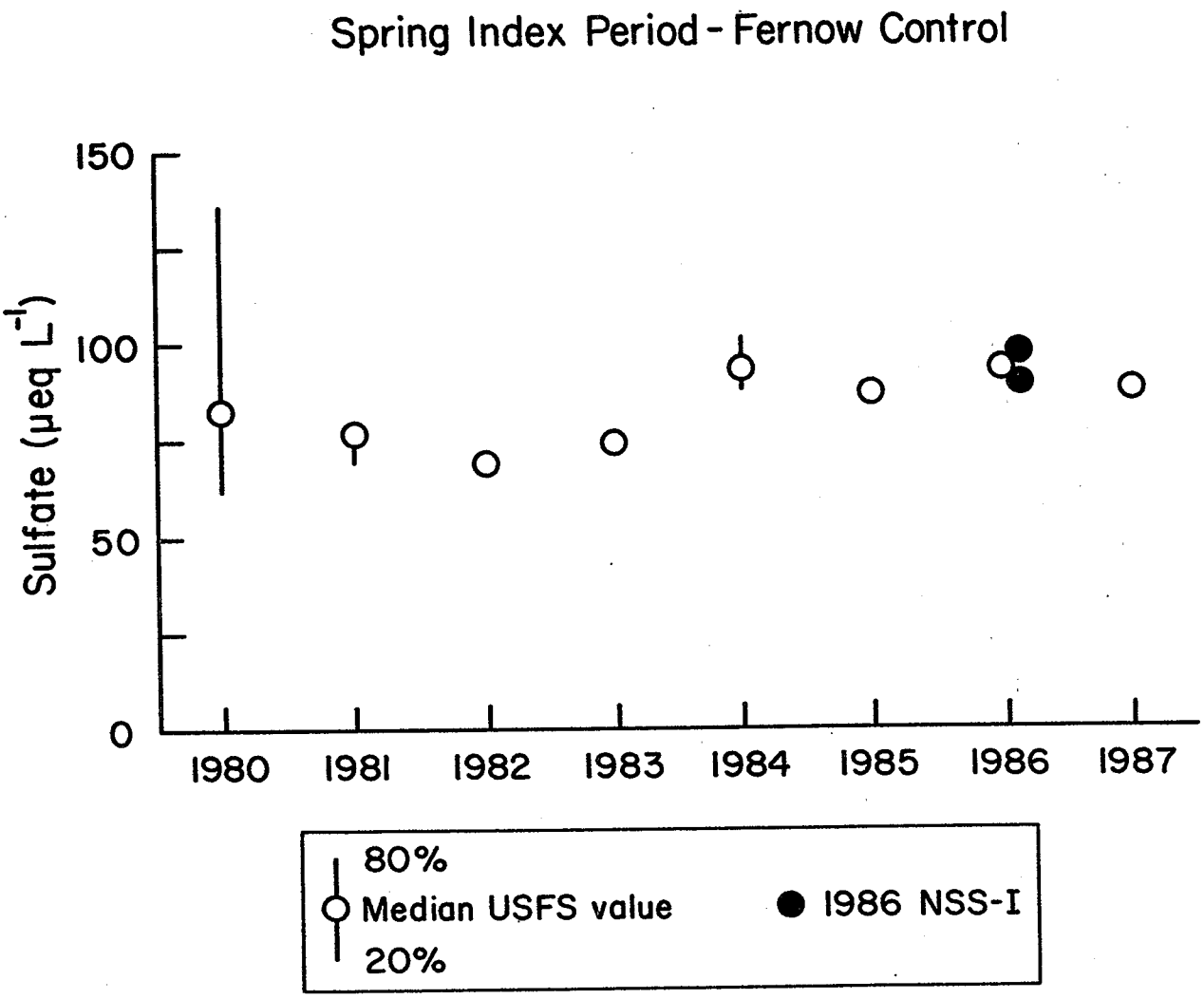


Figure 7-3. Sulfate concentration (μeq L^{-1}) in Fernow Control during the spring index period from 1980 to 1987. Data were provided by the USFS Timber and Watershed Laboratory in Parsons, West Virginia.

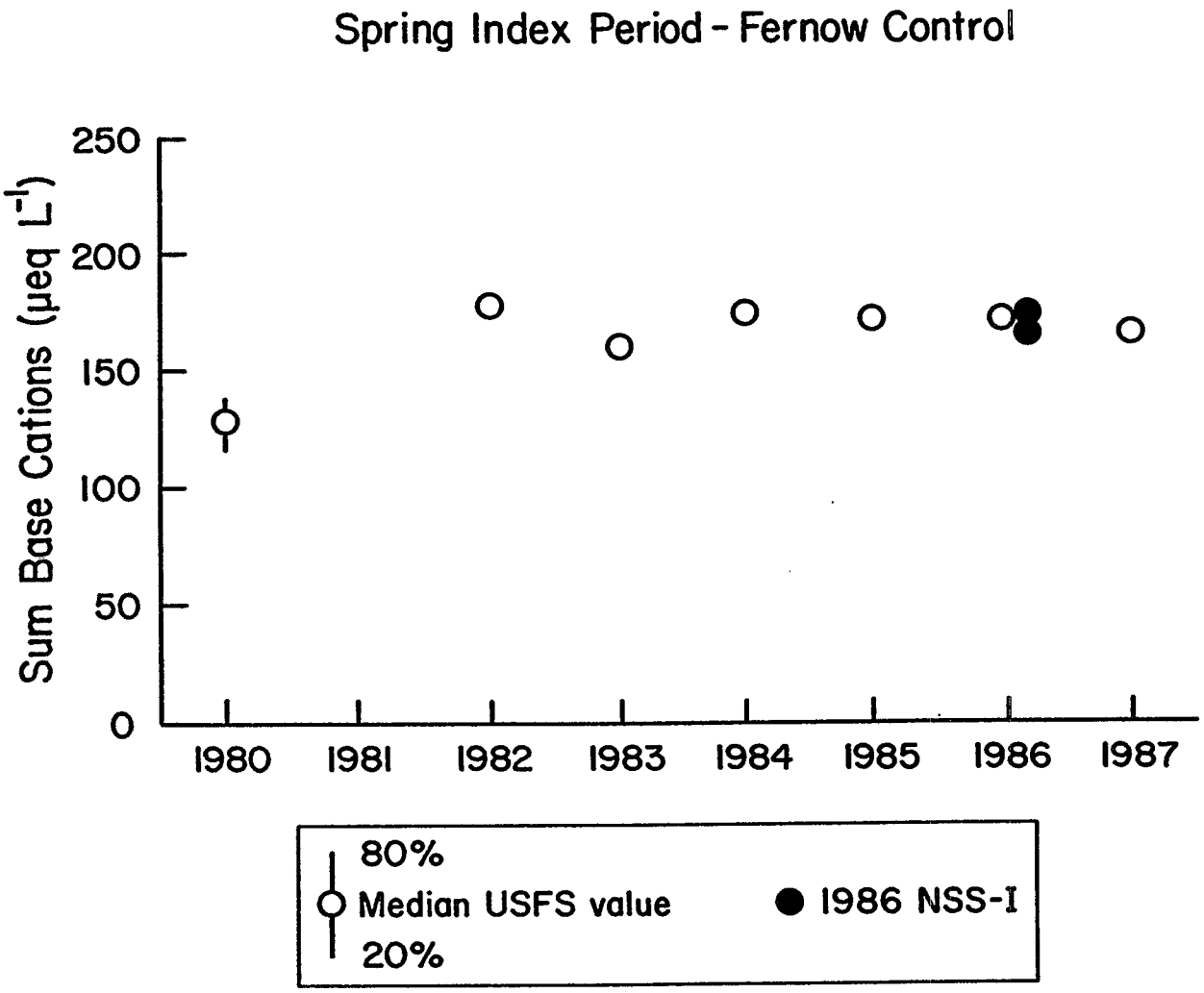


Figure 7-4. Sum of base cations (μeq L^{-1}) in Fernow Control during the spring index period from 1980 to 1987. Data were provided by the USFS Timber and Watershed Laboratory in Parsons, West Virginia.

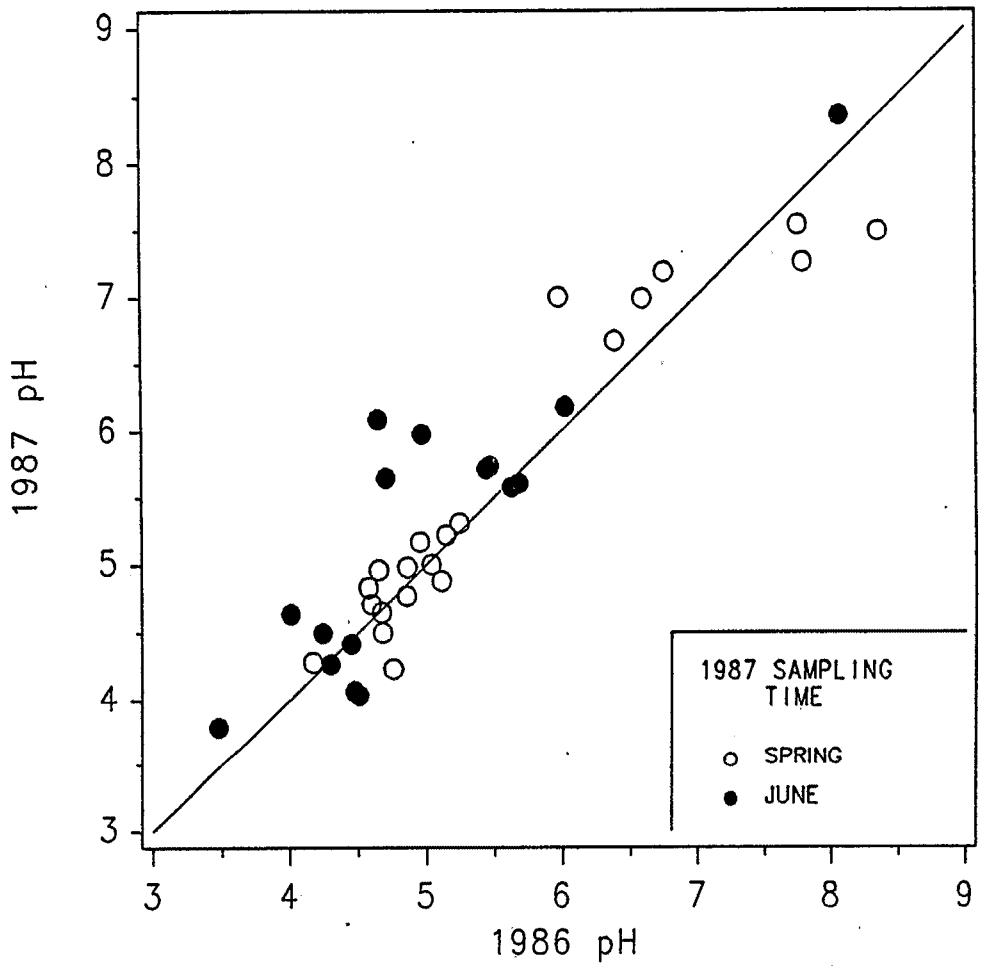


Figure 7-5. The pH observed in 1987 during the acid stream reconnaissance versus the 1986 NSS-I spring index field pH value in 37 mid-Atlantic stream nodes. The line is y = x. The best-fit regression line was 1987 pH = 0.914 (1986 pH) + 0.616, (r^2 = 0.836).

relationship ($r^2 = 0.881$; root mean square error = 25.9 $\mu S\ cm^{-1}$) between conductivity measured in 1986 and 1987 (Figure 7-6). Except for two high conductivity outliers, there was a strong one-to-one correspondence between the conductivities measured in 1986 and 1987.

As we would expect, there are differences in spring index period water chemistry between years. Although there is a certain amount of annual fluctuation, there does not appear to be any reason, based on the Mid-Atlantic acid streams reconnaissance data and Fernow Control data, to assume that the index chemistry in 1986 was atypical compared to recent years, despite the drought conditions. Thus in the Mid-Atlantic, in terms of annual variation, the NSS-I index data appear to be representative of stream water chemistry. Because the 1986 drought was more severe in the southeastern United States, further assessment of Southeast special interest site data needs to be done.

7.3 AMONG-SEASON VARIABILITY - THE INDEX TIME PERIOD

The sampling window chosen for indexing chemical characteristics in NSS-I sample reaches was the spring period between March 15 and May 15. The reasons for sampling baseflow chemistry during this season are discussed in detail in Section 2.5. The choice was made after consultation with hydrologists, biochemists, and fishery experts from Pennsylvania, Virginia, North Carolina, Florida, and Arkansas (U.S. EPA, 1985) and was supported by the results of recent studies of seasonal and short-term chemical variability in streams (Murdoch, 1986; Witt and Barker, 1986; Olem, 1986; Nix et al., 1986). These studies showed that minimum flow-weighted pH, ANC, and base cation concentrations occured during the spring at almost all sites (Ford et al., 1986). Sites with minima at other times of the year had winter minima and spring values nearly as low.

To illustrate the seasonal changes in streamwater baseflow chemistry, data were obtained from six streams studied during the EPA's Long Term Monitoring (LTM) Project (Newell et al., 1987) that were also NSS-I special interest sites (Section 2, Table 2-4 and Figure 2-1; Section 9, Table 9-12). Data in these streams were collected from fall 1984 to winter 1987. Three of these streams are in the Catskill Mountains of southeastern New York (Biscuit Brook, East Branch Neversink River, and High Falls Brook; Murdoch, 1986) and the other three streams are in the Laurel Hills of southwestern Pennsylvania (North Fork Bens Creek, North Branch Quemahoning, and Cole Run; Witt and Barker, 1986). Before using the data, samples suspected of having been influenced by hydrologic episodes were removed. Some of the LTM data were collected during precipitation events so that episodes could be studied. Thus when more than one sample was collected in a day, only the first sample was used in the present analysis because the remaining samples comprised sample sets taken during episodes. After this initial episode screening, the remaining data were examined by plotting discharge versus time. Two samples were removed because their discharges were an order of magnitude greater than the remaining discharges in the same streams. The remaining data appeared to be representative of baseflow conditions. The data were divided into seasons using the following criteria: summer (May 16 to September 15), fall (September 16 to December 15), winter (December 16 to March 31), and spring (April 1 to May 15). The spring season was selected to correspond with the spring index period used in the NSS-I for these streams (snowmelt to leafout).

Within-season chemical variation was roughly the same size as the among-season variation (Figures 7-7 to 7-10). The variability within spring and summer seasons was lower than that within fall and winter samples. The among-season data were analyzed using a two-way analysis of variance model with stream and season as the main effects. The season "variable" was divided into two groups, spring samples and nonspring samples (lumping the other three seasons

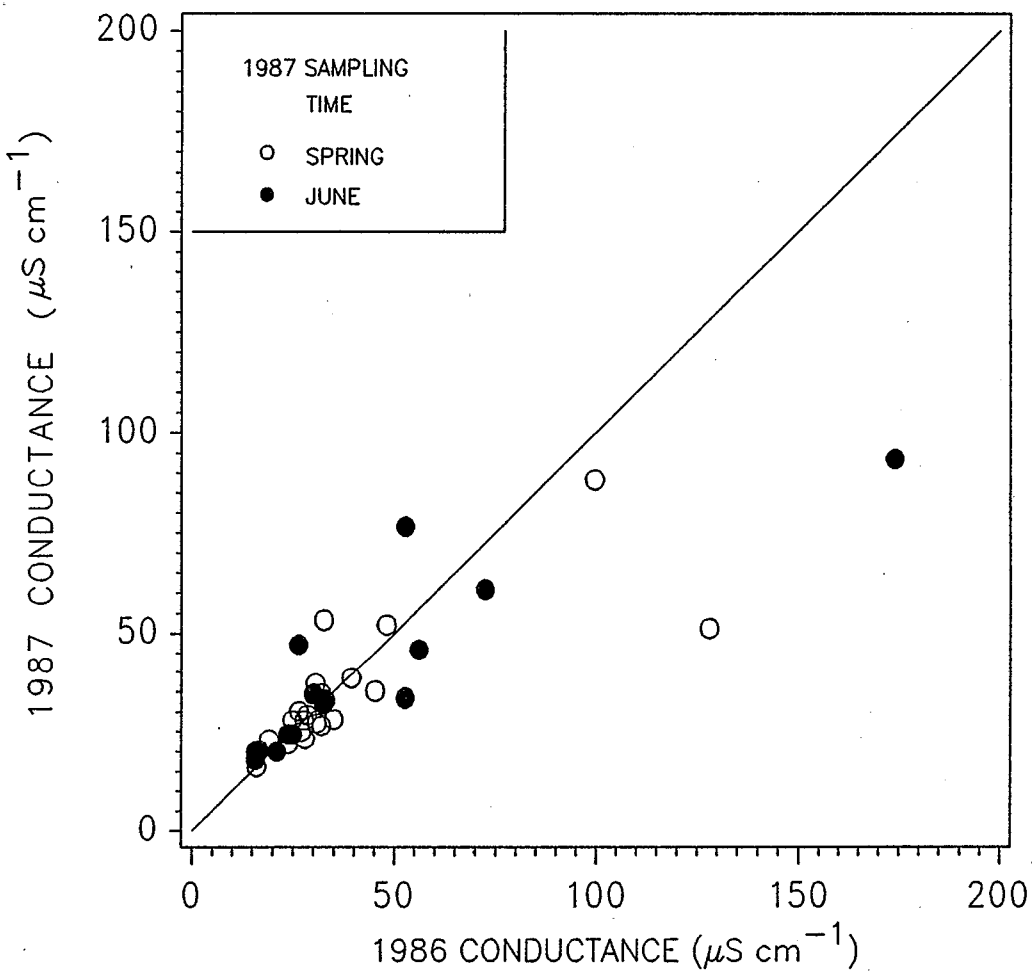


Figure 7-6. Conductivity observed in 1987 during the acid stream reconnaissance versus the 1986 NSS-I spring index in-situ conductivity value in 37 mid-Atlantic stream nodes. All conductivity data were corrected to 25°C for comparison. The line is y = x.

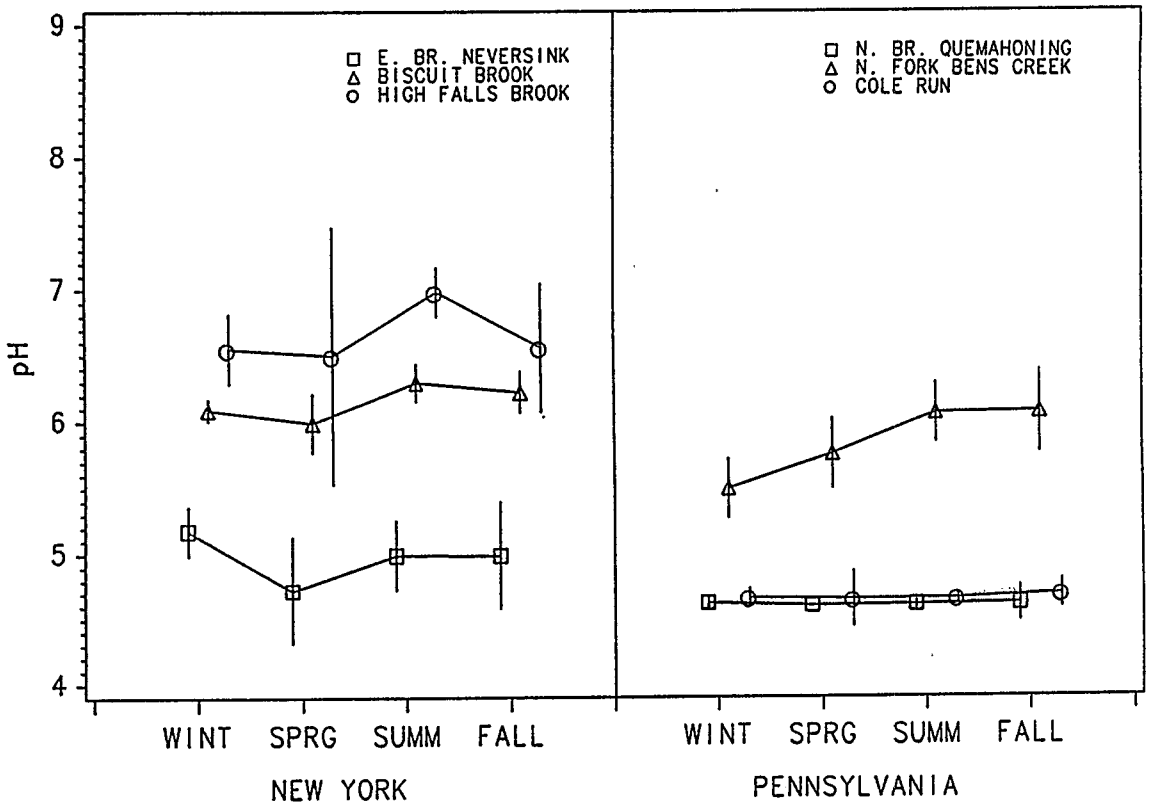


Figure 7-7. **The seasonal pattern in pH (mean plus 95% confidence interval) in three streams in the Catskill Mountains of New York (Murdoch, 1986) and three streams in the Laurel Hills of Pennsylvania (Witt and Barker, 1986). The spring season was defined as April 1 to May 15 (spring index period).**

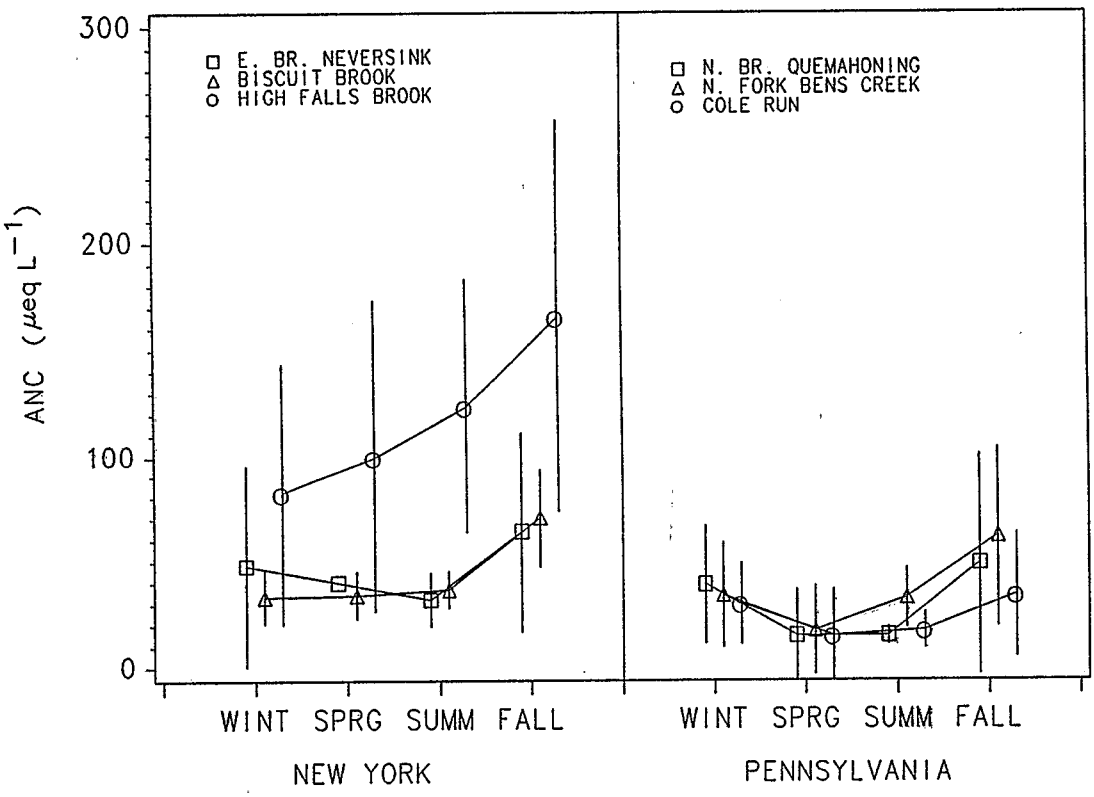


Figure 7-8. The seasonal pattern in ANC (mean plus 95% confidence interval) in three streams in the Catskill Mountains of New York (Murdoch, 1986) and three streams in the Laurel Hills of Pennsylvania (Witt and Barker, 1986). The spring season was defined as April 1 to May 15 (spring index period).

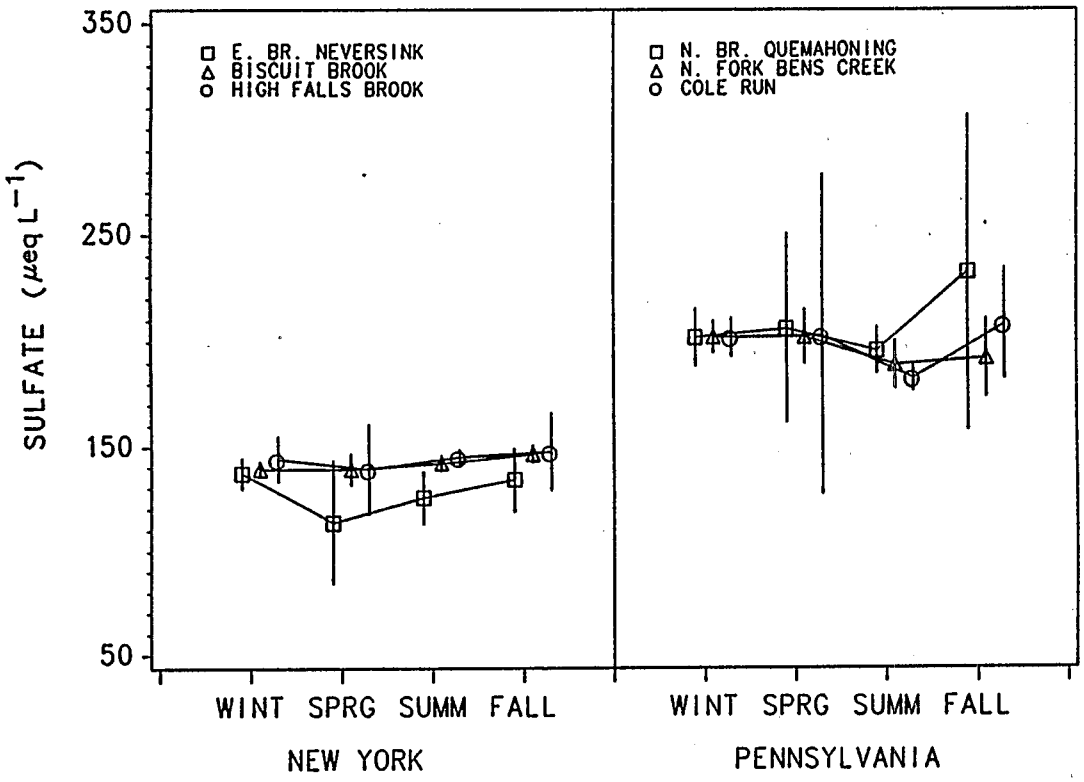


Figure 7-9. The seasonal pattern in sulfate concentration (mean plus 95% confidence interval in three streams in the Catskill Mountains of New York (Murdoch, 1986) and three streams in the Laurel Hills of Pennsylvania (Witt and Barker, 1986). The spring season was defined as April 1 to May 15 (spring index period).

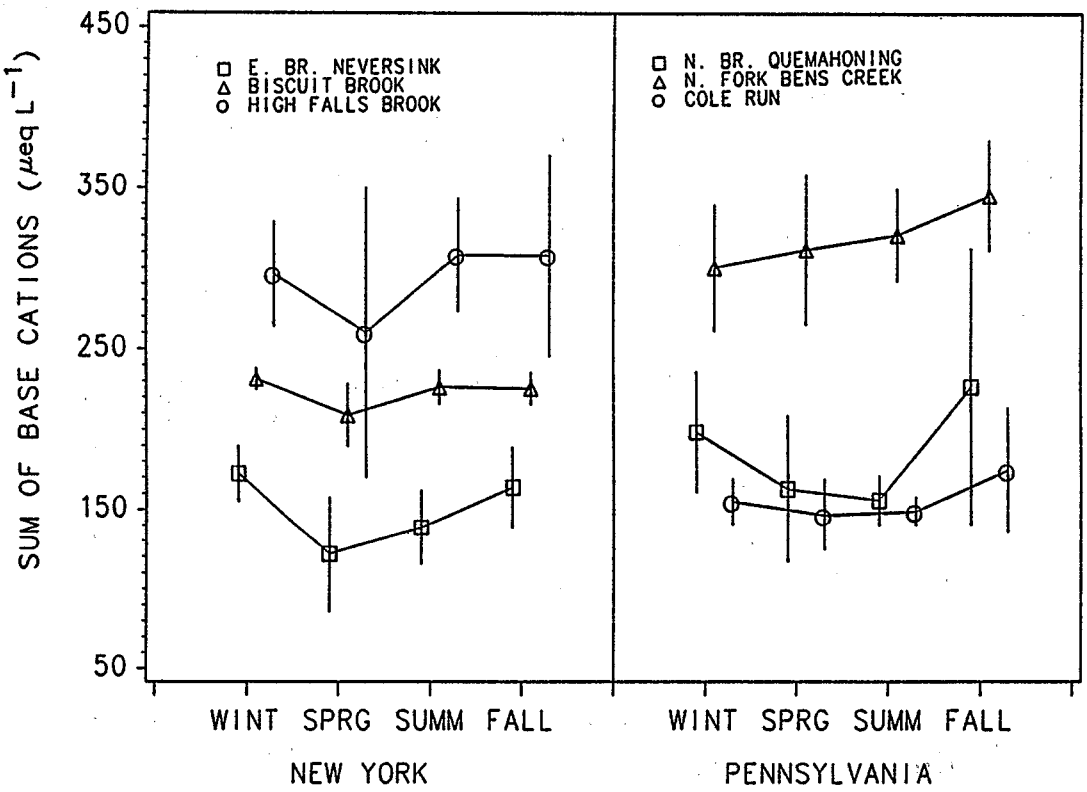


Figure 7-10. The seasonal pattern in the sum of base cations concentration (mean plus 95% confidence interval) in three streams in the Catskill Mountains of New York (Murdoch, 1986) and three streams in the Laurel Hills of Pennsylvania (Witt and Barker, 1986). The spring season was defined as April 1 to May 15 (spring index period).

together), to test the hypothesis that the spring samples were different than the samples in the other seasons. In all analyses, the stream main effect was always significant ($p < 0.01$).

pH values in the spring (Figure 7-7) were significantly lower than the pH values in other seasons ($F = 6.4$; $p < 0.05$). In general, mean ANC values were highest in the fall (Figure 7-8) and lowest in the spring. The spring ANC values, however, were not significantly lower than the values in the other seasons ($F = 3.01$; $p = 0.08$). Spring values were, however, significantly lower than fall values ($F = 13.24$ $p < 0.01$). Sulfate concentrations showed relatively small changes both within and between seasons (Figure 7-9) and sulfate concentrations in the spring were not significantly different from those in the other seasons ($F = 0.56$; $p = 0.45$). The seasonal mean concentration of the sum of base cations (Figure 7-10) was lower in the spring than in the other seasons combined ($F = 8.7$; $p < 0.01$).

These findings were essentially in agreement with those of Ford et al. (1986) and Messer et al. (1986, 1988) showing that spring and winter are typically seasons of low ANC and pH in Mid-Atlantic and Southeast streams. In combination with information citing the spring season as a time of the year when acid-sensitive fish life history stages are present (section 2.5; Bowman, pers. comm.), this data supports the selection of spring baseflow as the appropriate time for sampling streams in the NSS-I.

7.4 WITHIN-SEASON VARIABILITY

A potential source of uncertainty in the NSS-I population estimates presented in this report is the chemical variability within the spring index sampling period. The NSS-I Pilot Survey demonstrated that chemical variability among the three sample visits to Southern Blue Ridge streams between March 15 and May 15, 1985 had an insignificant effect on resultant population distributions of pH, ANC, sulfate, and a number of other major cations and anions (Messer et al, 1986, 1988). These results, however, do not necessarily apply outside the Southern Blue Ridge subregion. Within-season variability was examined in two ways: (1) through use of the LTM and special interest site data and (2) through comparison of the two sample visits to 226 upstream and 222 downstream reach sampling sites in the Mid-Atlantic during the NSS-I.

7.4.1 Within-Season Variability in Special Interest Sites

Analysis of the LTM project and special interest site data set of three Catskill Mountain and three Laurel Hill streams (discussed in Section 7.3) provided a finer resolution assessment of the variability within the spring index period than did the comparison of paired visits to numerous NSS-I sample reaches. The spring index period was defined as April 1 to May 15 to correspond to post-snowmelt/pre-leafout conditions in these streams. The LTM data presented here were collected in 1985 and 1986, whereas the NSS-I Mid-Atlantic data were collected only in 1986. In general, there was good agreement between the data collected by the NSS-I and that of the LTM researchers (Figures 7-11 to 7-14). There was more variability in the LTM data than in the NSS-I data, as would be expected, since the LTM data were collected for two different spring index periods and there were more samples.

The variability in spring index pH in the Pennsylvania streams (Figure 7-11) was fairly low (less than 0.1 pH unit change in Cole Run and the Quemahoning and 0.4 pH unit range in Bens Creek). In the New York Catskills streams, the pH variability was larger (0.7 to 1.1 pH unit ranges). Variability in spring index ANC (Figure 7-12) showed a similar but somewhat less variable pattern than pH. The largest ranges in ANC were observed in Biscuit Brook (57 μeq L^{-1})

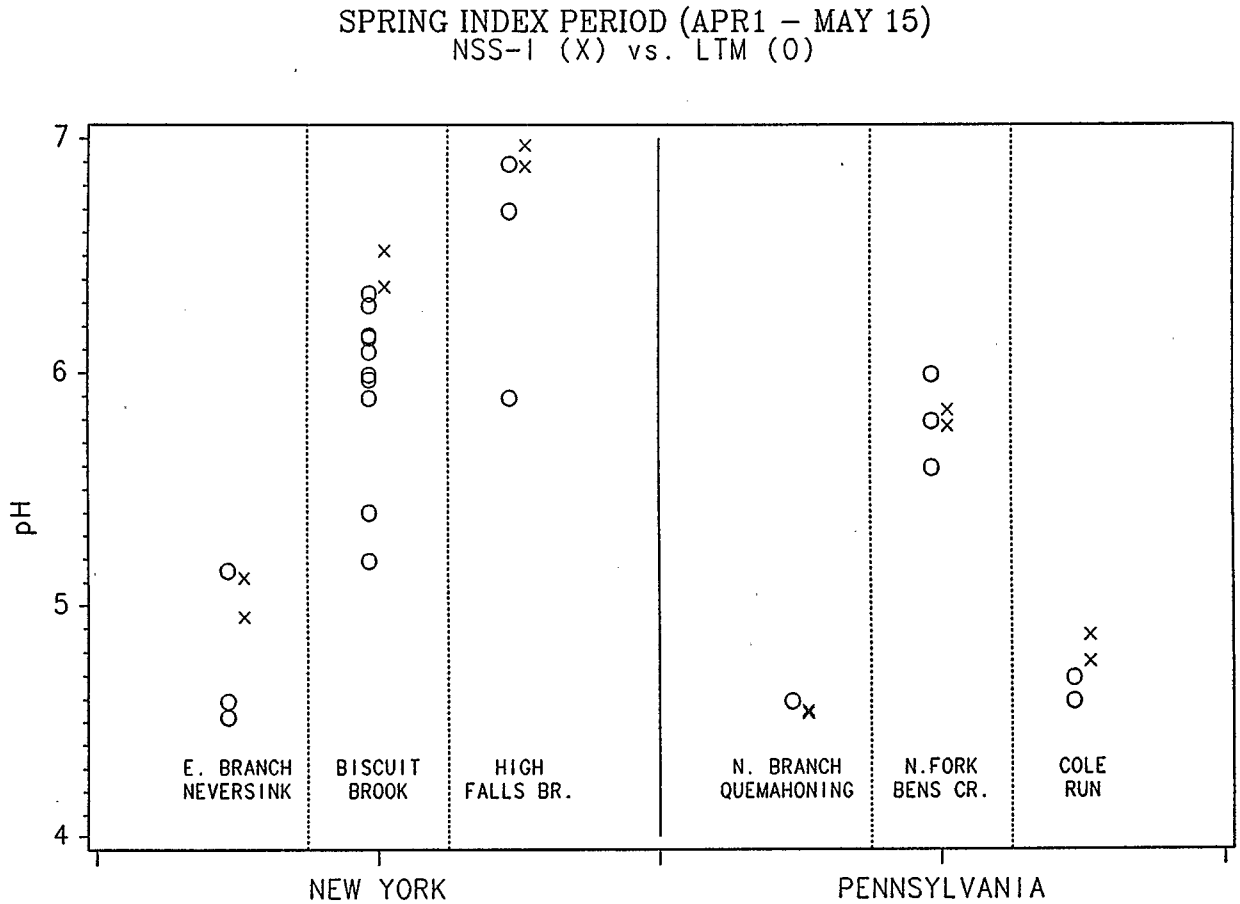


Figure 7-11. The pH range of NSS-I special interest site samples (1986) and Long-Term Monitoring (LTM) Project samples (1985-1986) within the spring index period (April 1 to May 15) in three streams in the Catskill Mountains of New York (Murdoch, 1986) and three streams in the Laurel Hills of Pennsylvania (Witt and Barker, 1986).

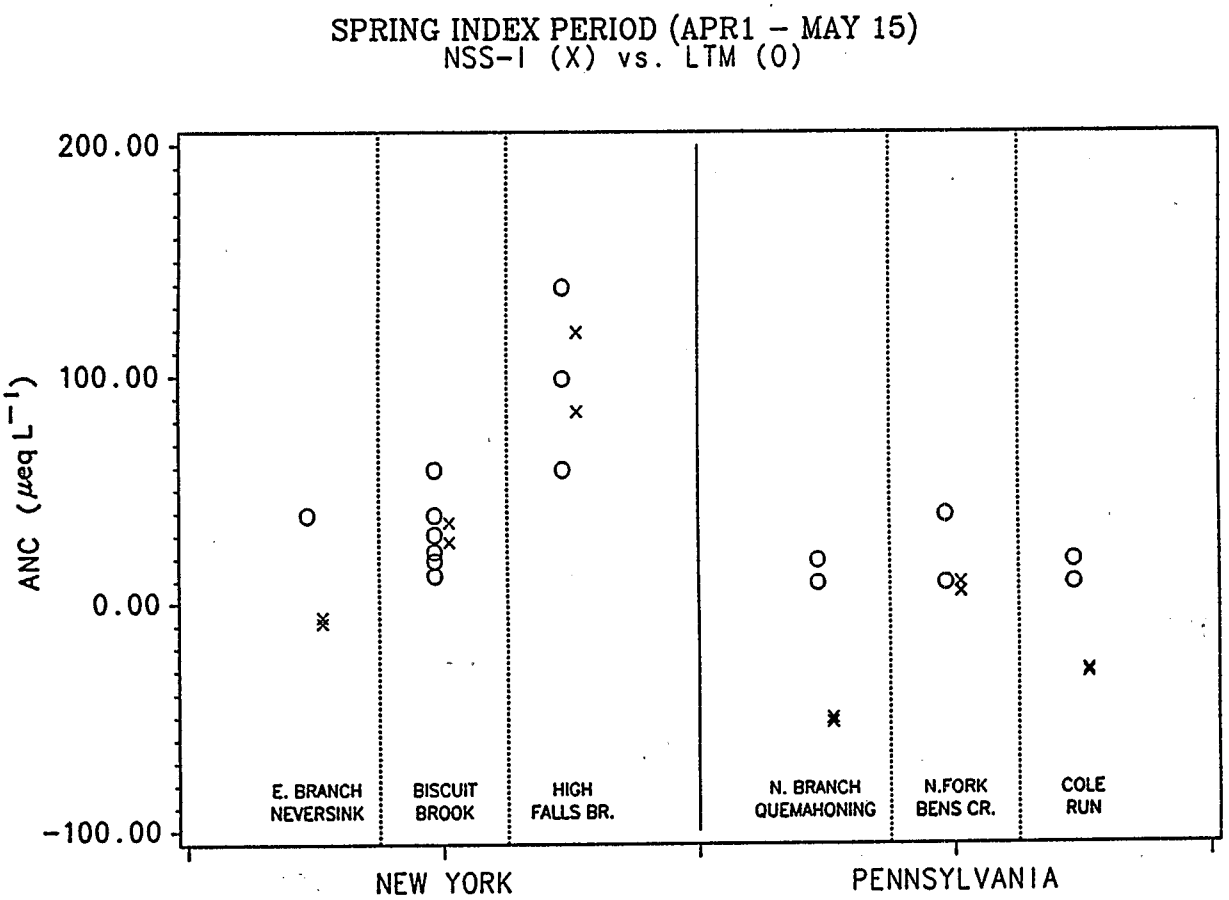


Figure 7-12. **ANC range of NSS-I special interest site samples (1986) and Long-Term Monitoring (LTM) Project samples (1985-1986) within the spring index period (April 1 to May 15) in three streams in the Catskill Mountains of New York (Murdoch, 1986) and three streams in the Laurel Hills of Pennsylvania (Witt and Barker, 1986).**

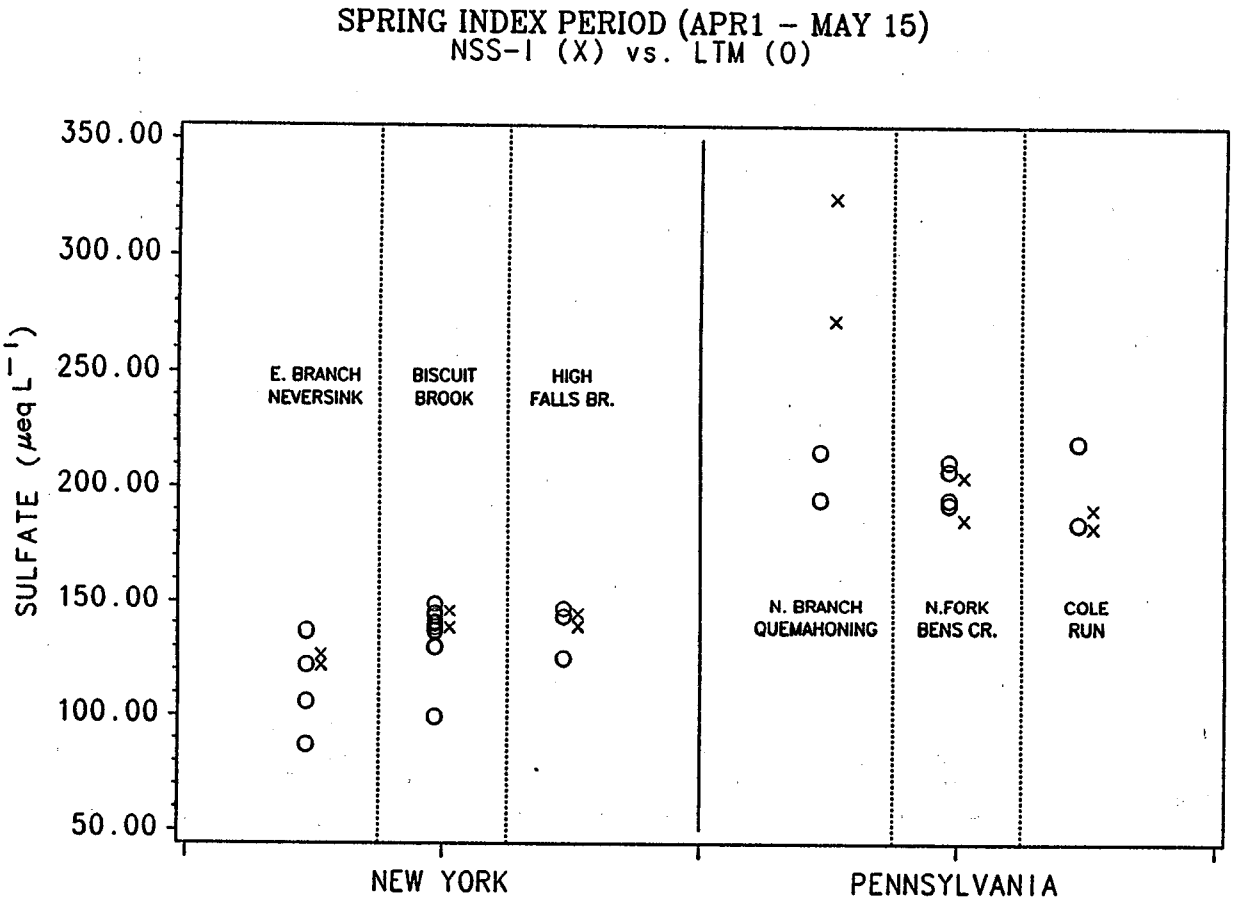


Figure 7-13. **Sulfate concentration range of NSS-I special interest site samples (1986) and Long-Term Monitoring (LTM) Project samples (1985-1986) within the spring index period (April 1 to May 15) in three streams in the Catskill Mountains of New York (Murdoch, 1986) and three streams in the Laurel Hills of Pennsylvania (Witt and Barker, 1986).**

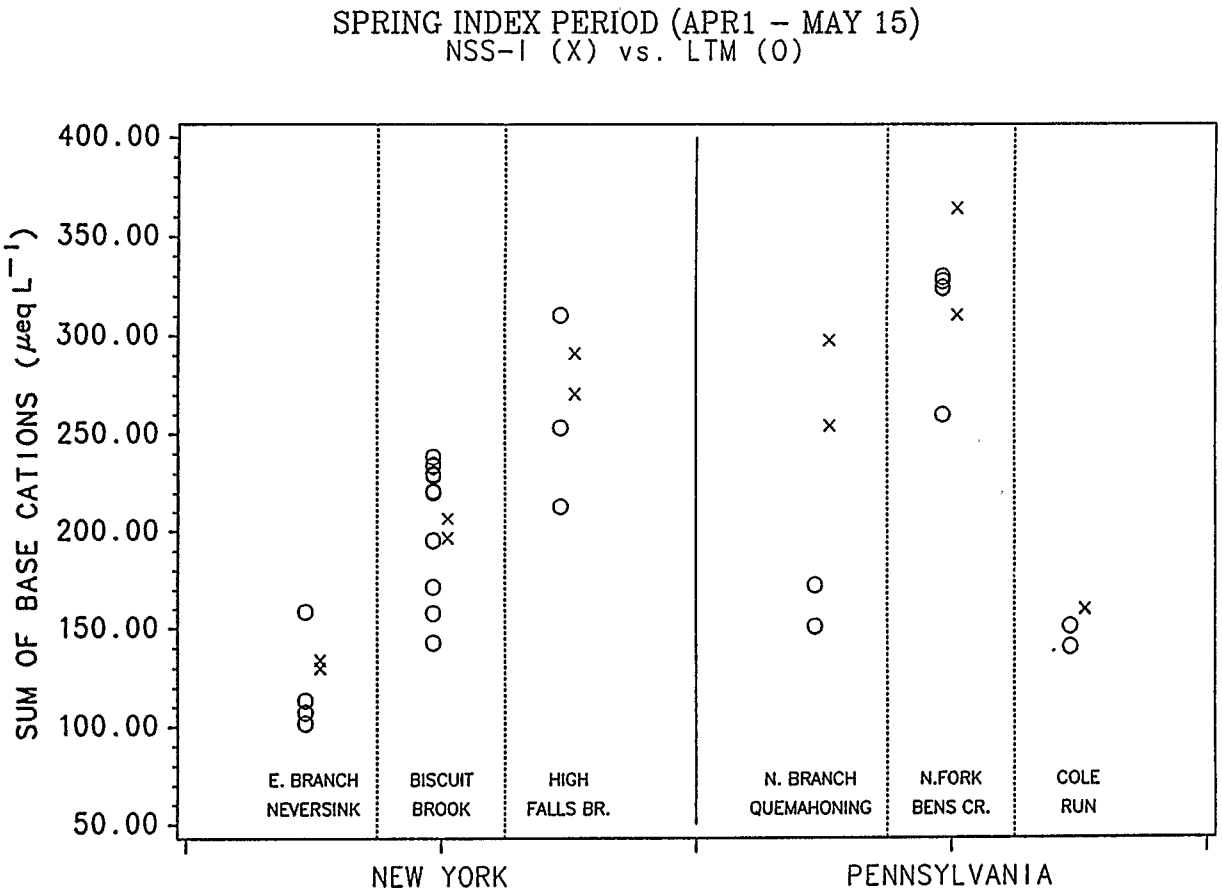


Figure 7-14. The range in the sum of base cation concentrations in NSS-I special interest site samples (1986) and Long-Term Monitoring (LTM) Project samples (1985-1986) within the spring index period (April 1 to May 15) in three streams in the Catskill Mountains of New York (Murdoch, 1986) and three streams in the Laurel Hills of Pennsylvania (Witt and Barker, 1986).

and High Falls Brook (80 μeq L^{-1}). Alkalinity variations in the other four streams were less than 30 μeq L^{-1}. In streams that had negative ANC, as measured by the NSS-I, the agreement between NSS-I and LTM project ANC data was not good. The LTM researchers used different procedures to deal with negative ANC samples and did not report them as negative values. Thus the LTM and NSS-I ANC data are not directly comparable for samples with negative ANC.

In general, the variability in spring index sulfate concentrations was lower than that of the other ions (Figure 7-13). The largest range in sulfate concentration was 50 μeq L^{-1} in Biscuit Brook. In comparison, the variability in the sum of base cations (Figure 7-14) was rather large (over 100 μeq L^{-1} in Biscuit Brook and High Falls Brook), indicating that base cations have a major terrestrial source component. Sulfate appears to behave as a more conservative ion. This suggests that there is not a major terrestrial source of sulfate and that the dominant sulfate source is probably atmospheric. The concentrations of sulfate and base cations measured in the North Branch of the Quemahoning during the NSS-I were twice those observed in the LTM project. A field visit to the Quemahoning during the Acid Streams Reconnaissance showed that it is affected by acid mine drainage along sections of its reach. It is possible that the LTM project and the NSS-I sampled slightly different locations along the stream. If the NSS-I sampling location was slightly downstream of the LTM sampling site, it could receive sulfate and base cations from mine drainage that was not present at the upstream LTM site.

7.4.2 Within-Season Variability in NSS-I Mid-Atlantic Sites

During the NSS-I field activities of 1986, Mid-Atlantic sites were visited twice during the spring, and Southeast sites were visited only once. The two sampling visits in the Mid-Atlantic subregion streams were typically two weeks apart. The NSS-I design intended them to be replicates, though their timing was not randomly set. The population distribution estimates presented for Mid-Atlantic subregions are based on the spring index chemistry, calculated by averaging values from the two spring visits--thereby obtaining more stable values with which to characterize each reach. This section evaluates, where possible, the effects of spring season baseflow chemical changes on estimates of the regional distribution of chemical characteristics. Of particular interest is the effect that such changes have on estimates of the number or fraction of acidic and low ANC stream reaches.

Figures 7-15 and 7-16 show that, for upper and lower reach sampling nodes in the Mid-Atlantic, the second spring sample ANC and pH are excellent predictors of values from the first sample, but there is evidence of a time trend of increasing ANC and pH between spring sampling visits. Linear regressions of the first visit versus the second visit are both highly significant ($p < 0.0001$) with r^2 values of 0.93. However, the second visit ANC and, to a lesser extent, pH, are consistently higher, as expressed by regression slopes of +0.82 and +0.97. This pattern is likely to result from a general decrease in streamflow over the spring season. During periods of decreasing baseflow, there is a general increase in the concentration of many chemical species in stream water. In particular, concentrations of base cations and other weathering products increase as the streamflow proportion contributed by older groundwater increases in relation to quickflow contributions from soil macropores and shallow soil horizons. The increase in alkalinity associated with base cations at lower base flows tends to neutralize acids derived from organic soil horizons and atmospheric deposition. (Note that the pattern observed with decreasing flow stage in reaches impacted by acid mine drainage was an increase in base cations and sulfate, with a reduction in ANC and pH.)

The magnitude of change observed in ANC and pH between the two NSS-I spring sampling visits was very dependent upon the concentration level on the first visit. With ANC, for

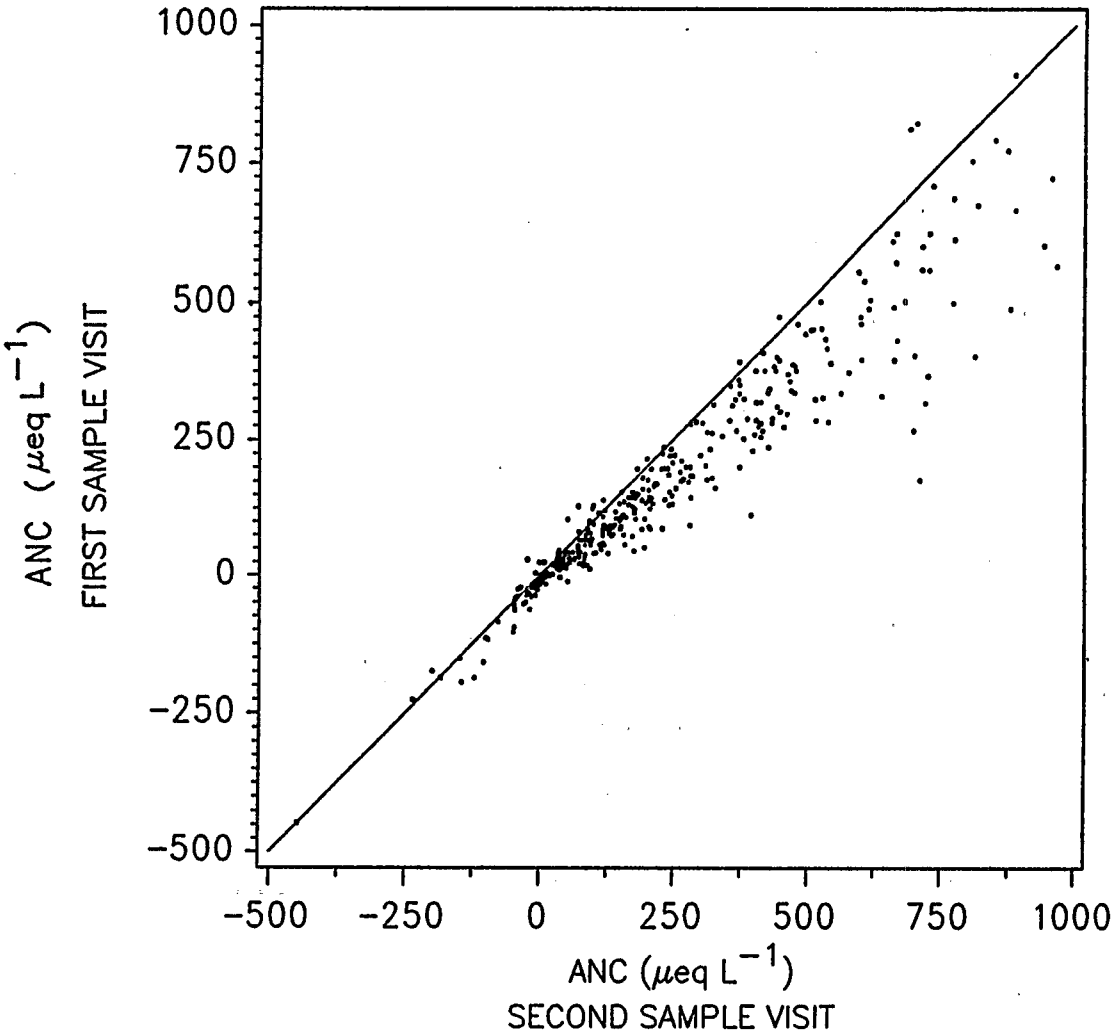


Figure 7-15. ANC on first visit versus second visit to NSS-I sample reaches in the Mid-Atlantic Region.

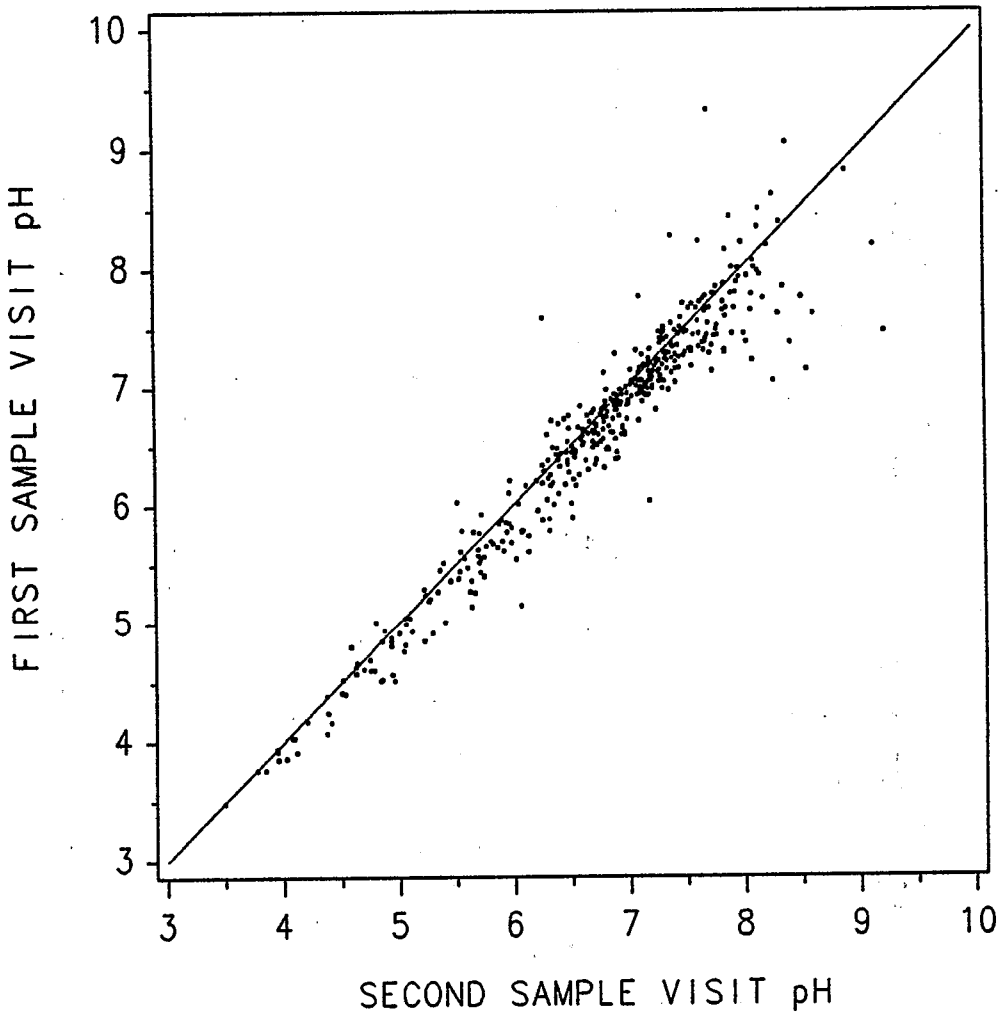


Figure 7-16. pH on first visit versus second visit to NSS-I sample reaches in the Mid-Atlantic Region.

example, the median absolute value of changes was 9.7 μeq L^{-1} in the range beween -50 and +50 μeq L^{-1} (Figure 7-17). For reaches with ANC between 50 and 100 μeq L^{-1} on the first visit, the median change was 29 μeq L^{-1}. Forty-nine percent of stream sample sites with ANC $\leq$ 50 μeq L^{-1} changed less than 10 μeq L^{-1} (Table 7-1). Sixty-seven percent of those with first visit ANC between 50 and 200 μeq L^{-1} changed by less than 50 μeq L^{-1}. The largest changes between visits were observed at sample sites with ANC > 400 μeq L^{-1} on the first visit. Seventy-one percent of sample reaches in this group experienced ANC changes (mostly increases) of greater than 100 μeq L^{-1}. The Northern Appalachians (2Cn) and the Poconos/Catskills (1D) tended to have changes greater than the regional median change in the higher ANC ranges (Figure 7-17). Within the ANC ranges of greatest interest (those below 100 μeq L^{-1}), the smallest median ANC changes were observed in the Valley and Ridge (2Bn) and the largest in subregion 1D (Figure 7-17). ANC changes observed within the lowest range are of the magnitude expected due to field sample collection, transport, and analysis (pooled standard deviation of field duplicate ANC measurements was 2.9 to 7.8 μeq L^{-1} in this range, Table 4-3).

A related pattern in the magnitude of change between sample visits was observed in pH (Figure 7-18 and Table 7-2). Stream water pH in reach sampling sites with pH lower than 5.5 tended to be less variable during baseflow than those with with pH above this value. However, the logarithmic nature of the pH variable must be taken into account. The change in hydronium ion concentration corresponding to a 0.25 unit pH change near pH 5 is 10 times greater than that associated with the same magnitude of pH change near pH 6. The median pH change (absolute value) for sample reaches with a first visit pH $\leq$ 5.5 was 0.08 (Figure 7-18), about twice the standard deviation of field duplicate pH measurements in this pH range (0.036). All sample reaches with pH $\leq$ 5.5 showed pH changes of less than 0.50 pH unit; 80% changed less than 0.25 unit. Considering the full pH range of streams, 94% experienced pH changes of less than 0.5 unit, whereas 75% showed smaller pH changes of less than 0.25 unit. The Poconos/Catskills (1D) showed the largest median between-visit pH changes in all ranges of pH (Figure 7-18), whereas the Valley and Ridge subregion (2Bn) showed the smallest median changes in the lower pH ranges of greatest interest.

The variability of stream baseflow chemistry between sample visits (or the apparent trend, for some variables and subregions) within the spring index sampling period has bearing on questions such as: "What is the number or fraction of the reach population that is acidic during the index period?" or "How many streams in the region have spring baseflow pH less than 5.0?" Figures 7-19 to 7-22 compare, in the combined Mid-Atlantic subregions, the population cumulative distribution functions (CDFs) for ANC, pH, sum of base cations (SBC) and sulfate, based on first visit, second visit, and spring index (average) measurements. Differences between first and second visits are greatest for ANC and minimal for the other three variables. The effect of greater within-season ANC increases in streams with ANC > 50 μeq L^{-1} is apparent in these plots, as is the greater apparent stability of baseflow (non-episodic) ANC and the other variables at upper reach nodes in comparison with lower nodes.

Table 7-3 summarizes the differences in population distributions of ANC based on the two different visits and the chemical index made by averaging the two. Considering the estimates for acidic (ANC $\leq$ 0 μeq L^{-1}) lower reach nodes in the target population, only the estimate for subregion 3B is different from that based on the chemistry averaged over the two visits (visit 1 estimates 10% are acidic, whereas the index chemistry estimates 7%). For the reach upper nodes, the population percentage of acidic reaches based on the chemical index is virtually the same for subregions 1D and 2Bn, but the index underestimates (by 3 percentage points) the fraction of acidic reaches during the first visit in subregions 2Cn and 3B. Similarly, the index-based CDFs made slightly lower estimates of reaches with pH < 5.0 at the lower nodes in

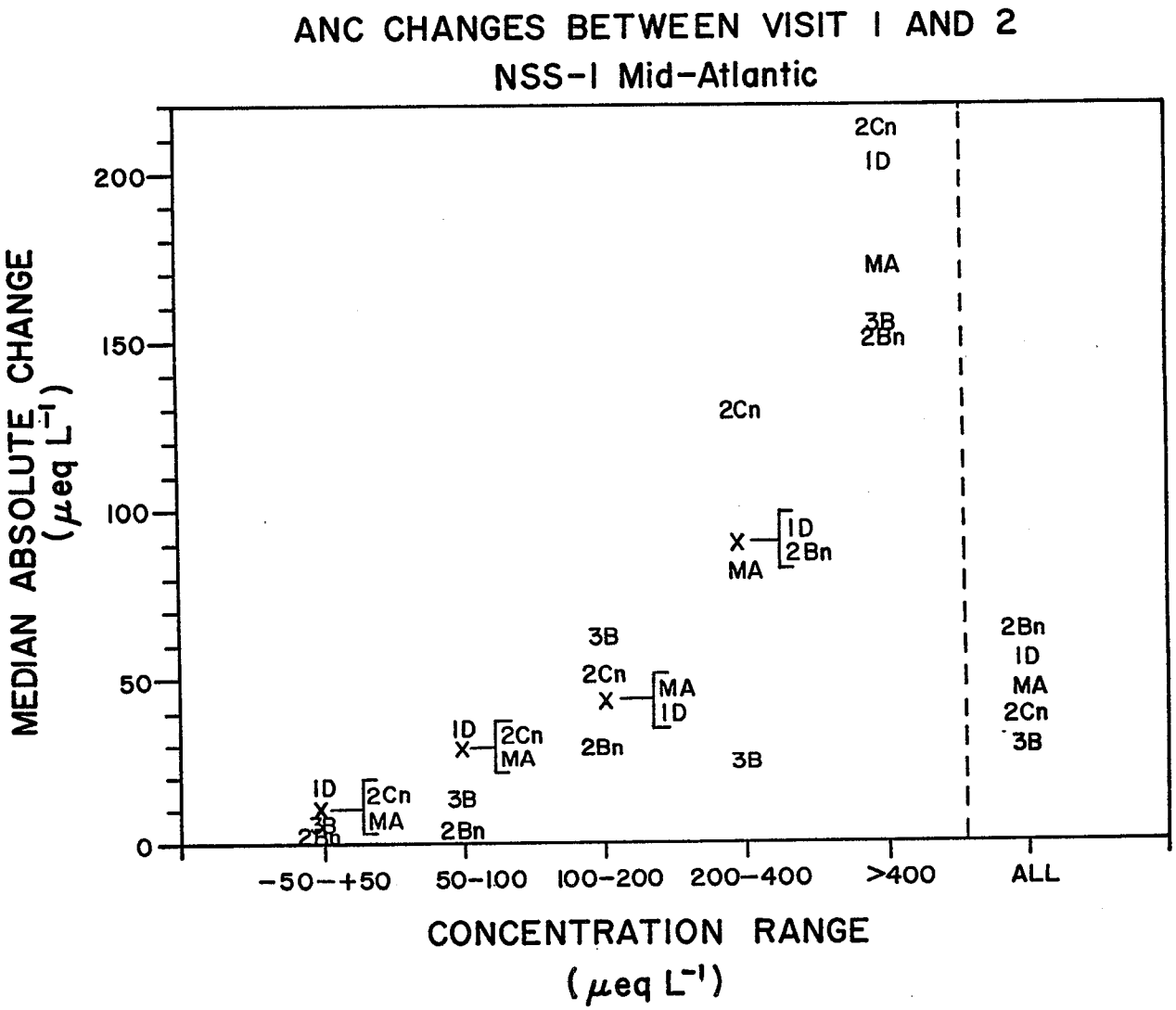


Figure 7-17. Median absolute changes in ANC (unweighted) between first and second visits to NSS-I sample reaches in four subregions of the Mid-Atlantic Region. MA indicates the median value for all Mid-Atlantic subregions.

Table 7-1. Distribution of Observed ANC Differences (unweighted) Between First and Second Visits to NSS-I Mid-Atlantic Sample Reaches

Index ANC	Absolute Change in ANC (μeq L^{-1})					
	≤ 5	>5 - ≤10	>10 - ≤25	>10 - ≤50	50 - ≤100	>100
ANC ≤ 0	13	8	15	4	3	-
ANC > 0 - ≤ 50	19	10	23	6	2	-
ANC > 50 - ≤ 200	8	6	23	46	32	9
ANC > 200 - ≤ 400	3	6	7	9	25	24
ANC > 400	2	1	3	11	20	90

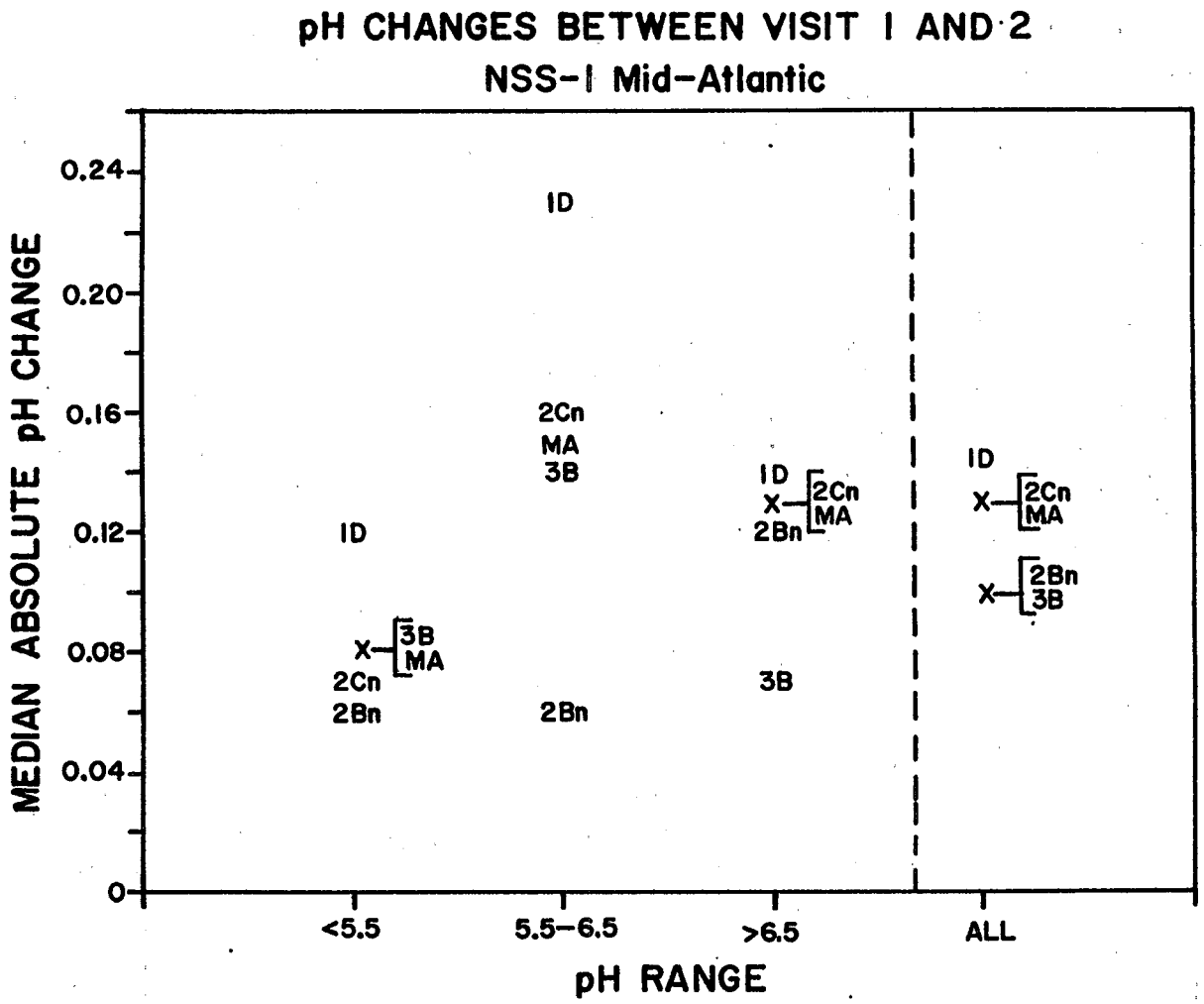


Figure 7-18. Median absolute changes in pH (unweighted) between first and second visits to NSS-I sample reaches in four subregions of the Mid-Atlantic Region. MA indicates the median value for all Mid-Atlantic subregions.

Table 7-2. Distribution of Observed pH Differences (unweighted) Between First and Second Visits to Mid-Atlantic Sample Reaches

Index pH	Absolute Change in pH			
	≤ 0.25	>0.25 - ≤0.5	>0.5 - ≤1.0	1.0 - ≤2.0
pH ≤ 5.0	34	6	-	-
pH > 5.0 - ≤ 5.5	13	6	-	-
pH > 5.5 - ≤ 6.0	25	9	3	-
pH > 6.0	249	59	17	7

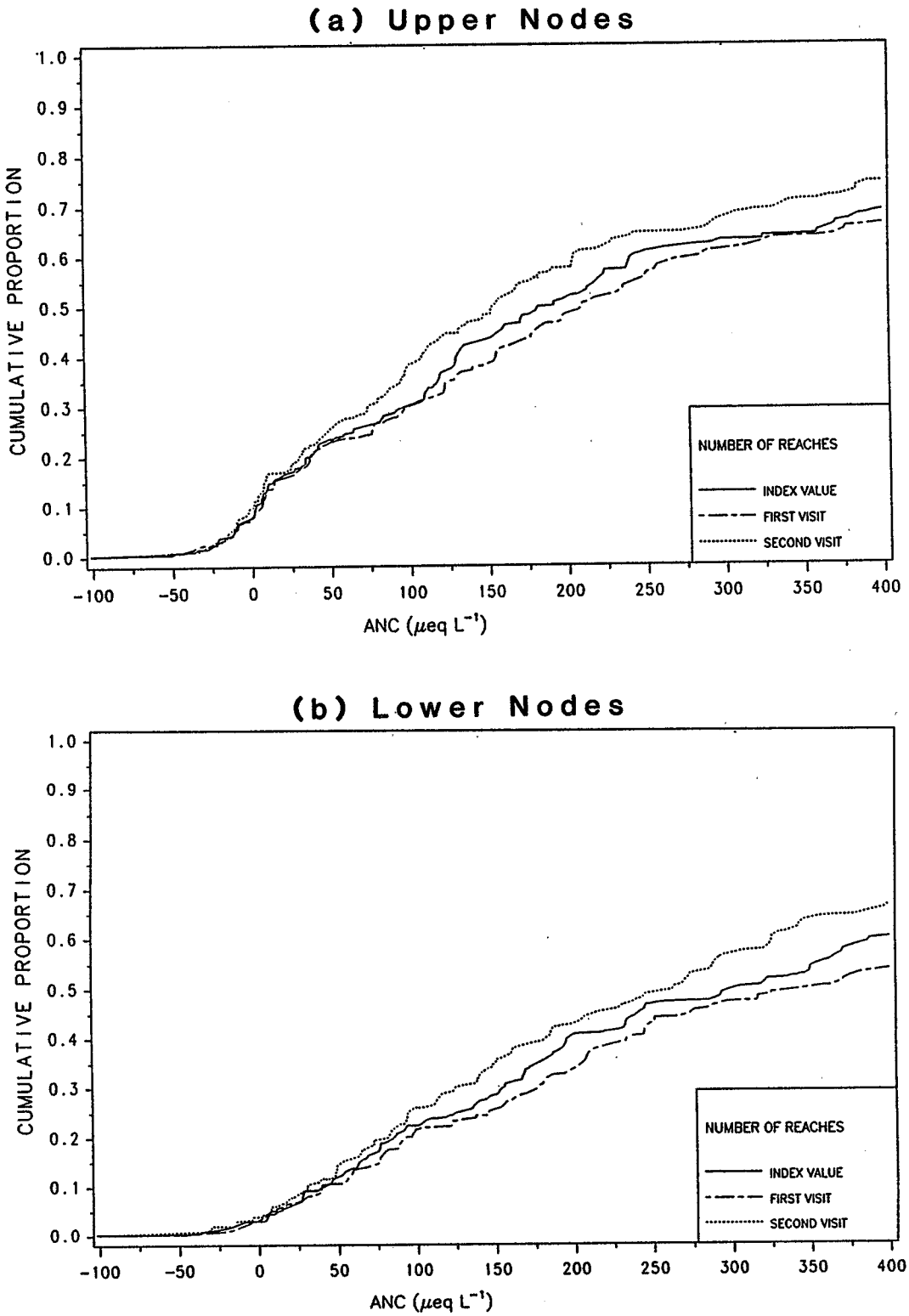


Figure 7-19. Population distributions for ANC in the NSS-I Mid-Atlantic Region based on first visit, second visit, and spring index (average) measurements for (a) upper nodes and (b) lower nodes.

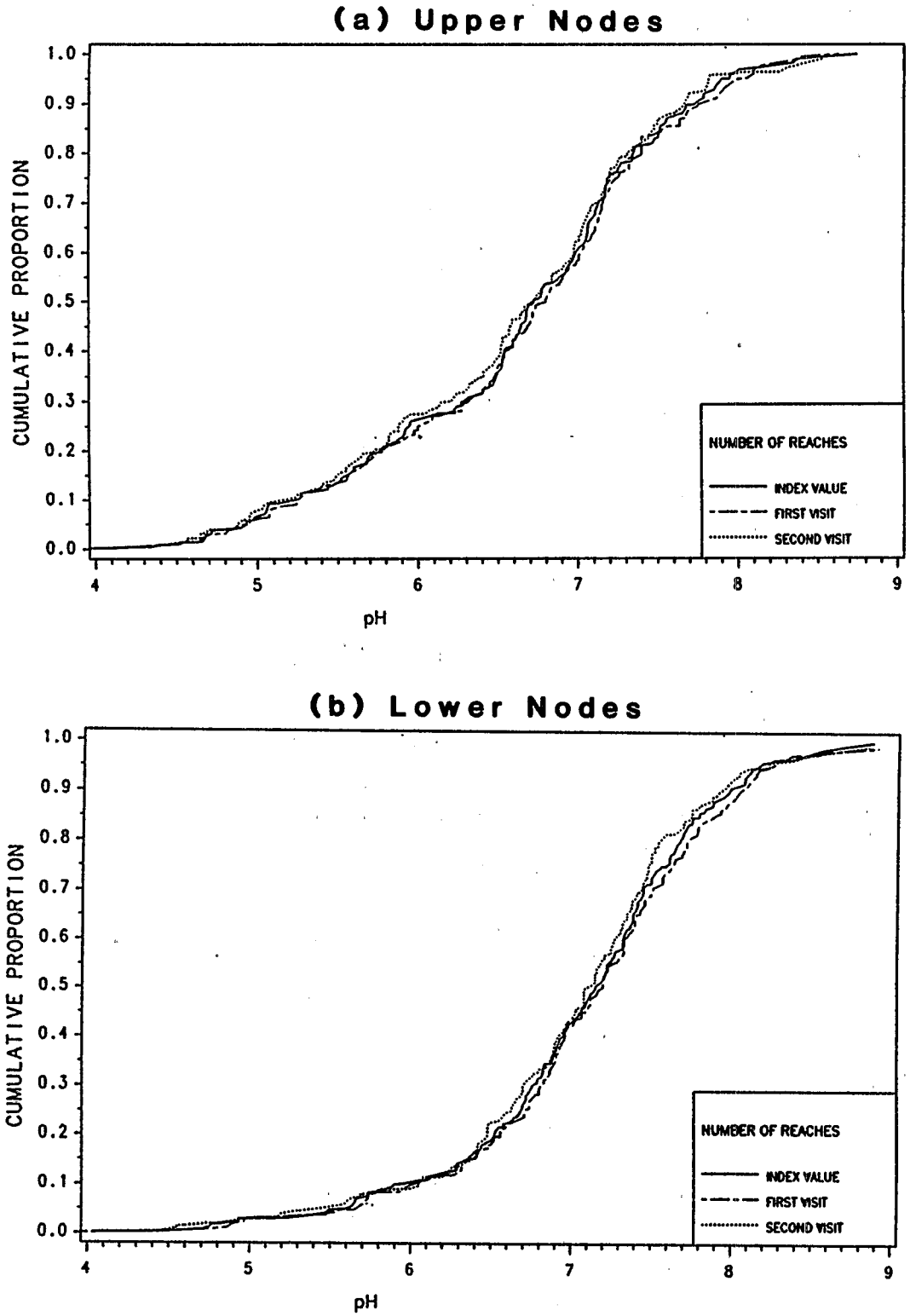


Figure 7-20. Population distributions for pH in the NSS-I Mid-Atlantic Region based on first visit, second visit, and spring index (average) measurements for (a) upper nodes and (b) lower nodes.

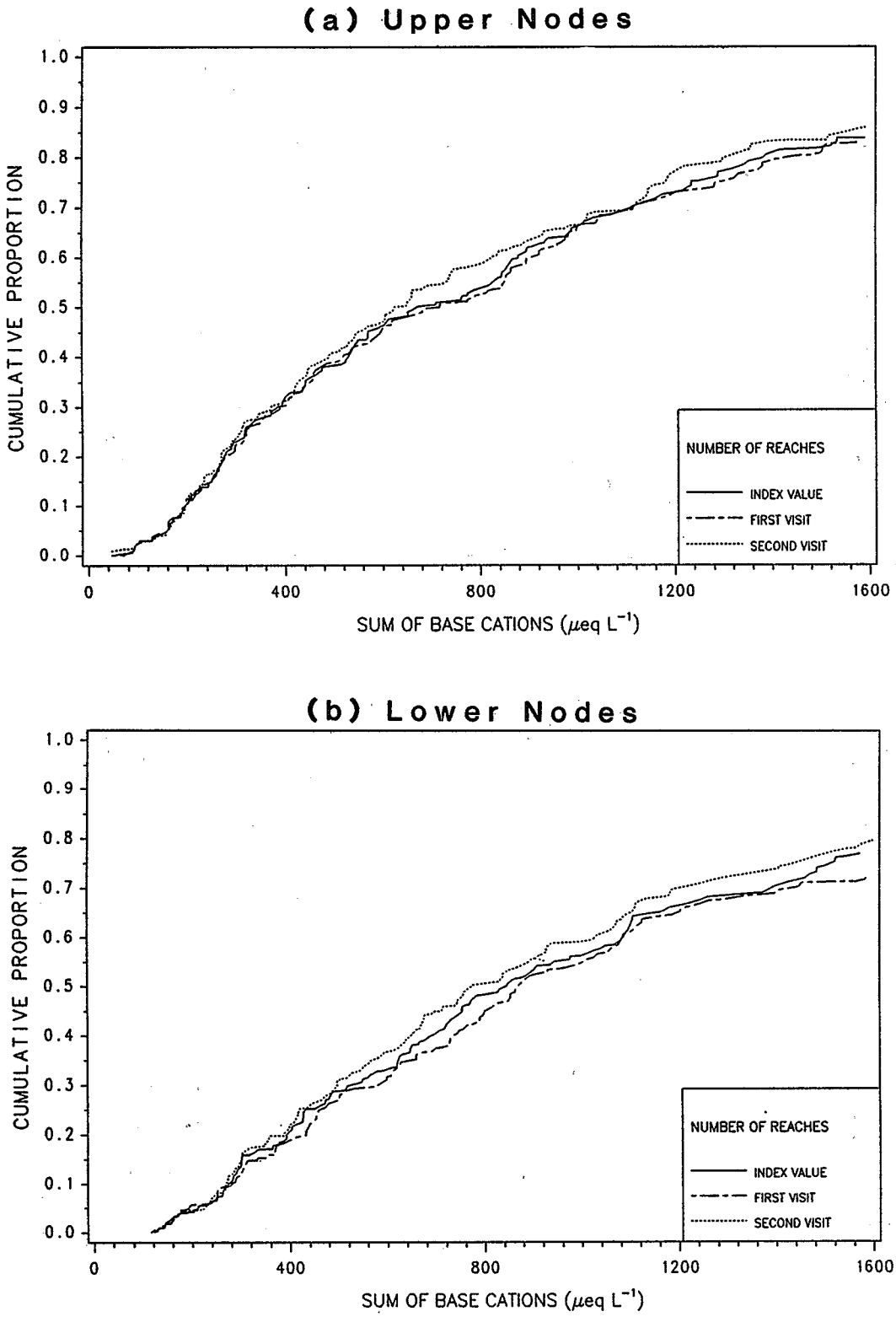


Figure 7-21. Population distributions for sum of base cations in the NSS-I Mid-Atlantic Region based on first visit, second visit, and spring index (average) measurements for (a) upper nodes and (b) lower nodes.

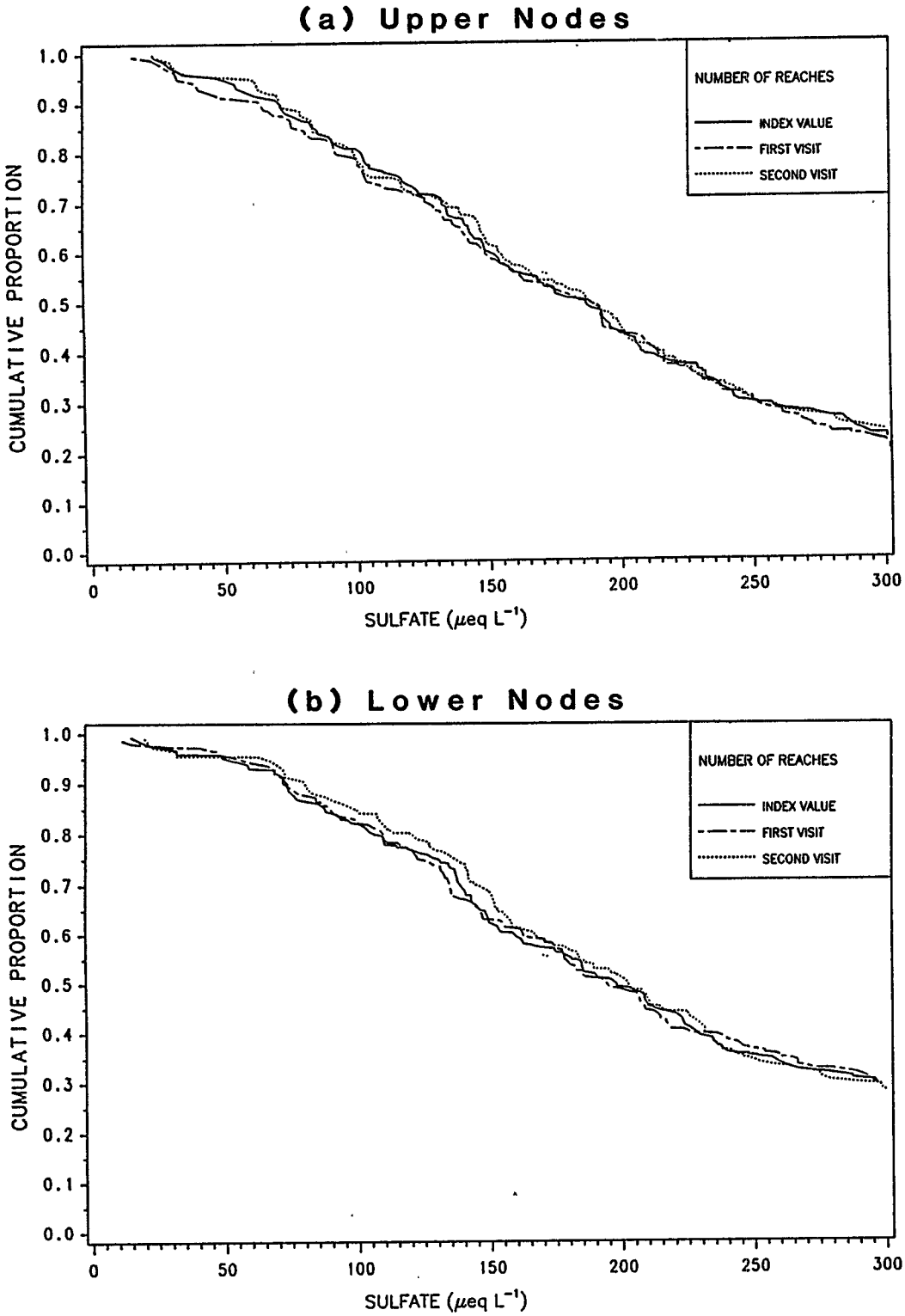


Figure 7-22. Inverse population distributions for sulfate concentrations in the NSS-I Mid-Atlantic Region based on first visit, second visit, and spring index (average) measurements for (a) upper nodes and (b) lower nodes.

Table 7-3. Population Estimates of the Percentage of Acidic and Low ANC Stream Reaches Calculated from First Visit, Second Visit, and Spring Index (Average) ANC at Upper and Lower Reach Nodes in NSS-I Mid-Atlantic Subregions

	ANC ≤ 0 μeq L^{-1}					
	Lower Node			Upper Node		
	visit 1	visit 2	Index (UCB)	visit 1	visit 2	Index (UCB)
1D (Poconos/Catskills)	*	*	*	6	7	6 (12)
2Bn (Valley and Ridge)	*	*	*	5	5	5 (10)
2Cn (N. Appalachians)	4	4	4 (8)	9	6	6 (11)
3B (MA Coastal Plain)	10	7	7 (12)	15	12	12 (19)

	ANC ≤ 50 μeq L^{-1}					
	Lower Node			Upper Node		
	visit 1	visit 2	Index (UCB)	visit 1	visit 2	Index (UCB)
1D (Poconos/Catskills)	11	5	5 (9)	25	17	23 (34)
2Bn (Valley and Ridge)	3	*	* (1)	11	11	11 (19)
2Cn (N. Appalachians)	30	22	23 (36)	41	34	34 (48)
3B (MA Coastal Plain)	20	16	20 (29)	29	29	30 (42)

(UCB) = Upper 95% Confidence Bound.
* = less than 1%.

two subregions (2Cn and 3B) than did those based on pH during the first visit (Figure 7-20). In subregions 1D and 3B, index-based estimates for reaches with pH $\leq$ 5.0 at their upstream nodes were lower than those based on the first visit (Table 7-4). In all cases, the single visit estimates of the number (or percentage) of acidic reaches are within the 95% confidence bounds of the figures based on the chemistry averaged over the two visits. These confidence bounds, based entirely on the spatial sampling frame (i.e., they do not incorporate within-season chemical variance) suggest that the variance resulting from the number and spatial distribution of sample sites is greater than that due to observed within-season chemical variability. However, the observation of a trend of increasing ANC over the portions of the index sampling period leaves open the possibility that, had all streams been sampled at the beginning of the index period, estimates of the number of acidic reaches might have been greater than reported. As described earlier in this section, the quantitative study of intensive data from special interest sites may allow extrapolation from index chemistry to the expected annual minimum baseflow ANC.

7.5 SUMMARY

In this section, we have examined the three major components of temporal variability (among-year, among-season, and within-season) that could affect the NSS-I population estimates. The limited data available for among-year variability suggest that: (1) the NSS-I year (1986) was not highly unusual with regard to several important chemical constituents, and (2) among-year variability probably would not cause population estimates to change substantially from year to year (in the short term). Chemical measurements (pH, ANC, sulfate, and sum of base cations) taken in 1986 from Fernow Control in West Virginia were very similar to those observed in 1980 - 1985 and 1987. On a regional scale, in 26 acidic stream reaches in the Mid-Atlantic, deviations between 1986 and 1987 spring pH and conductivity measurements were fairly small.

Data collected from six Mid-Atlantic special interest sites and LTM project streams showed that spring index samples had lower (or equally low) pH, ANC, and sum of base cation concentrations than samples collected in other seasons. Sulfate concentrations showed little seasonal change. Given the seasonal variation, and in light of the fact that populations of many fish species are most sensitive to acidic conditions in the spring when acid-sensitive life history stages are present, spring appears to be have been the appropriate season to conduct the NSS-I.

There was a fair amount of chemical variability within the spring index period, although it was not great enough to preclude the estimation of relatively robust spring baseflow population descriptions and classifications based on spring index values. However, quantitative models of stream baseflow concentrations incorporating seasonal change and flow variation may be necessary tools for assessing small long-term changes in stream chemistry--particularly if the monitoring programs incorporate baseflow indices calculated from one or several spring samples. Data collected from the first sample visit in NSS-I Mid-Atlantic streams were excellent predictors of ANC and pH in second visit samples. There was, however, a systematic trend of decreasing ANC and increasing pH from the first to the second sample visit in most streams. The median absolute change in ANC was around 50 μeq L^{-1}, and the median absolute change in pH was 0.13. Median changes in ANC were smaller (9.8 μeq L^{-1}) in streams within the ANC range of critical interest (-50 to +50 μeq L^{-1}). NSS-I population estimates made using only first visit samples were very similar to estimates made using only second visit samples or the spring index value (average of visits 1 and 2). Almost all work so far has been done on streams in the Mid-Atlantic and Southern Blue Ridge. Future work on temporal variability will incorporate data collected from special interest site streams throughout the southeastern United States.

Table 7-4. Population Estimates of the Percentage of Stream Reaches with pH Less than Reference Values Calculated from First Visit, Second Visit, and Spring Index (Average) pH at Upper and Lower Reach Nodes in NSS-I Mid-Atlantic Subregions

	pH ≤ 5.0					
	Lower Node			Upper Node		
	visit 1	visit 2	Index (UCB)	visit 1	visit 2	Index (UCB)
1D (Poconos/Catskills)	*	*	*	5	3	5 (9)
2Bn (Valley and Ridge)	*	*	*	2	2	2 (6)
2Cn (N. Appalachians)	4	3	3 (7)	6	6	6 (11)
3B (MA Coastal Plain)	8	7	7 (12)	15	10	12 (19)

	pH ≤ 5.5					
	Lower Node			Upper Node		
	visit 1	visit 2	Index (UCB)	visit 1	visit 2	Index (UCB)
1D (Poconos/Catskills)	*	*	* (1)	7	7	7 (12)
2Bn (Valley and Ridge)	*	*	*	6	6	6 (12)
2Cn (N. Appalachians)	6	4	6 (11)	16	13	13 (22)
3B (MA Coastal Plain)	12	9	13 (21)	25	24	24 (34)

(UCB) = Upper 95% Confidence Bound.
* = less than 1%.

SECTION 8
ION RELATIONSHIPS

8.1 OVERVIEW

Both natural and anthropogenic factors can influence the chemistry of streams and contribute to the intra- and inter-regional variation in their acid neutralizing capacity (ANC). These factors include differences in (1) the input of strong bases generated through weathering, (2) the input of strong mineral acids from natural (e.g., nitrification, sulfide oxidation) and anthropogenic (acidic deposition) sources of such acids, and (3) the input of naturally occurrring strong and weak organic acids leached from soils and wetland watersheds.

Because the stream survey data are for only a single point in time, and detailed information on the geology, soils, and hydrology of each watershed is not yet available, it is difficult to discern the sources of variation in acid/base chemistry. Such variation in stream water chemistry may result from generic differences in watershed geochemistry (e.g., weatherable and exchangeable pools of base cations) and hydrology (e.g., precipitation and evapotranspiration), as well as from differences in anthropogenic and natural sources of acidity deposited on, or generated within, the watersheds. Such survey data on the ion composition of stream water can, however, provide inferential evidence concerning the role of different factors in causing the observed patterns in ANC and pH within and among streams in the various subregions.

In this section, the relationships among various ions in stream water are examined to assess the factors associated with the observed differences in the acid/base chemistry within and among streams in the nine subregions sampled in the NSS-I. This is done through an examination of some bivariate and multivariate relationships that may be important in understanding the role of certain variables in stream acidification.

8.2 BASE CATIONS AND MINERAL ACID ANIONS

Information on the concentration of total and individual base cations is useful in assessing the role of various factors that potentially contribute to the between-stream differences in the acid/base chemistry of water. Trilinear plots of anion and cation distributions for each subregion (Figures 8-1 [a - i]) are particularly useful for characterizing intra-regional patterns in ion distribution and for assessing inter-regional differences and similarities in the composition of stream water. The ion distribution diagrams show the relative contribution of the respective cations and anions, expressed as a fraction of the total of those ions considered. For example, streams in which calcium is the dominant base cation would be clustered in the lower left portion of the base cation triangle (lower left), while streams dominated by sodium and/or potassium would be clustered in the lower right portion of the triangle. The diamond in the center of the trilinear plots illustrates the fractional contribution of the anions and cations combined. Thus, streams in which calcium and/or magnesium are the dominant cations are plotted on the left and upper portions of the diamond, whereas streams in which sodium and/or potassium are the dominant cations are plotted on the right and lower portions. Similarly, streams in which bicarbonate is the dominant anion are plotted on the left and lower portions of the diamond, whereas those in which sulfate and/or chloride are the dominant anions are plotted on the upper and right portions of the diamond.

These trilinear plots show that the cation composition varies from region to region but is generally dominated by a mixture of calcium and magnesium or calcium, magnesium, sodium, and potassium (Figures 8-1 [a - i]). Exceptions to this are in Florida (3C) (Figure 8-1i) and in the

Poconos/Catskills (1D)

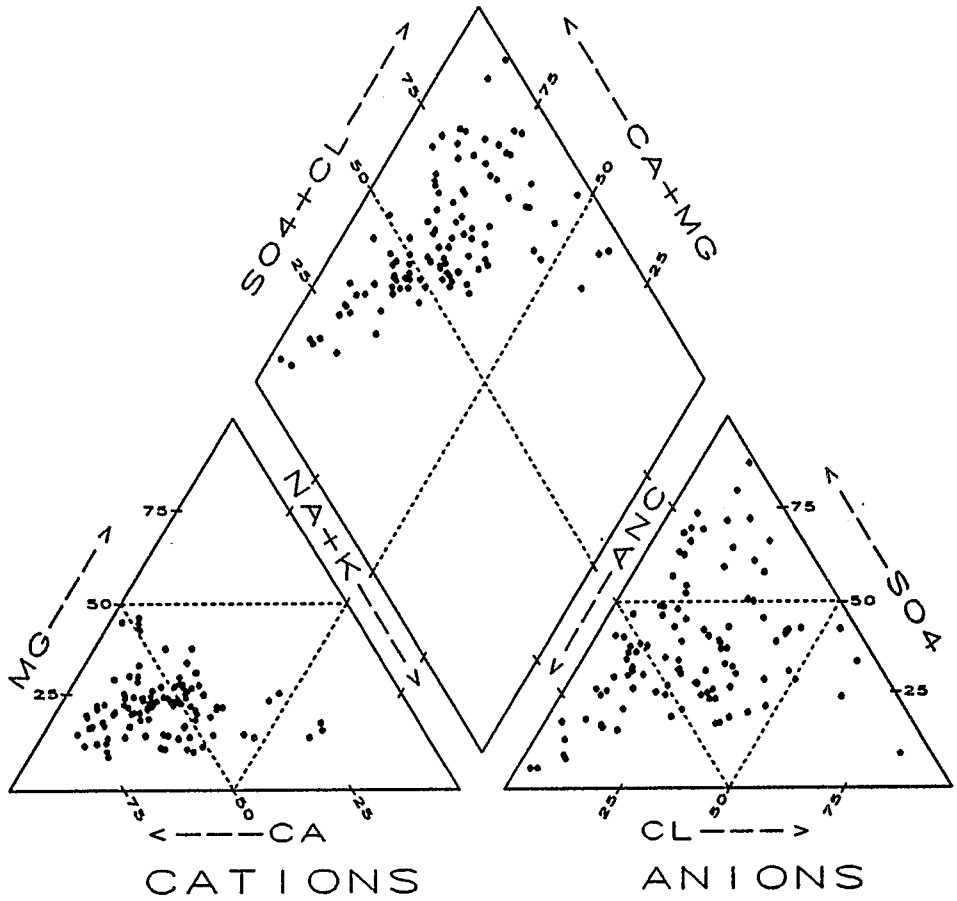


Figure 8-1a. Trilinear plots of major cations and anions in stream water at the upper and lower nodes combined in subregion 1D (Poconos/Catskills).

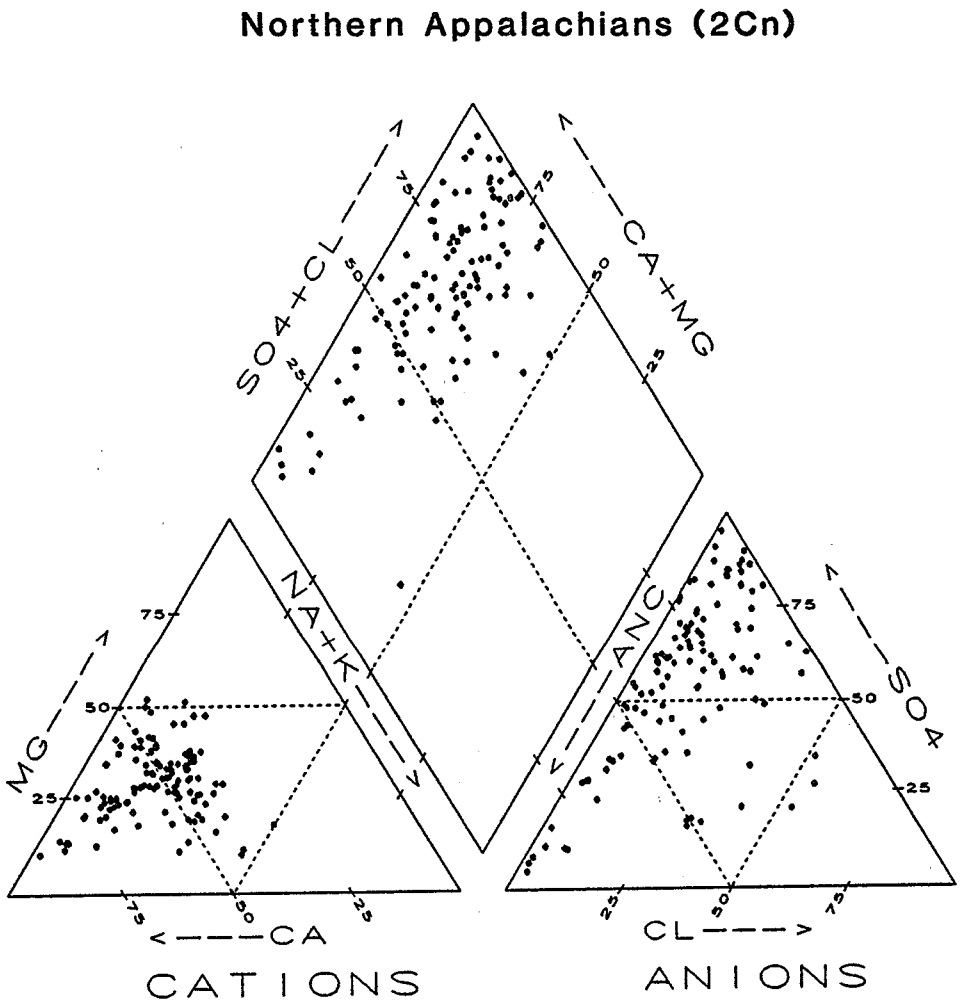


Figure 8-1b. Trilinear plots of major cations and anions in stream water at the upper and lower nodes combined in subregion 2Cn (Northern Appalachians).

Valley and Ridge (2Bn)

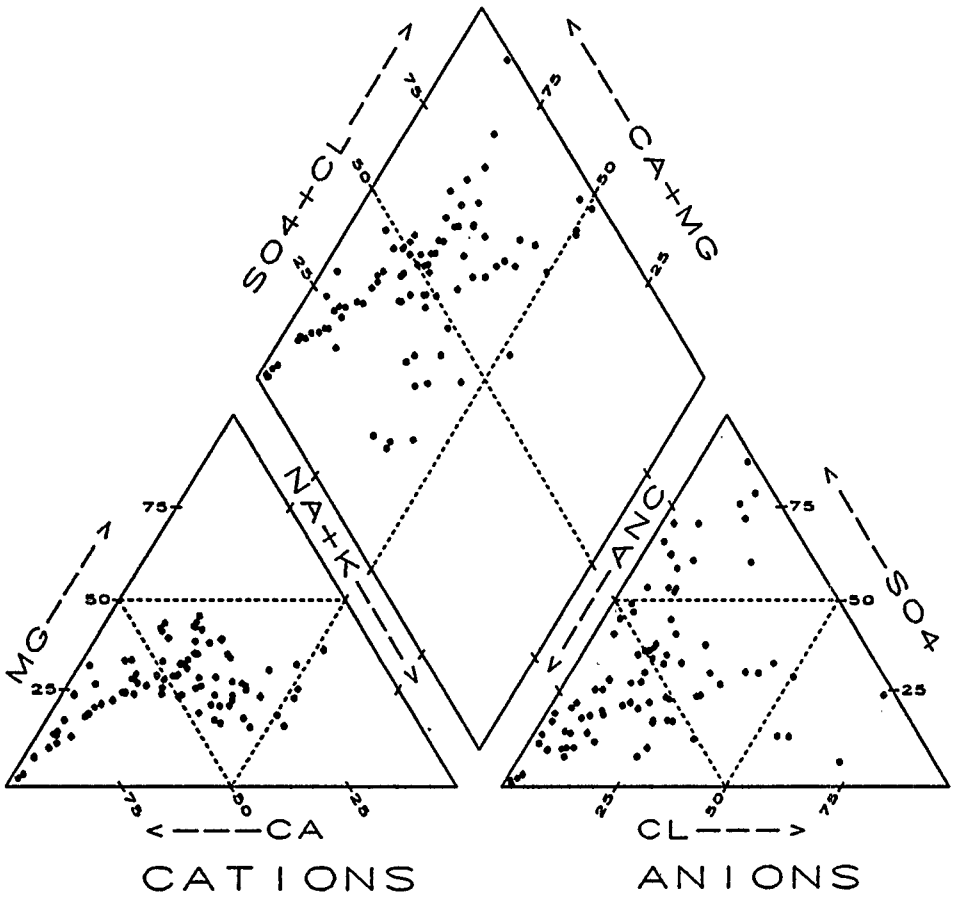


Figure 8-1c. Trilinear plots of major cations and anions in stream water at the upper and lower nodes combined in subregion 2Bn (Valley and Ridge).

Mid-Atlantic Coastal Plain (3B)

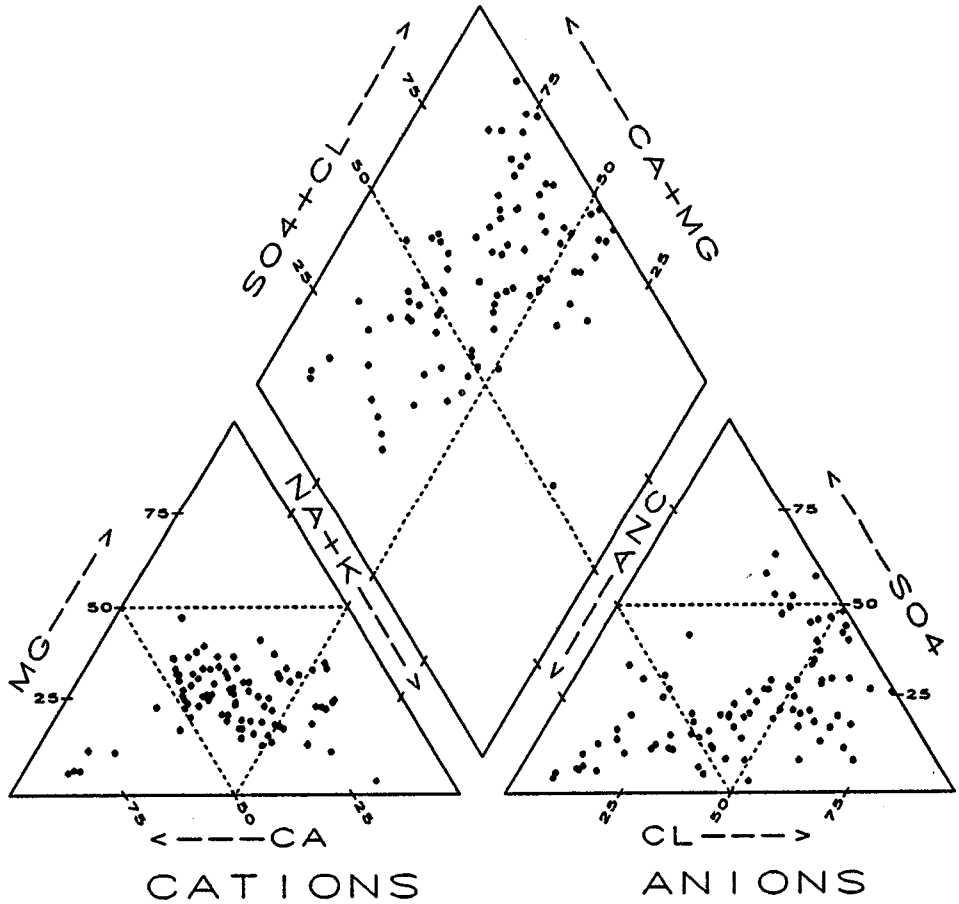


Figure 8-1d. Trilinear plots of major cations and anions in stream water at the upper and lower nodes combined in subregion 3B (Mid-Atlantic Coastal Plain).

Southern Blue Ridge (2As)

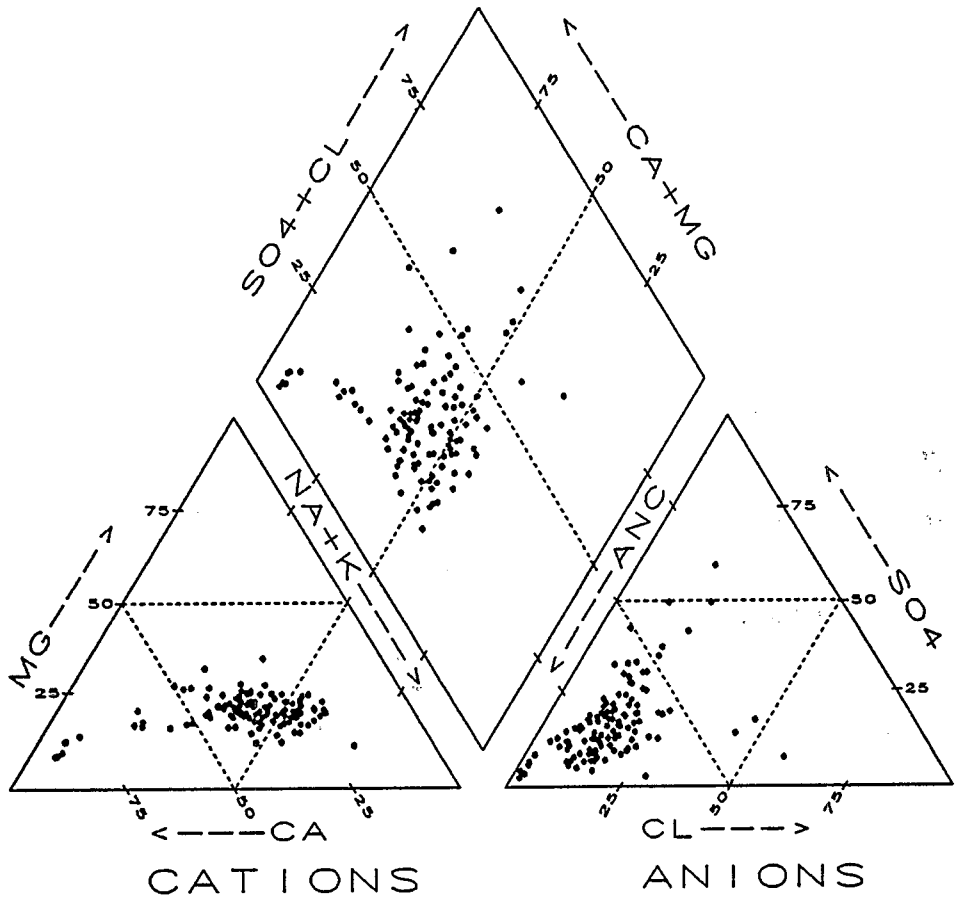


Figure 8-1e. Trilinear plots of major cations and anions in stream water at the upper and lower nodes combined in subregion 2As (Southern Blue Ridge).

Piedmont (3A)

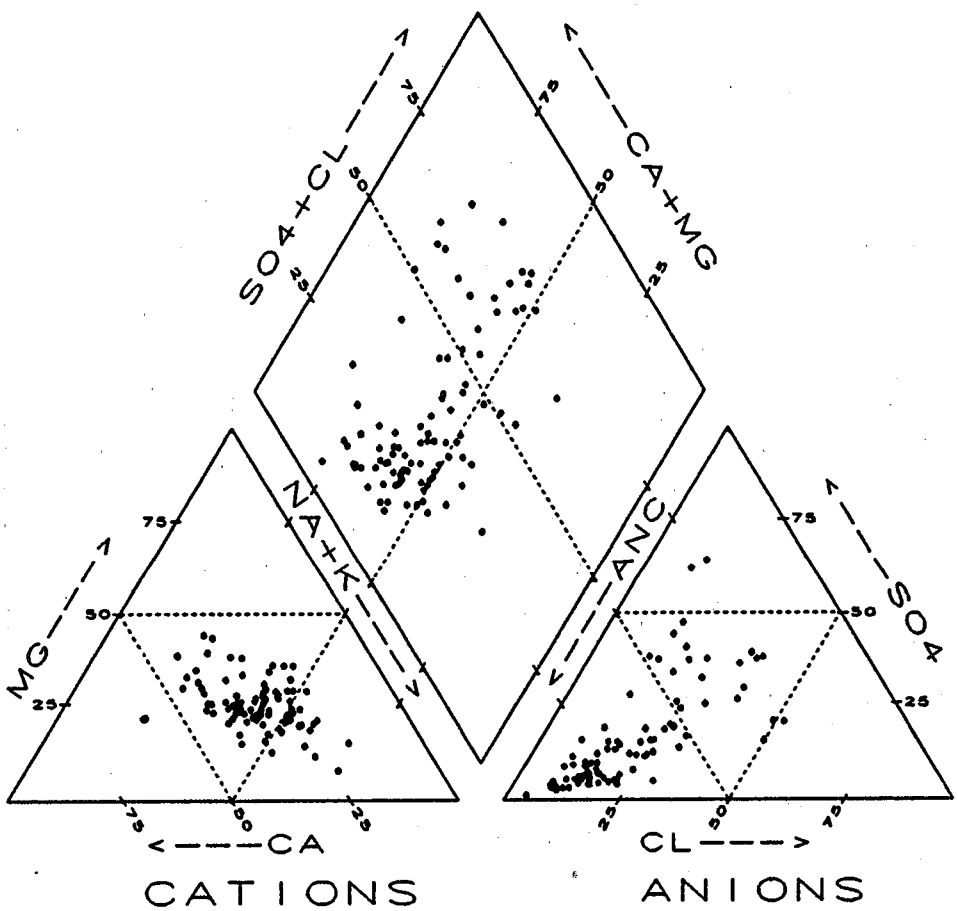


Figure 8-1f. Trilinear plots of major cations and anions in stream water at the upper and lower nodes combined in subregion 3A (Piedmont).

Southern Appalachians (2X)

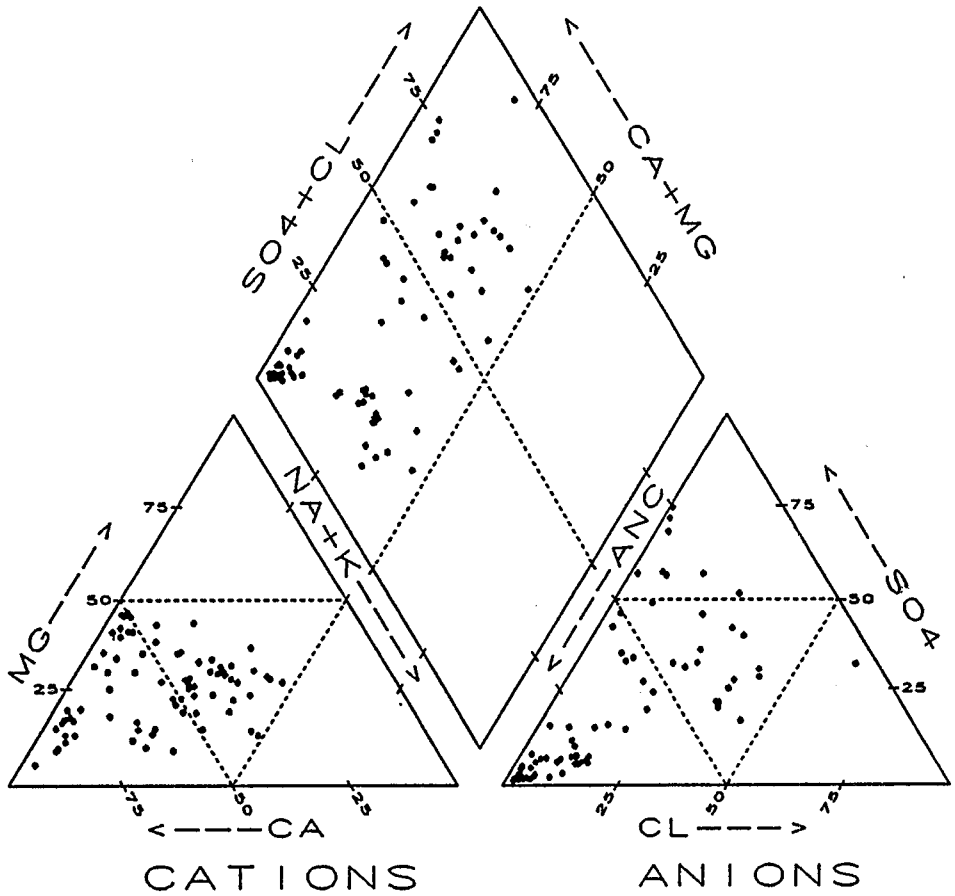


Figure 8-1g. Trilinear plots of major cations and anions in stream water at the upper and lower nodes combined in subregion 2X (Southern Appalachians).

Ozarks/Ouachitas (2D)

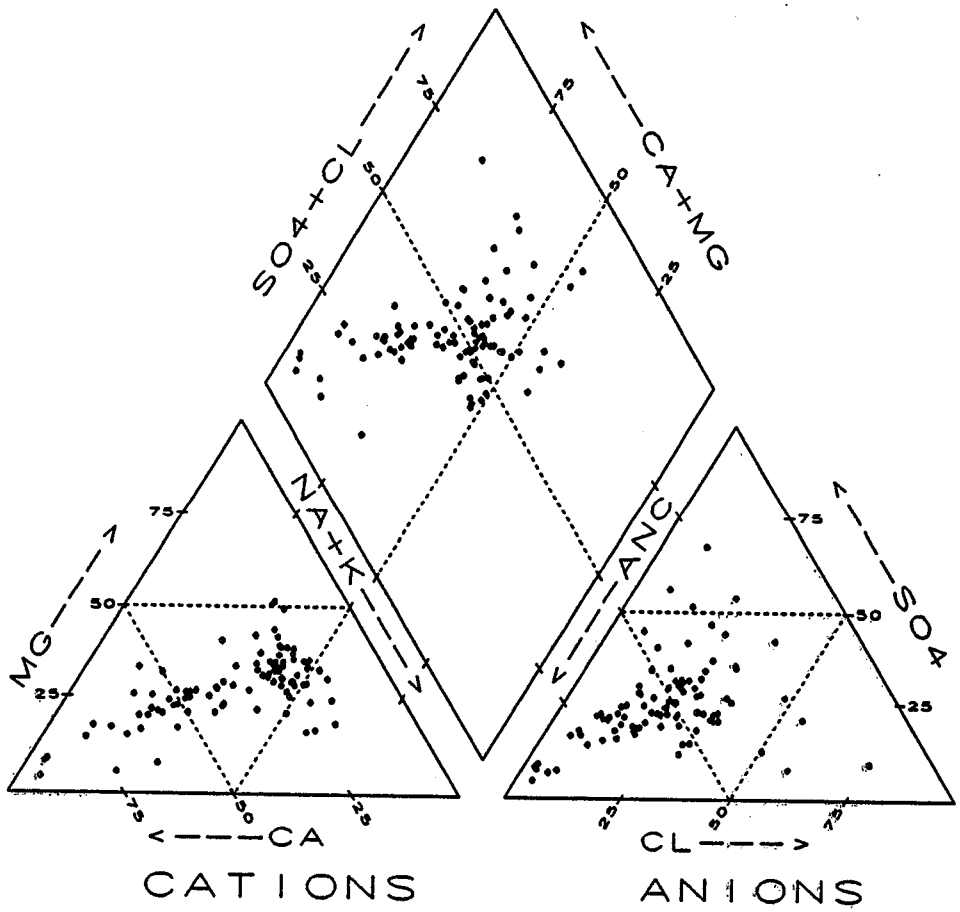


Figure 8-1h. Trilinear plots of major cations and anions in stream water at the upper and lower nodes combined in subregion 2D (Ozarks/Ouachitas).

Florida (3C)

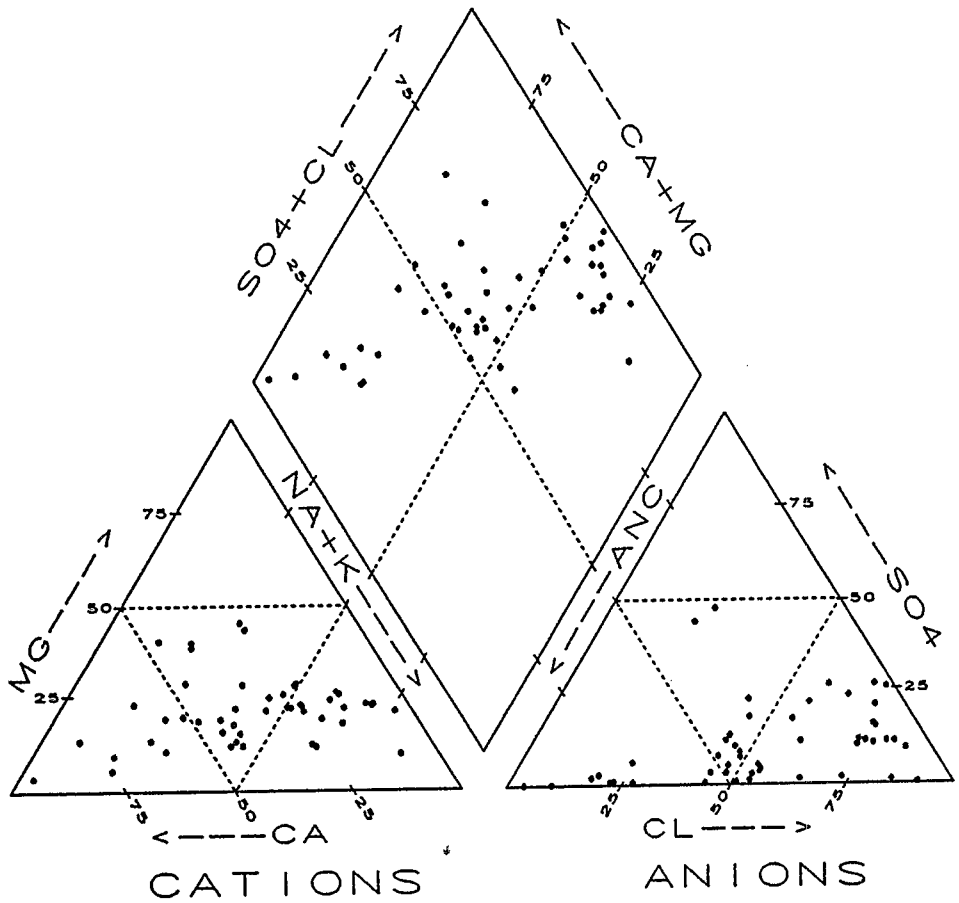


Figure 8-1i. Trilinear plots of major cations and anions in stream water at the upper and lower nodes combined in subregion 3C (Florida).

Mid-Atlantic Coastal Plain (3B) (Figure 8-1d), where sodium and/or potassium are the dominant cations in many of the streams. Sodium is a major fraction of the cation equivalents in both of these coastal subregions. The fact that chloride is also an important contributor to the anionic equivalence in both subregions suggests a sea salt contribution to the sodium and chloride content of stream water in both regions, although anthropogenic (e.g., road salt), and geological sources of chloride (groundwater flowing through salt-bearing formations) cannot be ruled out. However, given the proximity of both subregions to the coast, it is likely that sea salt deposition is the primary source of the higher sodium and chloride in stream water in both subregions.

The trilinear plots also show that sodium and/or potassium are important in some streams in the Ozark/Ouachitas (2D) (Figure 8-1h) and the Valley and Ridge (2Bn) (Figure 8-1c). Because chloride is also an important contributing anion in some streams in these subregions and the greater distance of the streams in subregion 2D from the coast compared to those in subregions 3C and 3B, it seems likely that geological and/or anthropogenic sources of salt, rather than sea salt deposition, are the primary causes of the higher contribution of sodium and chloride to the ion equivalents in these streams.

The fractional composition of anions is quite variable among the subregions. In most of the subregions, ANC, chloride, and sulfate dominate the anionic equivalents, although organic anions and nitrate are important in some streams in the Mid-Atlantic Coastal Plain (3B) (Figure 8-2d) and the Southern Appalachians (2X) (Figure 8-2g). Since nitrate is generally found in low concentrations in most pristine surface waters (Hem, 1985), these high nitrate levels suggest either agricultural (fertilizer) runoff, runoff from mature forests that are losing nitrate perhaps because of reduced nitrogen demand by the forest, or industrial/municipal inputs of wastes containing nitrate. Sulfate is the dominant anion in most of the streams in the Northern Appalachians (2Cn) and the Poconos/Catskills (1D) (Figures 8-1a,b; 8-2a,b]). Sulfate also contributes a major fraction of the anion equivalents in several sample streams in the Valley and Ridge (2Bn) and the Mid-Atlantic Coastal Plain (3B). In contrast, bicarbonate or bicarbonate plus chloride are the dominant anions in most streams in the Southern Appalachians (2X), the Piedmont (3A), the Ozarks/Ouachitas (2D), and the Southern Blue Ridge (2As) Figures 8-1 [e - h]). Bicarbonate is also the major anion in over half of the sample stream reaches in subregion 2Bn (Figure 8-1c). These plots thus show major differences in the ion composition of streams among the subregions, with sulfate being a major anion in many or most of the streams in the more northern subregions (2Cn and 1D). Streams in the Interior Southeast subregions (2X, 2D, 3A, and 2As), however, are dominated by bicarbonate or bicarbonate plus chloride. Streams in Florida (3C) are dominated by chloride, reflecting the apparent effect of sea salt deposition. Streams in subregions 1D and 2Bn exhibit no clear pattern, with some streams dominated by bicarbonate or sulfate and many of the streams containing almost equal fractions of bicarbonate, sulfate, and chloride (Figures 8-1 [a and c]).

The total ion content as well as the distribution of the major inorganic cations and inorganic and organic anions in stream water can also be examined as a function of pH or ANC classes by means of so-called ion fingerprint plots (Figures 8-2 [a - i]). These figures illustrate the population-weighted average distribution of ions in absolute concentrations in streams of different pH. The plots thus show not only the average ion composition of streams in each pH class in the various subregions but also the changes in average ion composition over the range of pH. In these plots, organic anions were assumed to be equal to the anion deficit.

The ionic strength of stream water in most of the regions exhibits a general pattern of decline with decreasing pH, although it does not decline monotonically in all subregions. The ionic content of streams in the lowest pH class in subregion 3C, for example, increases sharply,

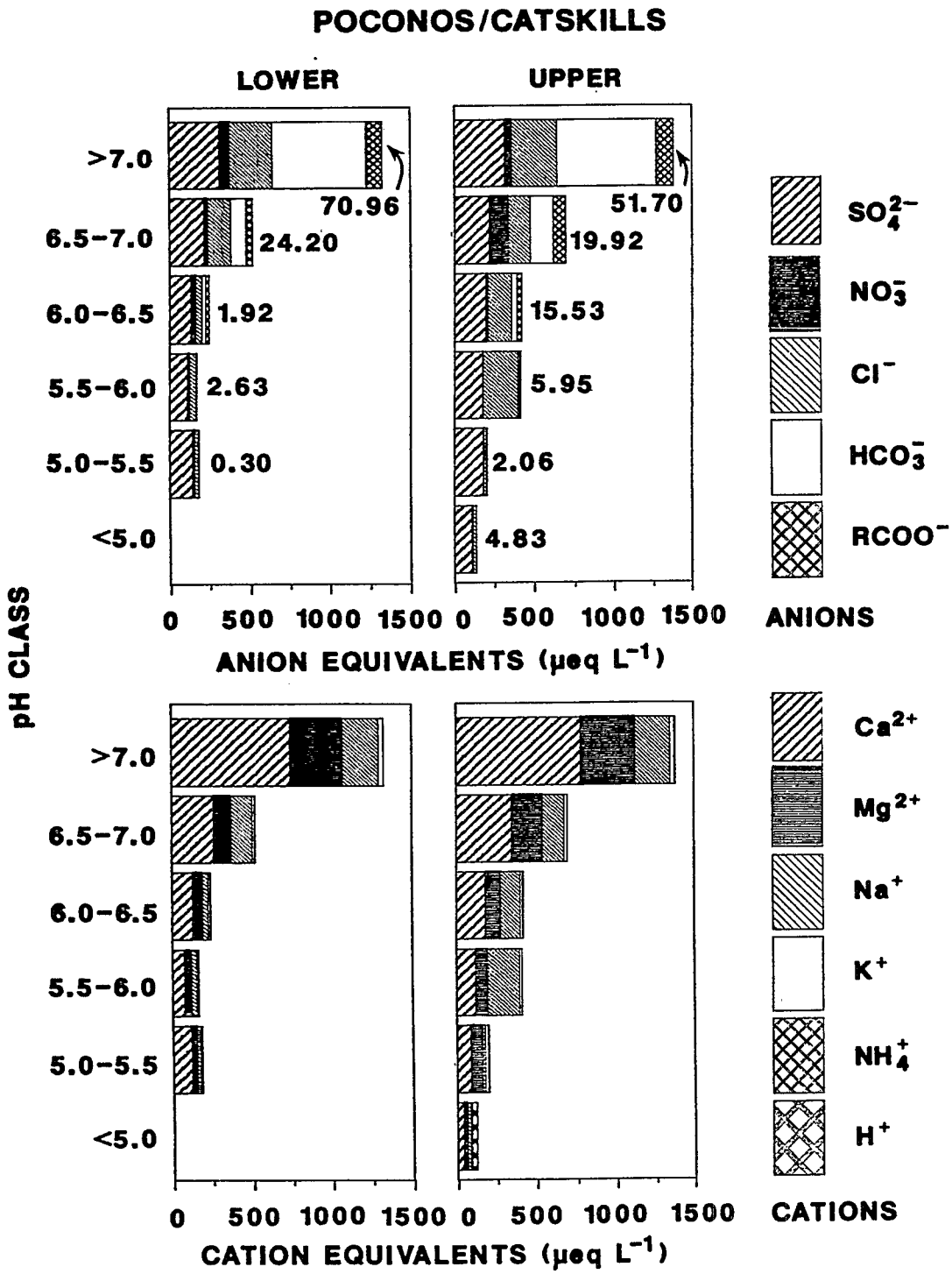


Figure 8-2a. Weighted average concentration of major anions and cations by pH class of stream water at the upper and lower nodes in subregion 1D (Poconos/Catskills). The numbers next to the anion bars give the estimated percentage of streams in each of the pH classes.

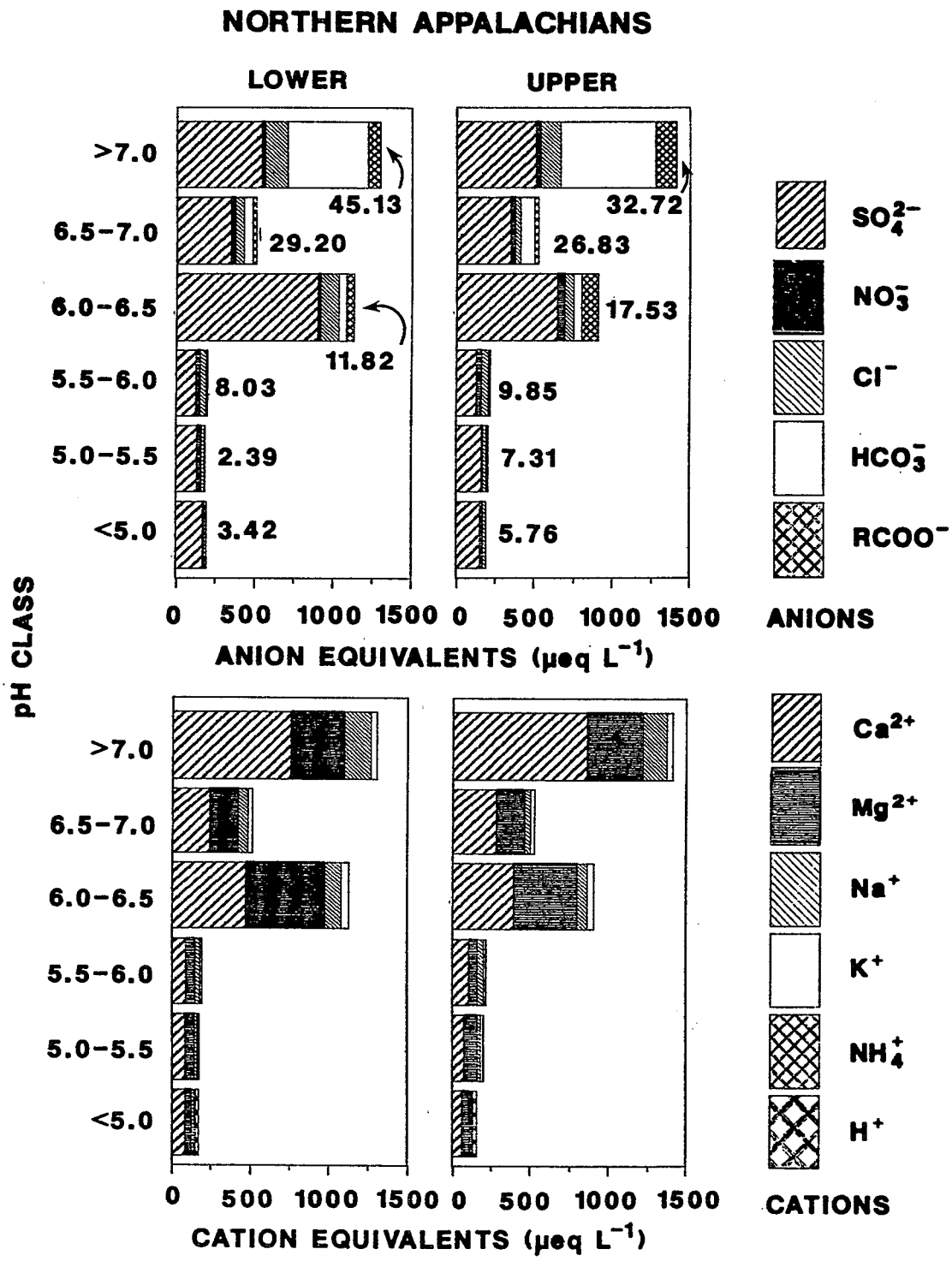


Figure 8-2b. Weighted average concentration of major anions and cations by pH class of stream water at the upper and lower nodes in subregion 2Cn (Northern Appalachians). The numbers next to the anion bars give the estimated percentage of streams in each of the pH classes.

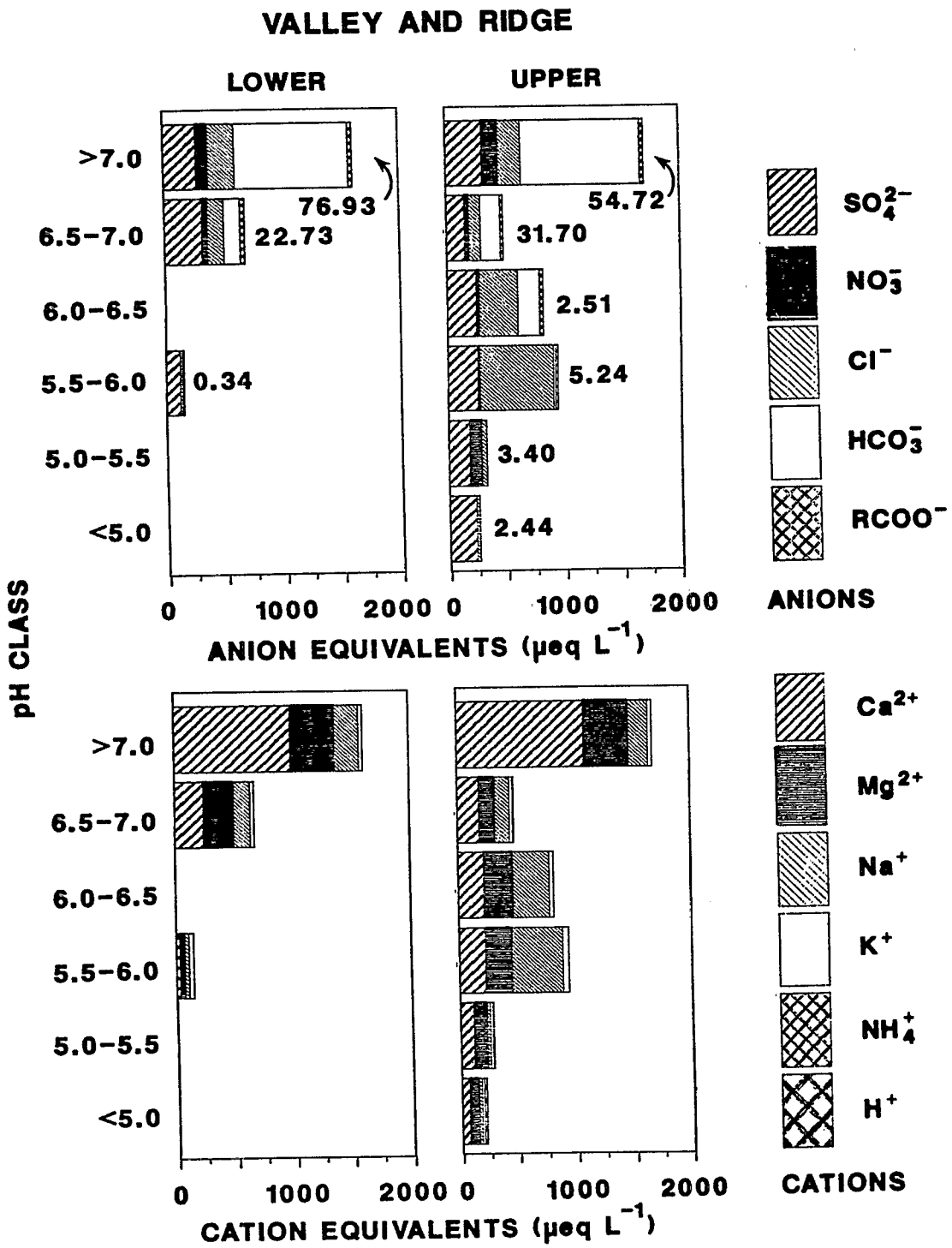


Figure 8-2c. Weighted average concentration of major anions and cations by pH class of stream water at the upper and lower nodes in subregion 2Bn (Valley and Ridge). The numbers next to the anion bars give the estimated percentage of streams in each of the pH classes.

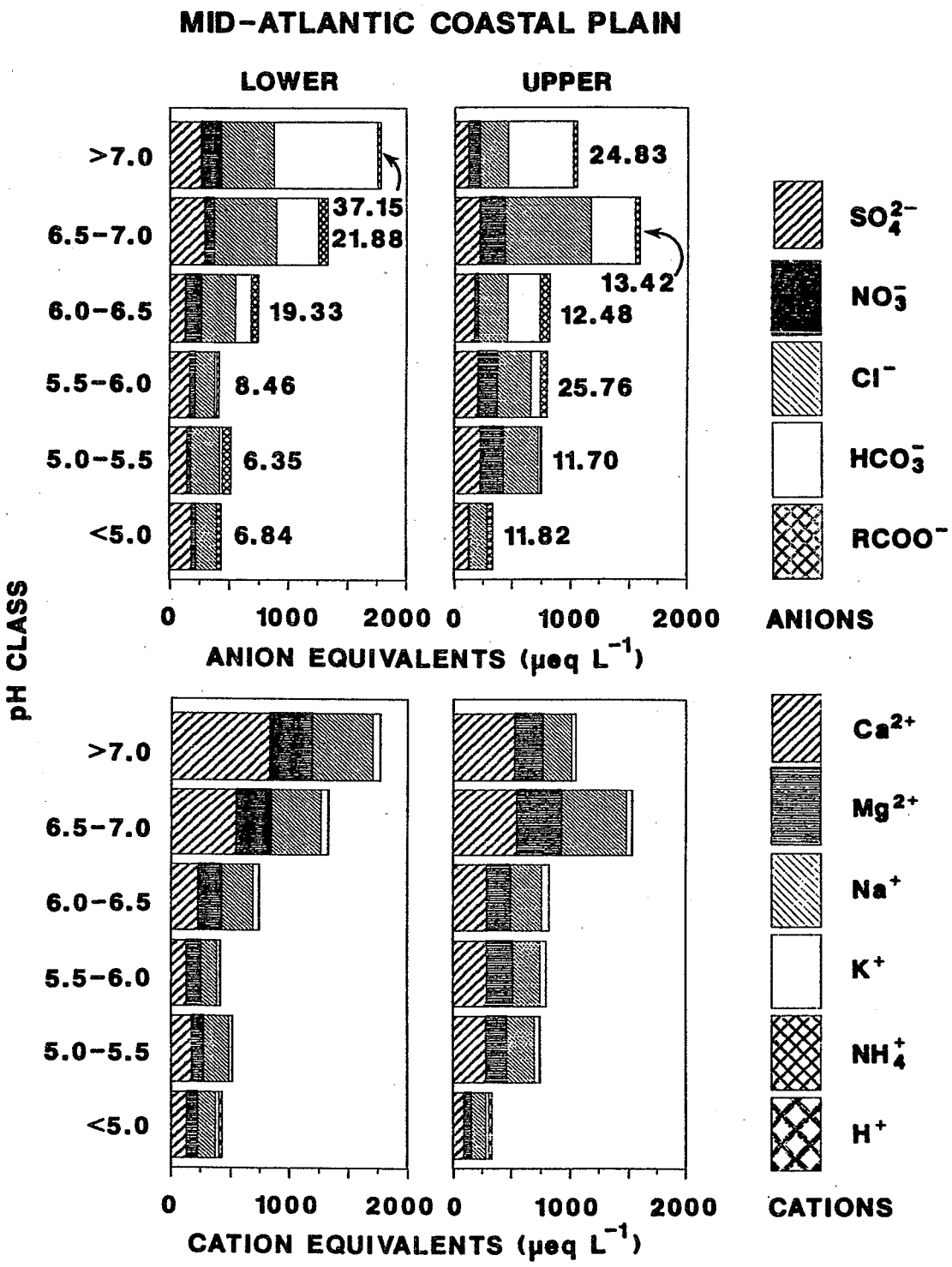


Figure 8-2d. Weighted average concentration of major anions and cations by pH class of stream water at the upper and lower nodes in subregion 3B (Mid-Atlantic Coastal Plain). The numbers next to the anion bars give the estimated percentage of streams in each of the pH classes.

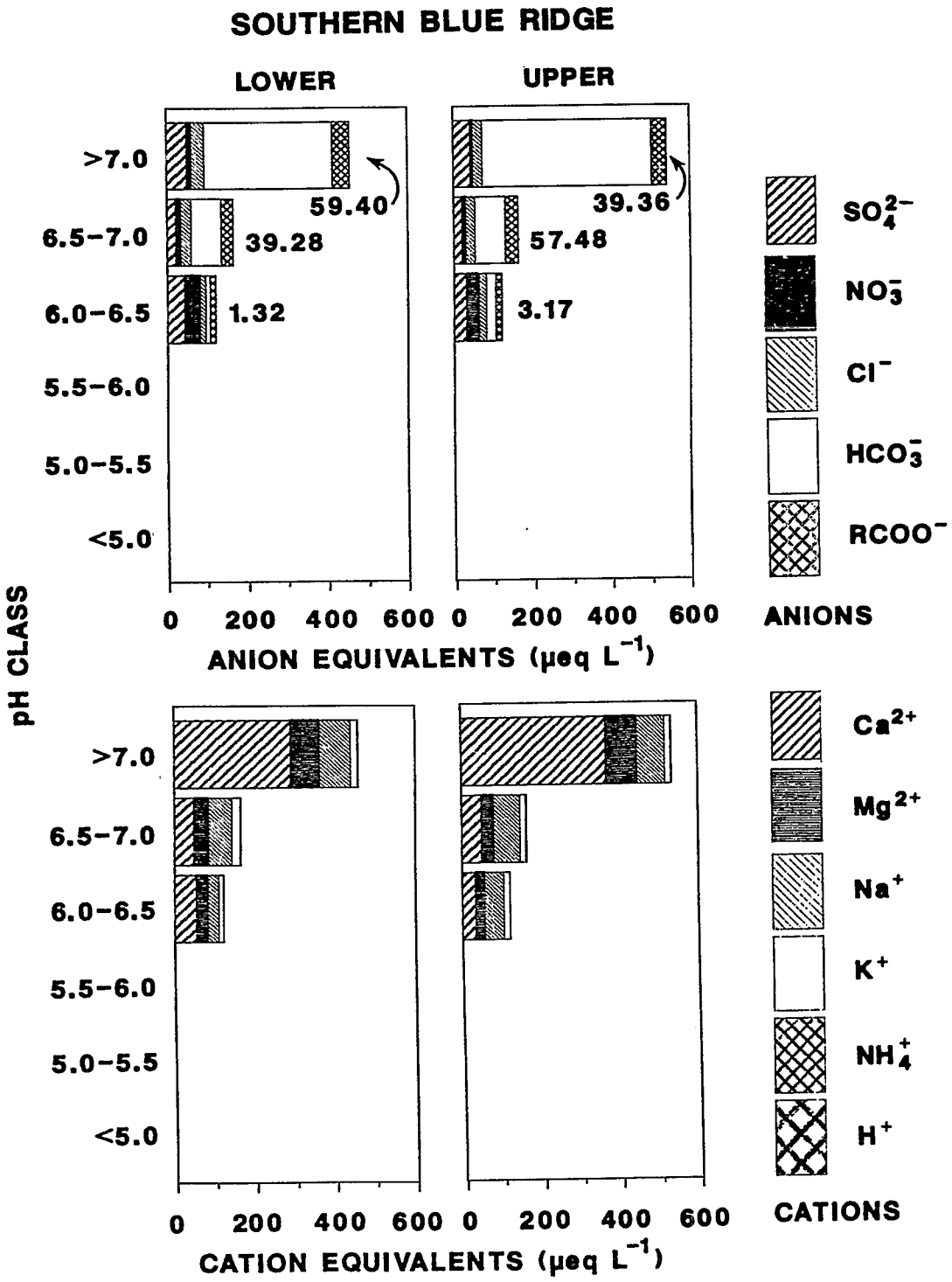


Figure 8-2e. Weighted average concentration of major anions and cations by pH class of stream water at the upper and lower nodes in subregion 2As (Southern Blue Ridge). The numbers next to the anion bars give the estimated percentage of streams in each of the pH classes.

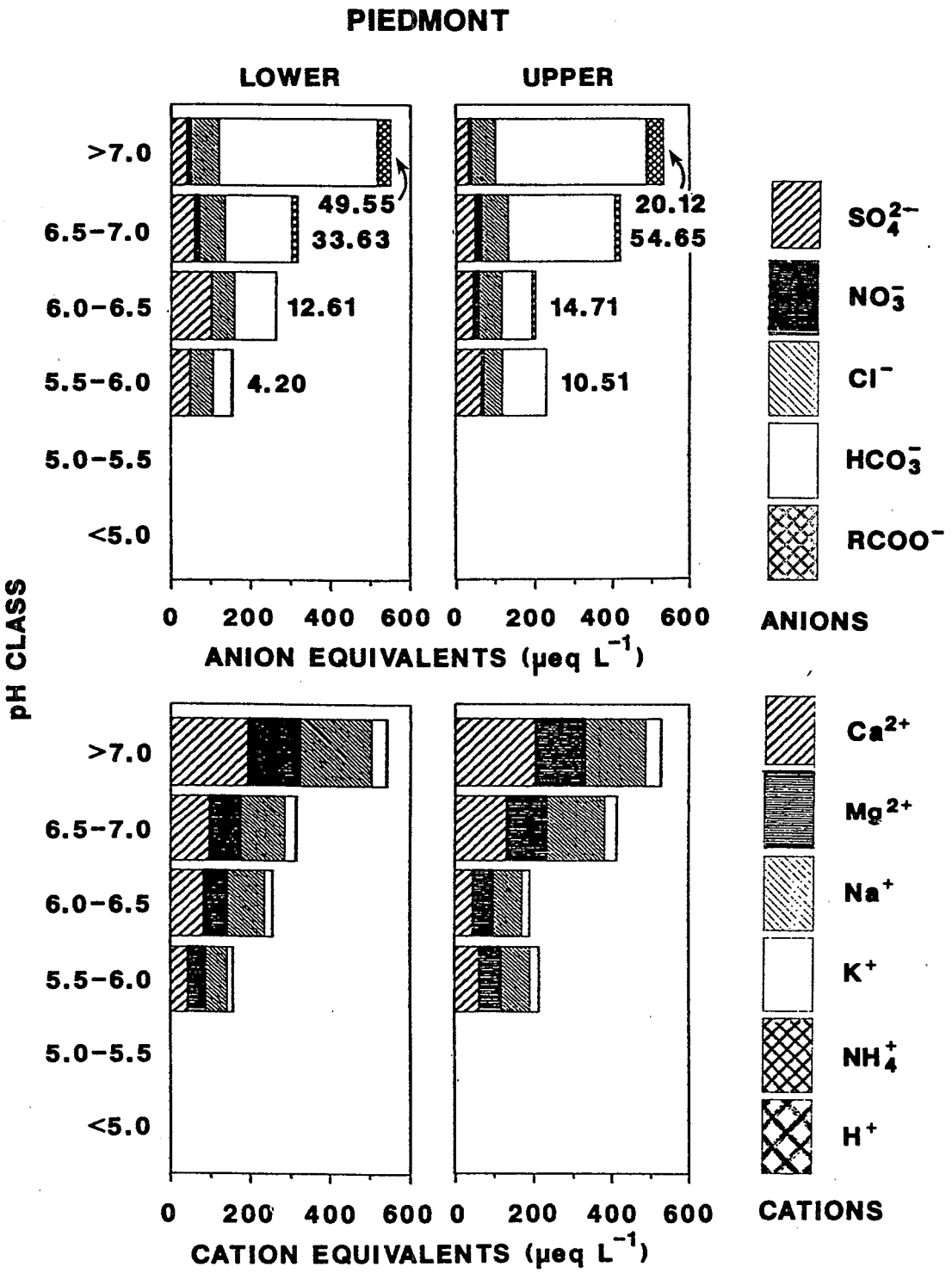


Figure 8-2f. Weighted average concentration of major anions and cations by pH class of stream water at the upper and lower nodes in subregion 3A (Piedmont). The numbers next to the anion bars give the estimated percentage of streams in each of the pH classes.

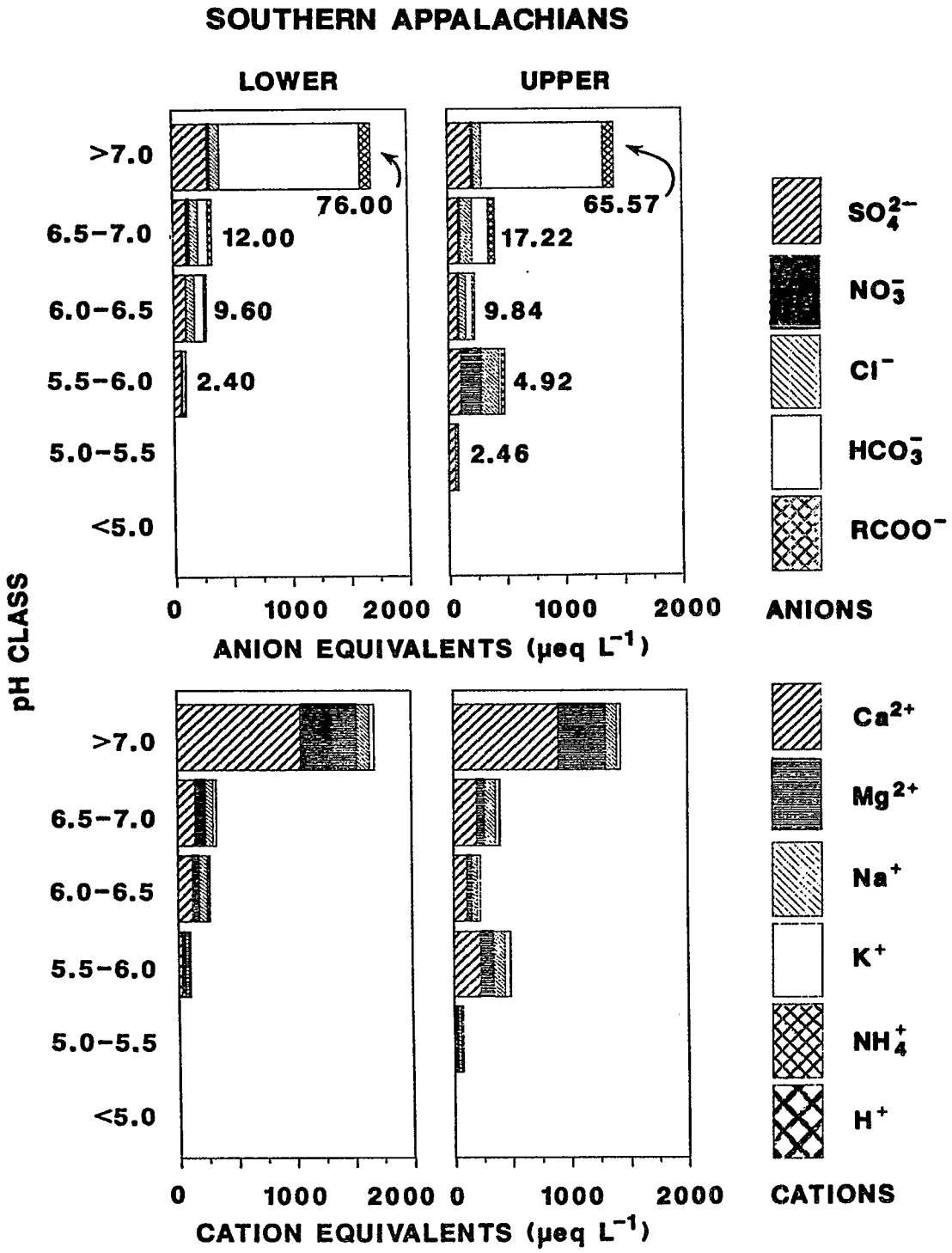


Figure 8-2g. Weighted average concentration of major anions and cations by pH class of stream water at the upper and lower nodes in subregion 2X (Southern Appalachians). The numbers next to the anion bars give the estimated percentage of streams in each of the pH classes.

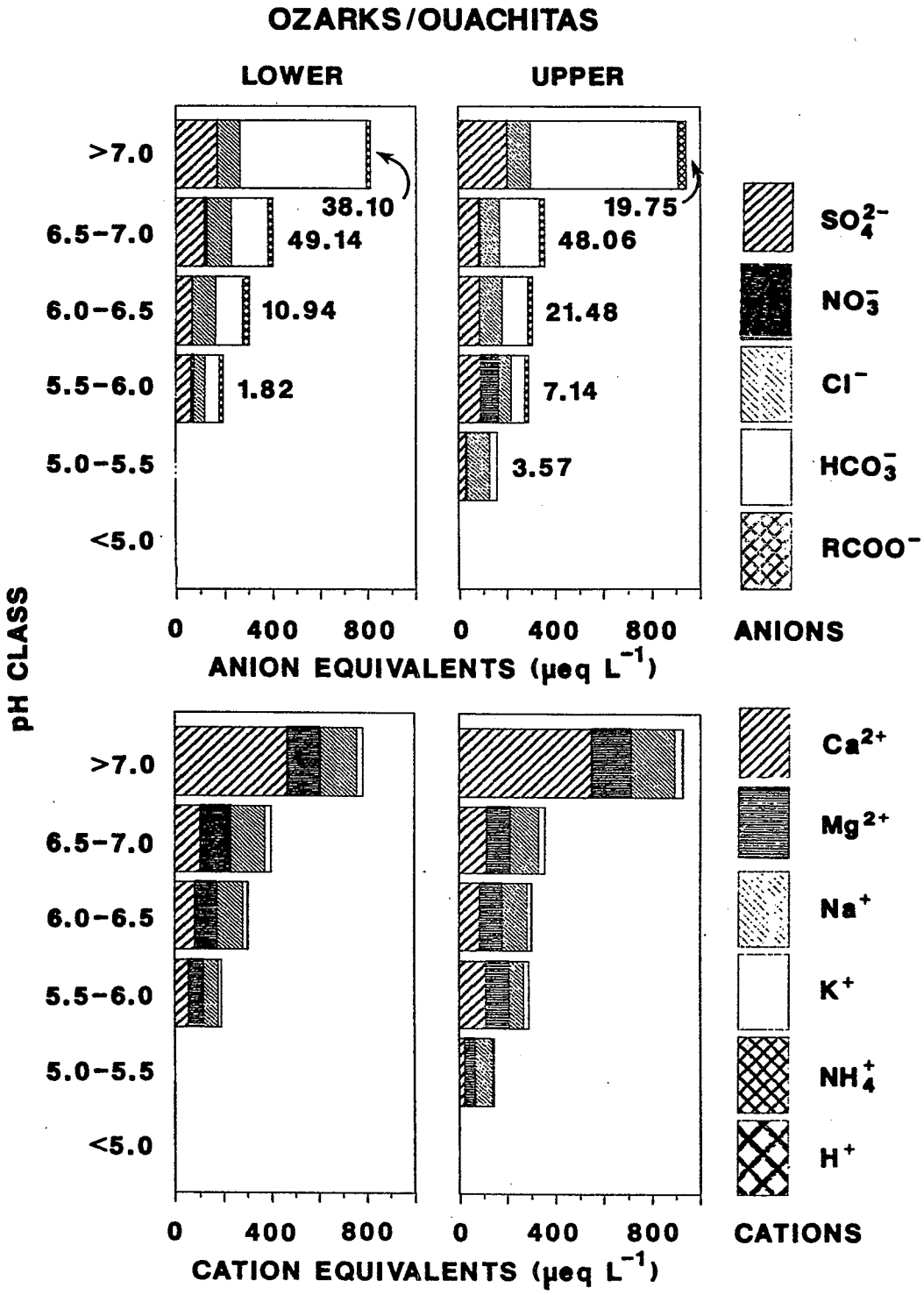


Figure 8-2h. Weighted average concentration of major anions and cations by pH class of stream water at the upper and lower nodes in subregion 2D (Ozarks/Ouachitas). The numbers next to the anion bars give the estimated percentage of streams in each of the pH classes.

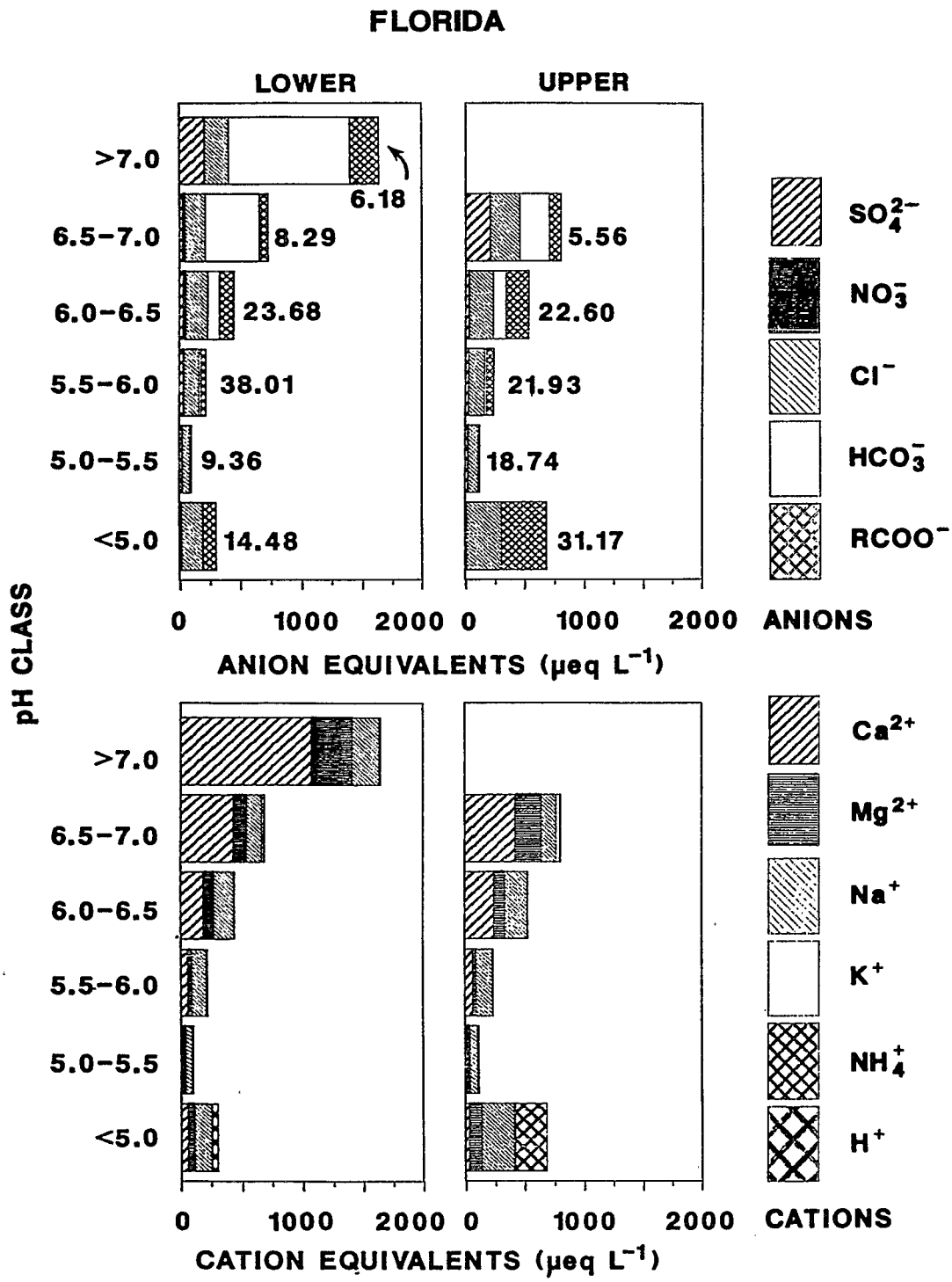


Figure 8-2i. Weighted average concentration of major anions and cations by pH class of stream water at the upper and lower nodes in subregion 3C (Florida). The numbers next to the anion bars give the estimated percentage of streams in each of the pH classes.

due primarily to increases in sodium, chloride, and organic anions (Figure 8-2 [a - i]). Because of the proximity of Florida streams to the coast, this suggests a sea salt influence on the ion composition of these streams.

In all of the other subregions, ionic strength either decreases monotonically with pH across the pH classes, or exhibits a biomodal distribution. Because streams of low ionic strength also have low concentrations of base cations, they also have a lower ANC and hence include those streams considered most sensitive to acidification. The association of lower pH and ANC with lower base cation concentrations is not in itself evidence of anthropogenic acidification, however, because the decline to a level approximately equal to the equivalence point for carbonic acid may simply reflect generic differences among watersheds in the production and export of alkalinity. Such differences could be due to variation among watersheds in the export of bases caused by geologic and hydrologic factors that control weathering and exchange of base cations associated with soils and bedrock.

The monotonic decline in ionic strength with decreasing pH is most obvious at both the upper and lower nodes in the Poconos/Catskills (1D) (Figure 8-2a), the Ozarks/Ouachitas (2D) (Figure 8-2h), and the Piedmont (3A) (Figure 8-2f), and in the lower nodes in the Valley and Ridge (2Bn) (Figure 8-2c), the Southern Appalachians (2X) (Figure 8-2g), and the Southern Blue Ridge (2As) (Figure 8-2e). This pattern is an indication that the differences in pH among streams with pH > 5.5, is due in part to generic differences among the watersheds in the generation of alkalinity through the weathering of base cations by carbonic acid--not solely due to differences in the extent of acidification resulting from inputs of strong acids. The ionic strength of stream water would be expected to remain the same, or to increase with declining pH, if the decrease in pH was due entirely to titration in which bicarbonate is replaced by strong acid anions, eventually resulting in an increase in acidic cations. For streams with pH far enough below the equivalence point for carbonic acid ($\approx$ 5.5), differences in carbonic acid weathering among watersheds cannot explain the low pH, because at this level, strong acids predominate (ANC < 0). It should be emphasized however, that use of the average ion composition of streams among pH classes may obscure major differences in the ion composition among streams within a given pH class. Hence, the presence of a monotonic decline in ionic strength with declining pH in a subregion should not be taken as evidence that no acidification has occurred.

If the differences in pH and ANC between streams in the different pH classes were due mainly to differences in recent, ongoing inputs of strong acids from the watersheds, and base cation export rates remained constant, the ionic content of stream water would be expected to remain the same or to increase with decreasing pH. In this case, as the carbonate alkalinity is replaced by strong acid anions (SO_4^{2-}, NO_3^-, Cl^-) and the concentration of acidic cations (H^+, Al^{n+}) increases, ionic strength increases or remains constant. The fact that the observed ionic strength tends to decrease across stream groupings of decreasing pH suggests that ongoing titration of the alkalinity is not occurring in the subregions where this pattern exists, unless base cation depletion is occurring.

The inherent or pre-existing differences in alkalinity generation among watersheds could be due entirely to natural differences in the geological, soil, and hydrological characteristics of each watershed, for example, differences in pool sizes of readily weatherable and exchangeable base cations, differences in hydrologic flow paths of water through the watershed, or differences in the production of natural organic acids. However, they could also be a result of anthropogenically caused differences: long-term deposition of strong acids and a resulting leaching of base cations from the soil. In areas where the base saturation of soils is low, a decline in the export of base cations could result from the reduction in the pools of readily weatherable or

exchangeable base cations due to soil acidification (i.e., reduction in base exchange capacity) (Reuss and Johnson, 1985).

The ion composition of stream water in those regions where ionic strength does not decline monotonically with decreasing pH suggests major geochemical or hydrologic differences between watersheds, major differences in atmospheric deposition of materials on the watershed, or both. Evidence of such intra-regional generic differences is illustrated by the data on cation and anion composition of stream water in the Valley and Ridge (2Bn) (Figure 8-2c) and the Northern Appalachians (2Cn) (Figure 8-2b). At the upper node in subregion 2Bn, streams with a pH > 7 have much higher calcium and magnesium concentrations than those with lower pH. The second peak in ionic strength, however, is due primarily to increases in sodium and chloride, suggesting an internal source of salt (e.g., road salt) in some of the watersheds in these intermediate pH classes. This pattern for calcium and magnesium content at the upper node indicates that streams with a pH > 7 drain watersheds with some carbonate or dolomitic bedrock, whereas those with a lower pH drain watersheds with little or no carbonate bedrock.

The pattern of increasing sodium and chloride content along the gradient between the pH > 7 group and the pH 5.5 - 6.0 group in subregion 2Bn (Figure 8-2c) suggests an internal source of chloride in these watersheds. Although the exact source is unknown, runoff of road salt and inputs of groundwater that has flowed through salt-bearing geological formations are suspected causes. The Valley and Ridge Province is known to contain marine shales that have a relatively high content of leachable sodium and chloride (Von Damm, 1987) and some of the watersheds have roads that may have been de-iced with road salt.

Both the upper and lower nodes of streams sampled in the Northern Appalachians (2Cn) (Figure 8-2b) and Florida (3C) (Figure 8-2i) and the upper nodes of streams in the Mid-Atlantic Coastal Plain (3B) (Figure 8-2d) and the Southern Appalachians (2X) (Figure 8-2g) exhibit bimodal distributions in ionic strength. In subregion 2Cn, the bimodal distribution of cations is due primarily to changes in calcium and magnesium content, while the trend in the anionic solute distribution is caused primarily by changes in sulfate and bicarbonate. This pattern could be caused by several factors, among them a high deposition rate of sulfate acidity or an internal source of sulfate acidity (e.g., pyrite oxidation), which enhanced the export of calcium and magnesium from the watersheds following increased weathering and/or cation exchange, an anthropogenic source of calcium that buffered some of the acidity (liming streams), or some combination of both.

In the Florida streams, the bimodal distribution in ionic content is associated primarily with changes in the calcium, sodium, organic anions, and chloride concentration (Figure 8-2i). The decreasing gradient in ionic strength between the pH > 7 group and the pH 5.5 - 6.0 group appears to be associated primarily with decreases in calcium, whereas the increasing ionic strength in the pH < 5.0 group is due primarily to increases in sodium, chloride, and organic anions. Because of the proximity of the Florida streams to the ocean, this pattern for sodium and chloride suggests that sea salt is probably the source of these ions. Whether these sources of sodium and chloride are related to wet and dry deposition, land use, or geologic sources is unknown. It is also possible that the low pH (< 5.0) is due to organic acidity as evidence by the large amount of organic anions in this pH group. The potential sources of acidity in Florida (3C) streams are discussed in more detail later in this section and in Section 9.

8.3 ALUMINUM

Cronan and Schofield (1979) hypothesized that mineral acids from atmospheric deposition have altered the natural process of soil weathering and development by augmenting the export

of aluminum from soil to surface waters. The mechanism responsible for this increased export of aluminum may involve cation exchange in soils with low base saturation, dissolution of primary and secondary mineral phases of aluminosilicate minerals, or some combination of both. Supporting evidence for the effect of acidic deposition on the mobilization and export of aluminum from watersheds is that in acid-sensitive regions receiving high atmospheric loadings of strong mineral acids, high concentrations of both H^+ and aluminum are observed in surface waters when the ratio of acidic anion equivalents (sulfate and nitrate) to basic cations exceeds one (Driscoll and Newton, 1985). Because the change in this ratio from < 1 to > 1 reflects a shift from carbonic acid weathering to mineral acid weathering, dissolution at low pH of aluminum in clay minerals by strong mineral acids is generally invoked to explain the aluminum increase in surface waters.

Because of the dependency of aluminum solubility on pH, extractable aluminum concentration is expected to increase with decreasing pH, particularly when the pH declines to < 5.5. Plots of both extractable (MIBK) aluminum and an estimate of inorganic monomeric aluminum (subsection 6.3.2) versus pH of streams in the NSS-I show that, in general, this relationship holds, with streams having a pH > 5.5 typically containing low and relatively uniform concentration of extractable and inorganic monomeric aluminum, whereas those with a pH < 5.5 exhibit higher concentrations of aluminum (Figure 8-3b,c). In contrast, total aluminum concentrations showed no relationship with pH, indicating that most of the aluminum in stream water is in a colloidal or particulate form (Figure 8-3a).

Aluminum appears to be toxic to fish at concentrations above the range of 100 to 200 $\mu g\ L^{-1}$, levels commonly observed in acidic surface waters. The extent of toxicity, however, appears to be dependent on the form of aqueous aluminum. Driscoll et al. (1980) and Baker and Schofield (1982) reported that aluminum toxicity to brook trout fry was greatly reduced when aluminum was complexed to organic matter. They also reported that fish survival was highly correlated with inorganic monomeric aluminum concentrations and pH. Because the labile or inorganic monomeric aluminum is thought to be the most toxic fraction, its concentration in water is of particular concern. At pH < 5.5, inorganic monomeric aluminum concentration is related to pH (Figure 8-3). However, only in the Mid-Atlantic Coastal Plain (3B) do streams with inorganic monomeric aluminum concentrations in excess of 100 $\mu g\ L^{-1}$ (3.7 μM) comprise more than 10% of the target population (Table 6-6). Population estimates for the various aluminum fractions are presented in subsection 6.3.2.

The concentration of nonlabile or organic aluminum (nonexchangeable, PCV technique) in streams sampled in the NSS-I is highly correlated with DOC concentration (Figure 8-3), a pattern consistent with that observed by Driscoll et al. (1984) for surface waters in the Adirondacks and by Turner et al. (1985) for streams in the New Jersey Pine Barrens. The nonlabile aluminum in stream water could be caused by leaching of organically complexed aluminum from plant litter and organic debris, complexation by dissolved organic matter of inorganic aluminum mobilized from soil minerals at low pH, or some combination of both.

8.4 SOURCES OF VARIATION IN ANC OF STREAM WATER

Although sulfate, nitrate, and chloride may not make up a major fraction of the anion equivalents in streams with pH > 7.0 (e.g., many Southeast streams), strong mineral acids may still contribute to the differences in pH and ANC among these streams. To determine the relative importance of mineral acid anions, organic anions, and base cations to the variation in ANC among streams, standardized multiple regression analysis (SAS, 1985) was conducted. Because NSS-I subregions are not extremely heterogeneous and because weighting factors do not

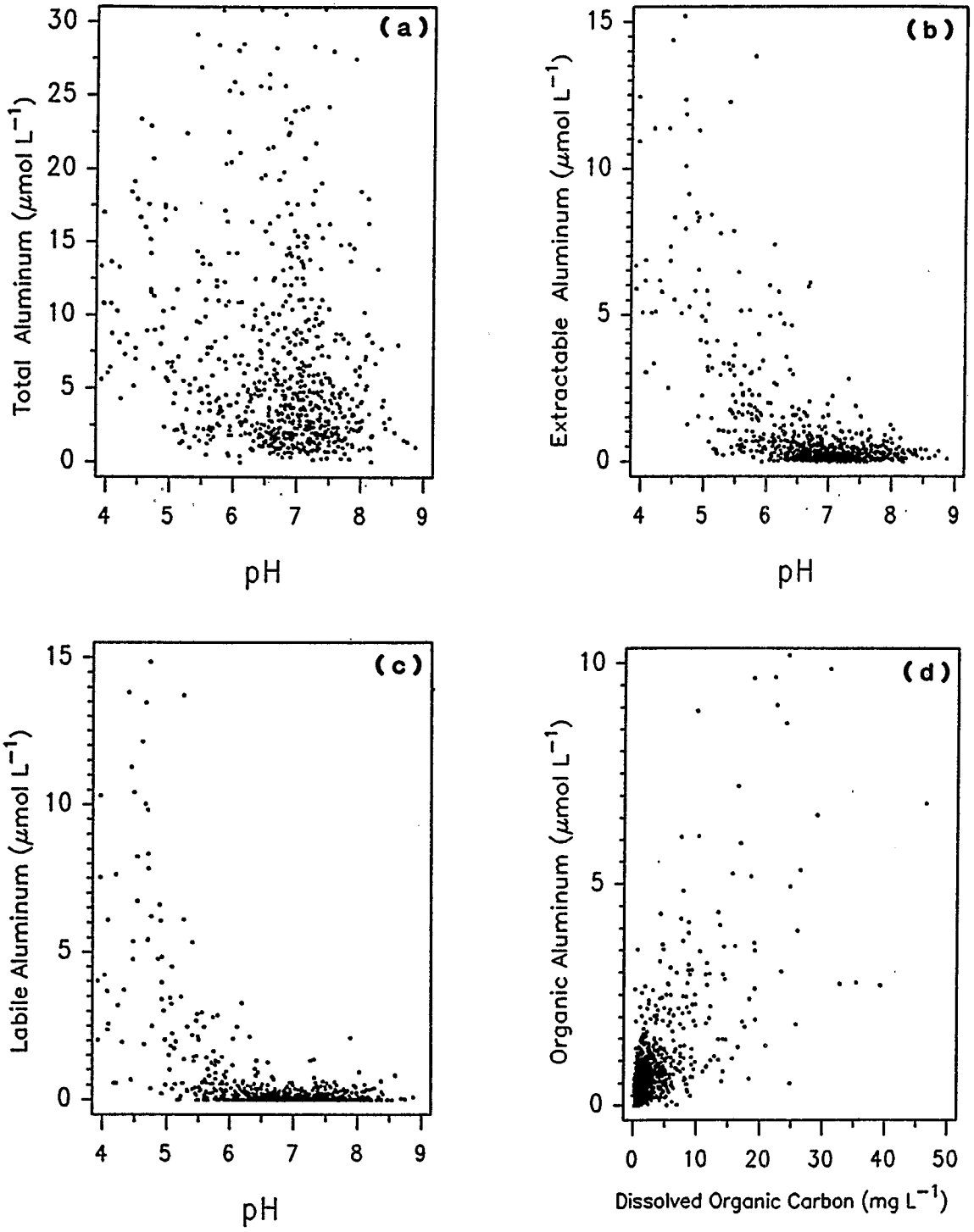


Figure 8-3. Plots of (a) total aluminum vs. pH, (b) extractable (MIBK) aluminum vs. pH, (c) labile or inorganic monomeric aluminum vs. pH, and (d) organic aluminum vs. DOC in streams of the NSS-I.

vary substantially within each NSS-I subregion, regressions employing unweighted sample data will not differ substantially from descriptions of population characteristics within NSS-I subregions. When weighting factors differ substantially, as they do among sample streams from different NSS-I subregions, multivariate models based on unweighted sample data may incorrectly describe a relationship for the regional stream population. This section describes the standardized multivariate regression analyses conducted within separate NSS-I subregions, removing the absolute necessity for using population weighting.

The standardized regression coefficient (b_i') is defined as:

$$b_i' = b_i\,[s_{xi}/s_y]$$

where b_i is the partial regression coefficient for the independent variable i, and s_{xi} and s_y are the standard deviations of the independent variable x_i and the dependent variable y, respectively.

Because the standard deviations of the dependent and independent variables are generally not the same, and because not all of the independent variables are measured in the same units (e.g., acid anions are measured in μeq L^{-1}, DOC is in mg L^{-1}), the partial regression coefficient does not provide a relative measure of the influence of each independent variable (sulfate, nitrate, chloride, base cations) on the dependent variable, ANC. By multiplying the regression coefficient (b_i) by the ratio of the standard deviations of x_i to y, the problems of unequal variation and different units of measurement are eliminated because the standardized regression coefficient has a unitless dimension that is normalized for differences in variance between the dependent and independent variable.

Comparison of the standarized regression coefficients thus provides a means to rank and compare the relative importance of each independent variable in terms of its ability to explain the variation in ANC among streams in each subregion. If the partial regression coefficient for sulfate is twice as great as that for nitrate, then sulfate can be considered to be twice as important as nitrate in terms of explaining the variation in ANC. The direction of this influence (i.e., positive or negative) is indicated by the sign of the slope. The results of these standardized multiple regression analyses describe associations among chemical species in the sample streams. They cannot be used to infer the cause of the observed ANC variation.

The relative influence on ANC of base cations, sulfate, nitrate, chloride, and organic anions, as reflected by DOC, was assessed using this approach. DOC was used as a surrogate for organic anions because the only estimates of the strong and weak acid organic anions are based on the calculated anion deficit and the difference between the measured ANC and the calculated carbonate alkalinity, respectively. The estimated anion deficit includes the other acid anions and base cations in the calculation and hence is not independent of the other indepedent variables used in the regression model. Further, the estimated strong acid organic anion concentration, as computed from the charge balance, is affected by the cumulative analytical errors associated with the measurement of the individual anions and cations used in the charge balance. Thus, for this purpose, and assuming that the strong organic acid anions are a constant proportion of DOC among the streams, strong organic acidity is probably more accurately estimated by DOC than by the charge imbalance (anion deficit). Similarly, the weak organic anions (estimated from the difference between the measured ANC and the calculated carbonate alkalinity) are not independent of ANC. Hence, they were not used in the regression analysis.

The absolute values of the standardized regression coefficient were plotted for the upper and lower nodes in each subregion (Figures 8-4, 8-5, and 8-6). In all nine subregions, the five independent variables together account for over 90% of the variation in ANC between streams,

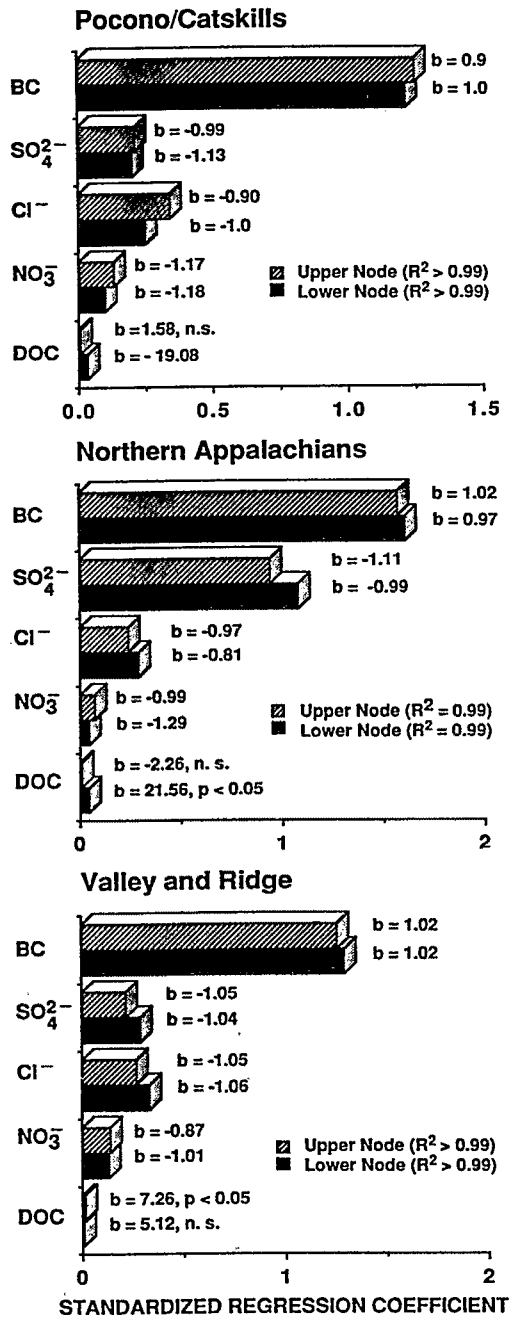


Figure 8-4. The absolute value of the standardized linear regression coefficient (b_i') for each of the independent variables that influence ANC in all streams in the population of interest in the Poconos/Catskills (1D), Northern Appalachians (2Cn), and Valley and Ridge (2Bn) subregions. Also shown is the estimated regression coefficient (b) (i.e., slope) for each independent variable. Unless otherwise indicated, the standardized regression coefficients were highly significant ($b_i' \neq 0$, $p < 0.001$) for the nodes plotted.

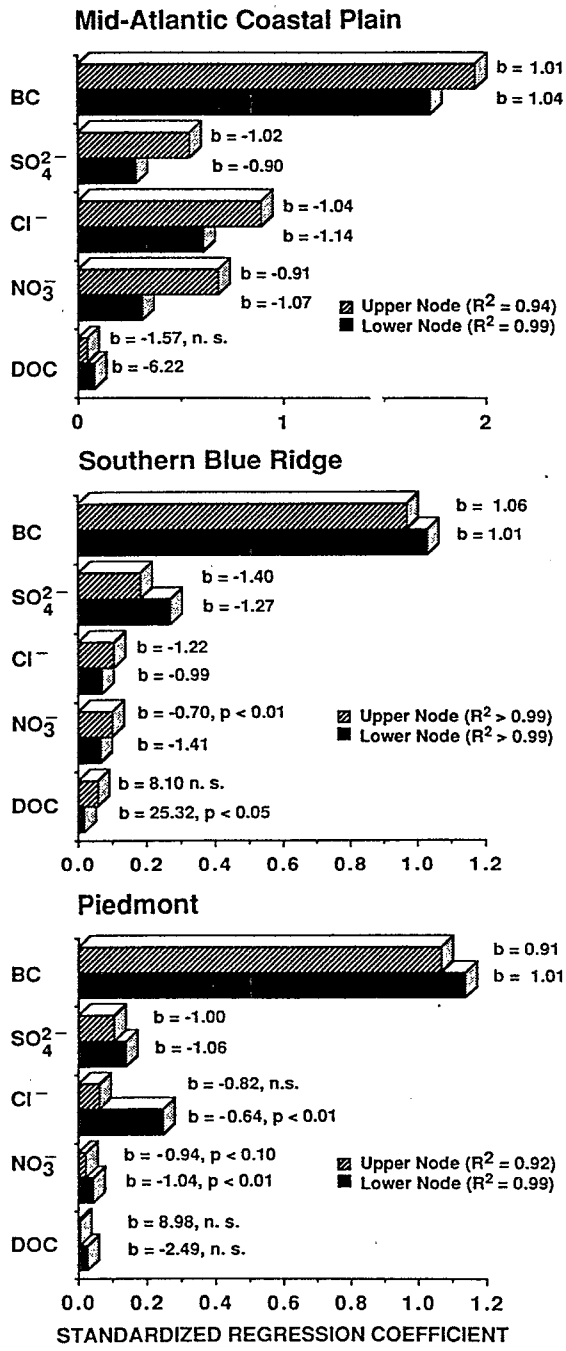


Figure 8-5. The absolute value of the standardized linear regression coefficient (b_i') for each of the independent variables that influence ANC in all streams in the population of interest in the Mid-Atlantic Coastal Plain (3B), Southern Blue Ridge (2As), and Piedmont (3A) subregions. Also shown is the estimated regression coefficient (b) (i.e., slope) for each independent variable. Unless otherwise indicated, the standardized regression coefficients were highly significant ($b_i' \neq 0$, $p < 0.001$) for the nodes plotted.

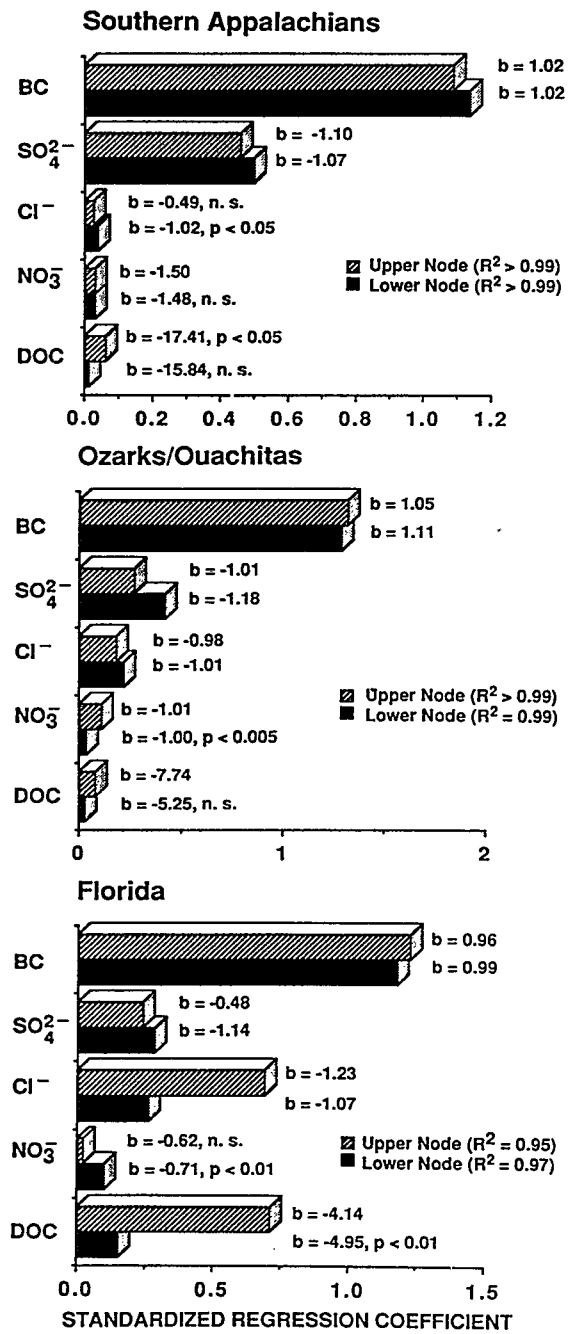


Figure 8-6. The absolute value of the standardized linear regression coefficient (b_i') for each of the independent variables that influence ANC in all streams in the population of interest in the Southern Appalachians (2X), Ozarks/Ouachitas (2D), and Florida (3C). Also shown is the estimated regression coefficient (i.e., slope) for each independent variable. Unless otherwise indicated, the standardized regression coefficients were highly significant ($b_i' \neq 0$, $p < 0.001$) for the nodes plotted.

and in most cases account for ≥ 99% of the variation. The sum of base cations, however, ranks as the variable of most importance in explaining the observed differences in ANC among streams. The only subregion where a strong mineral acid anion is of comparable importance to base cations is the Northern Appalachians (2Cn) (Figure 8-4), where sulfate is only slightly less important than base cations.

These results indicate that when all of the streams in the subregional populations of interest are considered together, sulfate is of major importance in explaining the variation in ANC among streams only in subregion 2Cn. In all other subregions, the contribution of sulfate as a predictor of variation in ANC among streams is substantially less compared to that for the base cations.

The important role of base cations in explaining differences in ANC among streams is to be expected when all streams in the target population are considered together, because of the wide range of base cations relative to the range of ANC. That differences in ANC among streams are associated primarily with differences in base cation concentration suggests that differences in weathering and exchange rates in soils and bedrocks among watersheds are the primary mechanism regulating ANC. Such differences could be caused by kinetic limitations associated with the extent to which drainage waters are in contact with weatherable and exchangeable pools of base cations in the soil and groundwater. These differences could also be due, in part, to a capacity limitation associated with differences in the pools of weatherable and exchangeable bases in the soil and bedrock (e.g., base-poor versus base-rich soils). Factors associated with the variation in the more acid sensitive streams (ANC < 200 μeq L^{-1}) are examined later in this section.

The apparent importance of base cations as a source of the observed variation in ANC among streams does not mean that mineral and organic acid anions do not contribute to that variation. In fact, the standardized regression analysis shows a highly significant negative relationship ($p < 0.0001$) between ANC and sulfate in all subregions, with the regression coefficient (b) being equal to or close to the theoretically expected value of -1.0.

Chloride also shows a significant negative effect on alkalinity in all the subregions except at the upper node in the Southern Appalachians (2X) and the upper node in the Piedmont (3A). Further, the slope is close to the theoretically expected value (-1.0). In the Mid-Atlantic Coastal Plain (3B), Pocono/Catskills (1D), Valley and Ridge (2Bn), and Florida (3C), the importance of chloride is comparable to or greater than that of sulfate in explaining the variation in ANC among streams.

Similarly, nitrate appears to exhibit a significant negative effect on ANC in all the subregions except at the upper nodes in subregion 3A and at the lower nodes in subregion 2X. Nitrate, however, is of less importance than base cations, sulfate, and chloride in most of the subregions. Only in subregion 3B is nitrate of comparable or greater importance than sulfate. The estimated slope for nitrate is also close to the theoretical value of -1.0.

In summary, analysis of the effect of mineral acid anions on the between-stream variation in ANC indicates that mineral acids play a less important role than base cations in explaining the overall variation in ANC among streams in all regions except for the Northern Appalachians (2Cn). In terms of the relative importance of the mineral acid anions, sulfate is at least twice as important as nitrate and chloride in subregions 2Cn, 2X, and 2D, but is of comparable or lesser importance than chloride or nitrate in subregions 2Bn, 1D, 3B, and 3C. The importance of organic acids in explaining the among-stream variation in ANC appears to be relatively minor in all subregions except at the upper node in 3C, where DOC is more important than any of the mineral acid anions and is within a factor of 1.7 of being comparable to base cations in importance. The role of organic acid anions in stream acidification is discussed further in the next section.

8.5 ORGANIC ANIONS

Surface water may contain varying amounts of strong and weak acids originating within the watershed. The weak acids are organic compounds and aluminum, whereas the strong acids may include organic compounds that behave like strong acids or mineral acids from natural sources (e.g., nitrification, sulfide oxidation). To assess the role of organic acids in the acidification of surface waters requires an analysis of the acid/base characteristics of dissolved organic matter (i.e., organic anions) to determine the amounts and relative contribution of the weak and strong organic acid anions. Weak organic anions are protolytic (react with H^+) and, depending on the pK_a of the weak acids, may behave like bicarbonate in terms of their reaction with protons. Inputs of weak acid organic anions (WAOA) thus can cause an increase in the ANC. In contrast, strong organic anions are nonprotolytic (do not react with H^+ for pH > 4.0) and behave like SO_4^{2-} and NO_3^- in terms of their proton dissociation properties. Because inputs of strong acid organic anions (SAOA) cause a decline in ANC, the primary concern is in assessing whether the effect of inputs of organic anions is acidifying (decrease in ANC) or alkalinizing (increase in ANC).

As discussed in Section 8.4, DOC is either a minor or nonsignificant contributor to the overall variation in ANC in all the subregions except Florida (3C), based on standardized regression analysis of the relationship between ANC and DOC. Although, this is only circumstantial evidence of the role of strong organic acids, it suggests that, except for Florida, organic acids are not a major source of the subregional variation in ANC among streams in any of the subregions. This does not preclude the possibility that individual streams or groups of streams (e.g., high organic, acidic streams) may be acidic because of organic acids. Because DOC was used as the independent variable and DOC can include both strong and weak acid organic anions, the effect of such anions on the ANC measured by Gran titration could be positive, negative, or neutral, depending on the proportion of strong and weak organic anions, the dissociation constant of these acids, and the pH of stream water. If the proportion of DOC made up of strong and weak acids varies among streams within a subregion, it is possible that the effect of these organic acids on the ANC within a subregion is masked when data for all streams are combined in the regression analysis.

The net effect of organic anions on the ANC of stream water is indicated by the results of the standardized regression analysis. This analysis shows whether there is a statistically significant relationship between the concentration of DOC and the variation in ANC among streams in each of the subregions. It also shows whether the relationship is negative ($b < 0$) or positive ($b > 0$), the former indicating that the DOC consists primarily of strong acid organic anions which depress the ANC, the latter indicating that the DOC consists primarily of weak organic protolytes that contribute to the noncarbonate component of the ANC.

At the upper nodes in Florida (3C), there is a significant negative relationship between DOC and ANC, suggesting that strong organic acids may be partly responsible for the low ANC in streams in this subregion (Figure 8-6). The regression coefficient between ANC and DOC is -4.14, indicating that the ANC declines by 4.14 μeq for every mg increase in DOC in stream water. The regression analysis suggests that DOC is more important than sulfate, chloride, and nitrate in explaining the variation in ANC among streams at the upper nodes in Florida. At the lower nodes, the effect of DOC on ANC is also negative; however, DOC is slightly less important than chloride and sulfate in explaining the variation in ANC among streams. This suggests that there are major changes in the organic acid/ANC relationship between the upstream and downstream nodes in subregion 3C streams.

Given the relatively high concentrations of DOC in many streams in the Mid-Atlantic Coastal Plain (3B), it is surprising that DOC ranks lowest in importance of the variables considered in explaining the variation in ANC among streams. Further, DOC accounts for a significant fraction of the variation in ANC in subregion 3C streams only in the lower reach nodes. The negligible effect of DOC on ANC in this subregion may be due to the use of bulk DOC as the independent variable in the regression model. If the equivalents of strong and weak acid organic anions per mole of DOC is quite variable among streams, use of bulk DOC as a measure of organic anions would tend to obscure the effect of such differences on the ANC.

An additional reason why DOC may not explain the subregional variance in ANC in the coastal plain is that the variation in DOC is small relative to the variation in ANC. Comparison of the partial regression coefficients and the standardized regression coefficients at the upper and lower nodes in subregion 3B indicates that this is the case. This observation points out a potential pitfall in the interpretation of these standardized regression analyses. If, for example, ANC in all streams in a subregion is depressed the same amount by equal concentrations of a strong acid anion, the variation in ANC is likely to be best explained by among-stream base cation concentration (buffering) or by a different strong acid anion that shows greater variation. The partial regression coefficients show a high potential for DOC to influence ANC as indicated by the negative slopes of -6.22 and -1.57 for the lower and upper nodes, respectively. The partial regression coefficient is not significantly different from zero at the upper node, suggesting that the variation in the concentration of DOC in this subregion is small relative to that for ANC. As such, DOC would not be expected to account for a significant fraction of the variation in ANC among streams. This analysis, however, assumes that the equivalents of strong acid organic anions per mg of DOC are the same among all streams. The variation among the regions in both the sign and magnitude of the partial regression coefficients for DOC indicates that this is not a valid assumption. Thus, it may be tenuous to assume that the DOC in all streams within a subregion is the same in terms of the fraction that behaves as a strong acid.

Strong acid organic anions (SAOA) alone were also estimated from the difference in the charge balance (measured cations and anions):

$$\text{SAOA} = [\text{sum of measured cations}] - [\text{sum of measured anions}],$$

where [sum of measured cations] = $Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} + NH_4^{+} + H^{+}$, and [sum of measured anions] = $SO_4^{2-} + NO_3^{-} + Cl^{-} + F^{-} + (ANC + H^{+})$. ANC + H^{+} includes both carbonate and non-carbonate protolytes (ANC = $HCO_3^{-} + CO_3^{2-} + OH^{-}$ + weak noncarbonate protolytes - H^{+}). The anion deficit was then regressed against DOC and the results of this analysis are shown in Table 8-1. Only regressions with slopes significantly different from zero ($p > 0.05$) are shown. The slope of these regressions is a measure of the strong organic acid equivalents per mg of DOC.

In all cases, positive slopes were observed, indicating a significant positive relationship between anion deficit and the concentration of DOC in stream water. The slopes, however, vary from region to region and from the upper to the lower nodes within a subregion, ranging from 4.0 at the upper nodes in the Ozark/Ouachitas (2D) to 12.4 μeq mg^{-1} DOC at the upper nodes in the Southern Blue Ridge Province (2As).

This three-fold range in the regression coefficient supports the results of the standardized regression analysis which showed that the equivalents of strong acid organic anions per mg of DOC varied not only from region to region, but also between the upper and lower nodes within a region. The high slope for the Southern Blue Ridge (2As) implies that for every mg increase in DOC in stream water, the ANC will decline by approximately 12.4 μeq. However, the DOC

Table 8-1. Estimates of the Strong Acid Organic Anion Equivalents per mg Organic Carbon in Stream Water at the Upper (U) and Lower (L) Sample Reach Nodes in NSS-I Subregions Based on Linear Regression of the Calculated Anion Deficit and DOC

SUBREGION/NODE[$]	SLOPE (μeq mg^{-1})	r^2	p
Poconos/Catskills (L)	8.0	0.48	< 0.01
Mid-Atlantic Coastal Plain (U)	6.2	0.54	< 0.001
Mid-Atlantic Coastal Plain (L)	7.9	0.52	< 0.001
Southern Blue Ridge (U)	12.4	0.61	< 0.001
Ozarks/Ouachitas (U)	4.0	0.31	< 0.001
Ozarks/Ouachitas (L)	5.5	0.88	< 0.001
Florida (U)	6.2	0.59	< 0.001
Florida (L)	7.0	0.93	< 0.001

[$] For those nodes and subregions not listed, the slope of the regression was not significantly different from zero ($p > 0.05$).

levels in streams in subregion 2As (median < 1 mg L^{-1} DOC) are typically lower than in most of the other subregions. Thus, despite the apparently higher equivalents of strong acid organic anions per mg of DOC in stream water in this subregion, the watersheds export very little DOC during baseflow, with the result that organic acids do not play a major role in contributing to the variation in ANC between streams under baseflow conditions.

DOC also had a significant positive relationship with ANC in the lower nodes in some subregions (e.g., the Northern Appalachians [2Cn] and the Southern Blue Ridge [2As], and in the upper nodes in the Valley and Ridge [3B]), indicating that the DOC in these subregions and nodes consisted of mainly weak organic protolytes. Because the concentration of weak organic anions was low in these subregions, DOC was not a major source of the variation in the ANC among streams. In all of the remaining nodes and subregions, the relationship between DOC and ANC was not statistically significant ($p > 0.10$), suggesting that variation in DOC among streams in these subregions and nodes was also not a contributing source of the variation in the ANC.

In those subregions with a significant negative relationship between DOC and ANC, DOC appears to be of major importance in explaining the variation in ANC among streams only in Florida (3C) because of the high concentrations of DOC. In this case, DOC was comparable to base cations and chloride in importance as a source of variation in ANC among streams in both the upper and lower nodes. In Florida streams with an ANC < 200 μeq L^{-1}, however, DOC was important only at the upper nodes. In the other subregions (Mid-Atlantic Coastal Plain [3B], Pocono/Catskills [1D], Southern Appalachians [2X], and Ozark/Ouachitas [1D]), DOC ranks substantially lower in importance than the sum of base cations and mineral acid anions as a source of the variation in ANC among streams.

8.6 SOURCES OF ANC VARIATION IN LOW ANC (< 200 μeq L^{-1}) STREAMS

The previous analysis of factors that account for the among-stream differences in ANC included all streams in the population of interest within a subregion. Because of the concern about the acidification of streams having the lowest buffering capacity and the possibility that inclusion of streams with a high ANC would obscure the role of mineral acids as a source of variation, the data were reanalyzed using only those sites with an ANC < 200 μeq L^{-1}.

Variation in ANC between streams was analyzed for each subregion using the standardized linear regression analysis described in Section 8.4. The importance of variation in base cations, sulfate, nitrate, chloride, and DOC in explaining the variation in ANC was determined by regressing these variables on ANC. The absolute values of the standardized regression coefficients are plotted for the upper and lower nodes in each subregion (Figures 8-7, 8-8, and 8-9).

These plots show that for all the subregions except the Northern Appalachians (2Cn) (Figure 8-7) and Florida (3C) (Figure 8-9), the sum of base cations is again the most important variable in explaining the variation in ANC among the more acid-sensitive streams. In subregion 2Cn, sulfate is of comparable importance to base cations, indicating that sulfate is as important as base cations in explaining the variation in ANC among streams in this subregion. Differences in ANC among streams within most of the remaining subregions are still largely associated with base cation differences, despite the statistical significance of the association between ANC and strong acid anions in these subregions.

In Florida streams (Figure 8-9), however, chloride is of comparable importance to base cations at the lower nodes, although at the upper nodes, base cations, chloride, and DOC are of approximately equal importance in explaining the variation in ANC among streams. Sulfate is not associated with a significant portion of the ANC variation at either the upper or lower nodes in subregion 3C stream reaches. Surprisingly, DOC does not contribute significantly to an

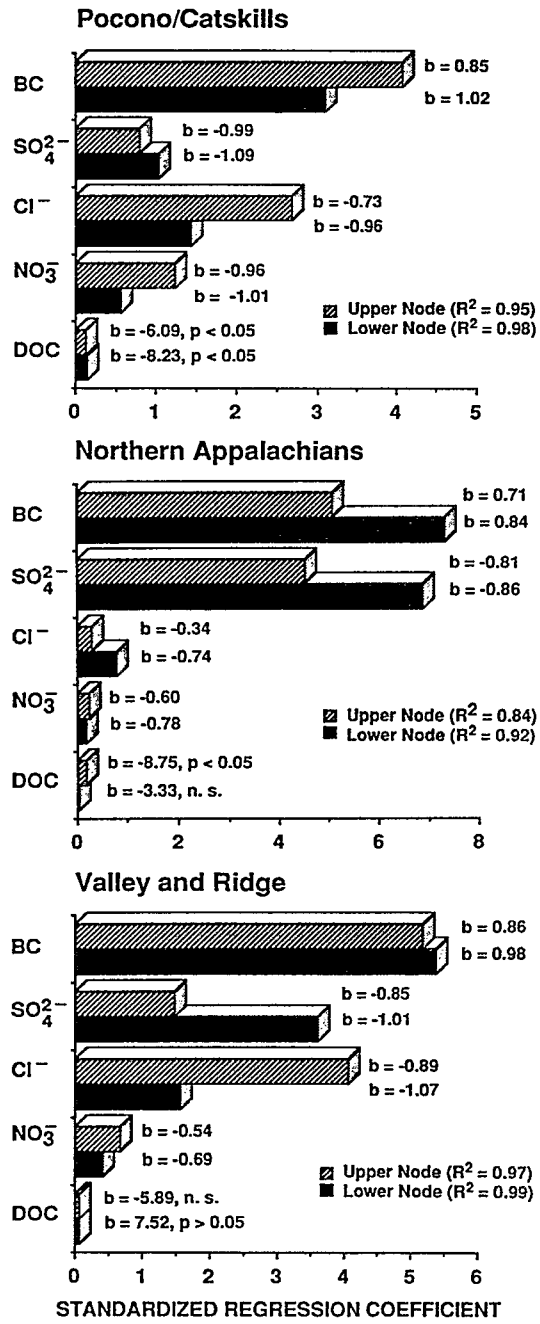


Figure 8-7. The absolute value of the standardized linear regression coefficient (b_i') for each of the five independent variables considered in streams in the Poconos/Catskills (1D), Northern Appalachians (2Cn), and Valley and Ridge (2Bn) subregions, with ANC $\leq$ 200 μeq L^{-1}. Also shown is the estimated regression coefficient (b) for each independent variable. The standardized coefficients are highly significant ($p < 0.001$) unless otherwise indicated.

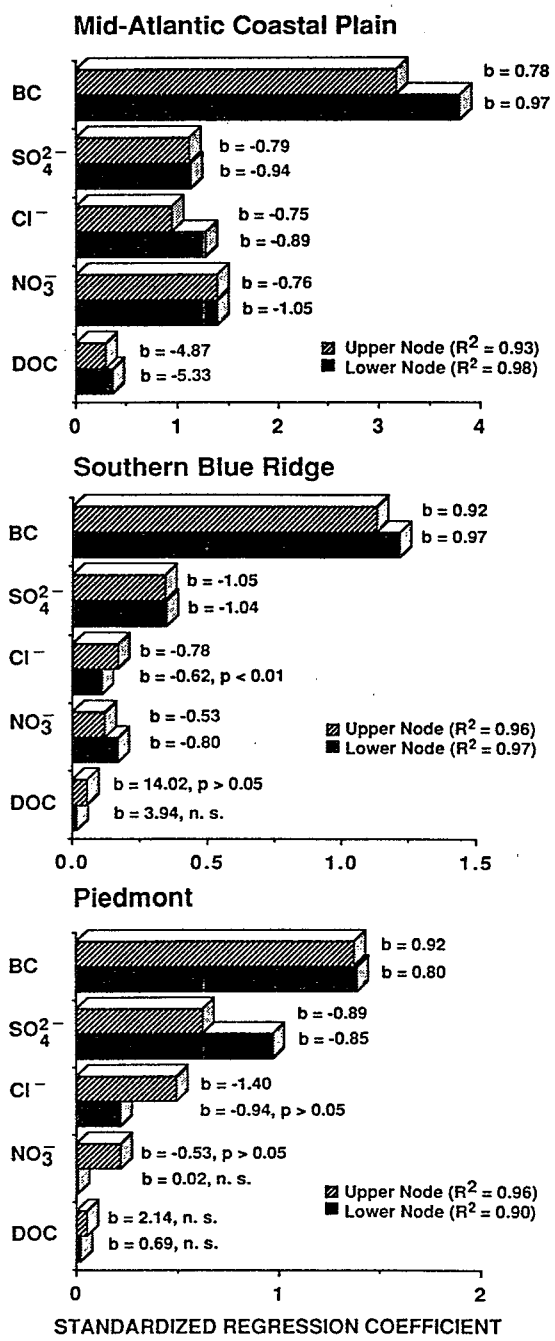


Figure 8-8. The absolute value of the standardized linear regression coefficient (b_i') for each of the five independent variables considered in streams in the Mid-Atlantic Coastal Plain (3B), Southern Blue Ridge (2As), and Piedmont (3A) subregions, with ANC $\leq$ 200 μeq L^{-1}. Also shown is the estimated regression coefficient (b) for each independent variable. The standardized coefficients are highly significant ($p < 0.001$) unless otherwise indicated.

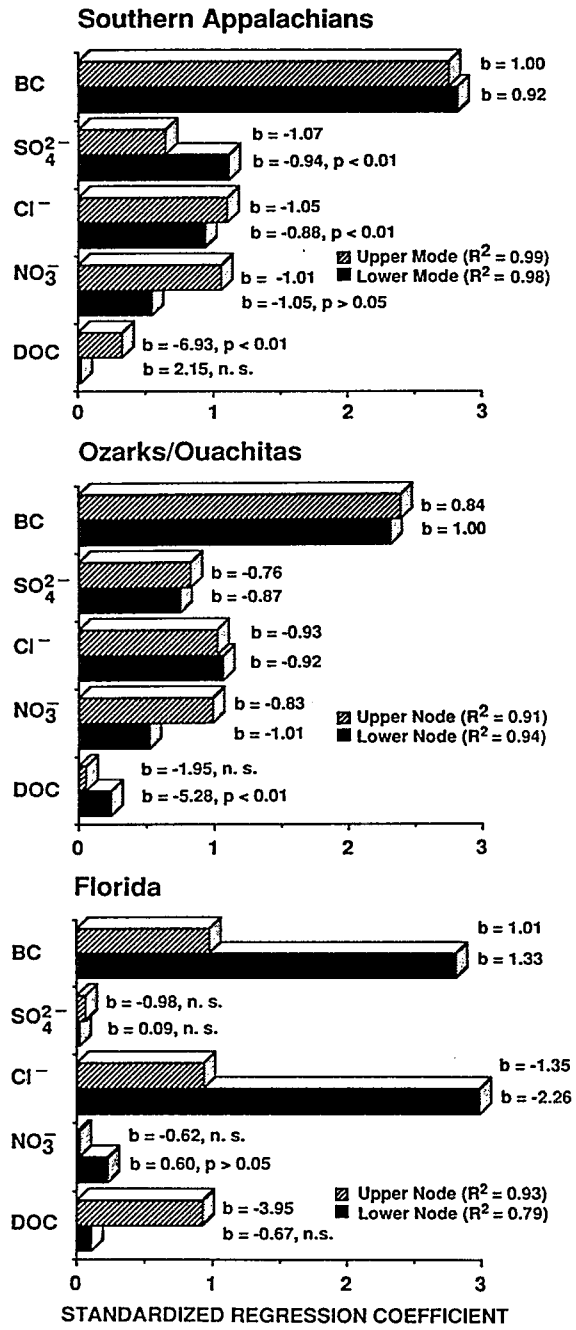


Figure 8-9. The absolute value of the standardized linear regression coefficient (b_i') for each of the five independent variables considered in streams in the Southern Appalachians (2X), Ozarks/Ouachitas (2D), and Florida (3C) subregions, with ANC $\leq$ 200 μeq L^{-1}. Also shown is the estimated regression coefficient (b) for each independent variable. The standardized coefficients are highly significant ($p < 0.001$) unless otherwise indicated.

explanation of the variation in ANC at the lower nodes in Florida streams, suggesting that (1) the variation in DOC is small relative to that observed in ANC or (2) the acidic functional groups are either lost from water or are so diluted during transport from upstream to downstream that they no longer contribute to the variation in ANC. Both the median concentration and the range of DOC decreases from the upper to the lower nodes, indicating either a loss or dilution of the soluble organic matter.

8.7 EFFECTS OF CARBONIC ACID ON pH - (CO_2 EFFECTS)

Carbon dioxide (CO_2) is not an inert gas. When dissolved in water, CO_2 becomes hydrated to form carbonic acid (H_2CO_3), as shown in the following reaction:

$$CO_2\ (g) + H_2O = H_2CO_3.$$

Depending on the pH of the water in which the CO_2 is dissolved, carbonic acid can dissociate and depress the pH. At pH $< \approx 5.5$, CO_2 should have little or no effect on pH because essentially all of the carbonic acid present will be undissociated (i.e., exist as H_2CO_3).

In contrast to other strong or weak acids, changes in carbonic acid content will have no effect on the ANC unless there are phase changes in the carbonate system (e.g, carbonate precipitation). This lack of an effect of CO_2 on alkalinity is because the increase in HCO_3^- is balanced by an increase in H^+ according to the reaction:

$$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^-.$$

Hence, there is no net change in alkalinity as CO_2 increases or decreases.

The effects of CO_2 on the pH of stream water was assessed by comparing the closed-system pH measured in the processing laboratory with that measured in the analytical laboratory after equilibration with atmospheric CO_2 ($pCO_2 = 10^{-3.5}$ atm). The latter was determined by bubbling 300 ppm CO_2 air through the stream water samples for 20 minutes. If the air-equilibrated pH is greater than the closed-system pH, the difference is assumed to be due to CO_2 supersaturation. Similarly, a decrease in pH indicates that the sample was undersaturated with respect to the pCO_2 in the atmosphere.

Plots of the difference between closed-system and air-equilibrated pH versus the air-equilibrated pH suggest that almost all of the streams in every subregion are supersaturated with CO_2 (Figure 8-10). The small differences between the air-equilibrated pH and the closed-system pH at pH levels < 5.5 are consistent with the decrease in the dissociation of carbonic acid with declining pH, and suggest that systematic errors in the measurement of pH are not the cause for the difference in pH between air-equilibrated and closed-system samples.

The increase in pH when the samples are air equilibrated (i.e., excess CO_2 is degassed) ranges from approxiately 0.25 units to one full pH unit, indicating that carbonic acid alone has an important effect on the pH of stream water in almost all subregions, particularly Florida (3C), the Piedmont (3A), the Mid-Atlantic Coastal Plain (3B), and the Ozarks/Ouachitas (2D). This suggests that streams in these subregions are more supersaturated with CO_2 than those in the other subregions. Possible reasons for these apparent regional differences in CO_2 supersaturation may be related to the gradient of the streams and the resulting differences in the outgassing rate of excess CO_2 that enters the stream channel in groundwater and soil water (in equilibrium with higher pCO_2), regional differences in biological activity that generates CO_2 in soil solutions, or some combination of both.

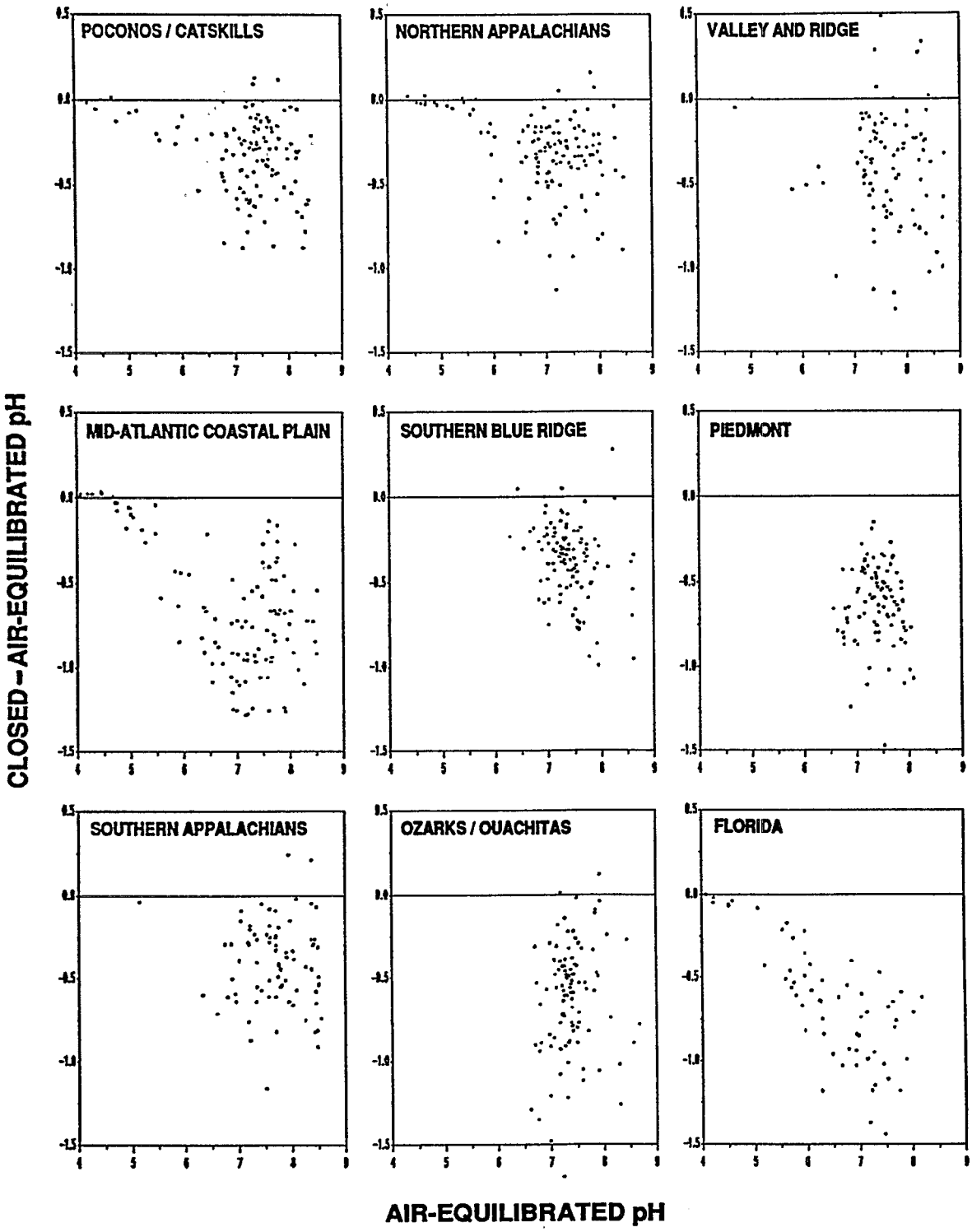


Figure 8-10. Plot of closed-system minus air-equilibrated pH vs. air-equilibrated pH of stream water in NSS-I subregions. Points plotted below the line indicate the samples were supersaturated with CO_2; points above the line indicate undersaturation.

To assess whether the air-equilibrated pH was close to the theoretical pH of water with carbonate species in equilibrium with atmospheric CO_2, the measured air-equilibrated pH was compared to the theoretical air-equilibrated pH for different ANC values (Figure 8-11). The theoretical air-equilibrated pH curve was calculated assuming that the ANC was made up entirely of carbonate species. The plot shows that in almost all subregions, many of the streams with air-eqilibrated pH > 6.0 plot below the theoretical value based on carbonate ANC alone. The exception is the Southern Blue Ridge (2As), where the measured air-equilibrated pH of almost all streams was close to the theoretical value.

Reasons for the deviations from the theoretical curve include errors in the measurement of air-equilibrated pH, failure to equilibrate the samples with atmospheric CO_2 before measurement of air-equilibrated pH, the presence of weak organic acids that dissociate near the measured air-equilibrated pH, and the presence of other weak acids (e.g., aluminum). Since aluminum is present in low concentrations at pH > 6.0, where the air-equilibrated pH difference in most subregions is the greatest, aluminum is unlikely to be the cause for the differences between the theoretical and air-equilibrated pH values in these cases. Aluminum, however, will contribute to the pH difference in the acidic streams with elevated aluminum levels.

Organic anions will cause the air-equilibrated pH to be lower than expected because these weak organic anions have a lower pK_a than that for bicarbonate. Subregions with the highest DOC levels--Florida (3C) and the Mid-Atlantic Coastal Plain (3B)--also have large differences in air-equilibrated pH, suggesting that weak organic acids contribute to this difference.

Differences in the response of pH electrodes resulting from DOC interferences could also account for the apparent air-equilibrated pH differences. Herczeg and Hesslein (1984) reported that high levels of DOC in lake waters interfered with the response of pH electrodes, resulting in air-equilibrated pH values lower than expected. pH bias due to DOC interference could account for the observed differences in the air-equilibrated pH of streams only if the bias were not linear over the entire pH range. Since there was little or no difference between the expected and observed pH of most streams with air-equilibrated pH $\leq$ 6.0, this suggests either that the air-equilibrated pH difference is not due to DOC interference with the pH measurement or that DOC interference is not constant over the entire air-equilibrated pH range.

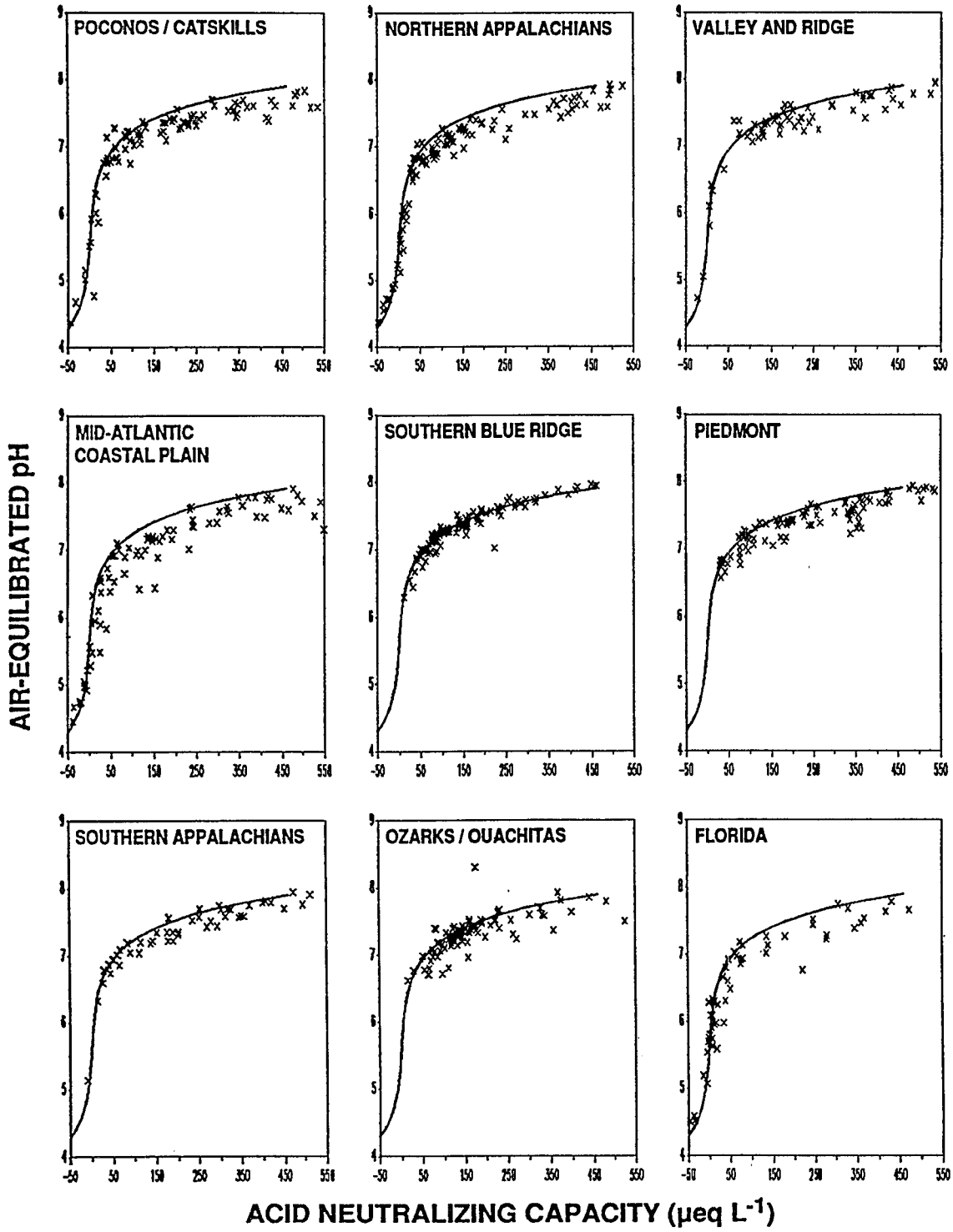


Figure 8-11. Observed air-equilibrated pH vs. ANC in NSS-I subregions. The solid line represents the theoretical pH calculated from ANC, assuming all of the ANC is due to carbonate protolytes in equilibrium with atmospheric CO_2 at 15°C.

SECTION 9
NATURE AND DISTRIBUTION OF ACIDIC AND LOW ANC STREAMS

9.1 OVERVIEW

In order to determine the status and extent of acidic and low ANC streams that may have been affected by acid deposition, stream reaches acidified by other sources (e.g., acid mine drainage, organic acidity, neutral salt hydrogen ion substitution) must first be identified. In this section, all NSS-I stream reaches with spring index ANC values ≤ 200 μeq L^{-1}, a number commonly used to indicate sensitivity to acid deposition, were classified according to probable sources of acid anions. Streams classified as being affected by acid anion sources other than acid deposition, and those affected by significant watershed sources of sulfate that would mask atmospheric contributions, were removed from the list of streams possibly impacted by acid deposition. These include streams affected by acid mine drainage or natural sulfide mineral weathering, non-acidic sulfate inputs (e.g., sulfate mineral weathering or fertilizers), organic acidity, and displacement of hydrogen ion by sea salt. The remaining streams constitute a high-interest subpopulation of streams with anion balances dominated by strong inorganic acid anions at concentrations that could reasonably be produced by evaporative concentration of anions in precipitation. Acidic streams in this high-interest group are likely to have been affected by acid deposition. Although streams with ANC between 0 and 200 μeq L^{-1} may have naturally low ANC, it is also possible that acid deposition could cause ANC depressions in these streams. Within each stream chemical classification, population estimates of the numbers of acidic (ANC $\leq$ 0 μeq L^{-1}), very low ANC ($0 <$ ANC ≤ 50 μeq L^{-1}), and low ANC ($50 <$ ANC ≤ 200 μeq L^{-1}) stream reaches were made. The distribution of streams by chemical groupings in the NSS-I subregions and geographic site classes are also presented.

9.2 BACKGROUND

In addition to acid deposition, other mechanisms, both natural and anthropogenic, can cause acidic conditions in streams. One of the most severe acid generating mechanisms in streams is acid mine drainage, which has acidified streams (damaging or eliminating their fish populations) in many mining regions of the United States (Barnes and Romberger, 1968; Ahmad, 1972). When mine spoils containing sulfide (e.g., pyrite in coal tailing piles) are exposed to air and water, the reduced iron and sulfur are oxidized by a series of microbial and chemical processes according to the following overall reaction (Stumm and Morgan, 1981; Dugan, 1985):

$$4\ FeS_2 + 15\ O_2 + 14\ H_2O \quad \text{--->} \quad 4\ Fe(OH)_3 + 16\ H^+ + 8\ SO_4^{2-}$$

The products of this reaction can be hydrologically transported into surface waters and cause their acidification. Acidity is generated from both sulfide oxidation and iron hydrolysis. Streams affected by acid mine drainage are characterized by high iron, manganese, and sulfate concentrations, high specific conductance, and low pH. Typical pH values in these streams range from 2.0 to 4.0; sulfate concentrations range from 1000 to 25,000 μeq L^{-1}, whereas iron concentrations range from 1 to 100 mg L^{-1} (Mills, 1985).

Weathering of sulfide minerals in undisturbed watersheds (e.g., those in the Anakeesta formation in parts of the Southern Blue Ridge) may also generate acidity as shown in the above reaction (Huckabee et al., 1975; King et al., 1968; Hadley and Nelson, 1971). The rates are limited, however, because the minerals are underground and are only slowly exposed to oxygen

and water through natural weathering processes. It is only when the sulfide minerals are disturbed (as is done in mining activities) that accelerated weathering and hydrologic flow cause the severe acidification typical of streams affected by acid mine drainage (Dugan, 1985; Dick et al., 1986). Chemical conditions similar to acid mine drainage may occur when slumps or road cuts expose sulfide containing material to air and water.

Waters with high concentrations of dissolved organic matter can be naturally acidic (pH 3.0 - 5.0) due to the leaching of organic acids from the natural decay of biotic material (Gorham et al., 1984). Not all organic carbon, however, contributes to organic acidity in aqueous systems. In natural waters, dissolved organic carbon (DOC) is typically composed of roughly 50% humic substances (10% humic acids, 40% fulvic acids), 30% hydrophillic acids, 5% - 10% carbohydrates, 5% - 8% carboxylic acids and phenols, and 4% amino acids (Thurman, 1985). The analytical procedures that measure any one of these groups of organic compounds are quite complex, and in most cases are operational definitions (rather than analyses of specific compounds). In the NSS-I, therefore, DOC concentration was used as a composite measure of the organic contribution to stream water chemistry. Unfortunately, DOC determinations measure all of these organic carbon forms and represent a group of compounds that vary greatly in their acid/base characteristics. DOC is, therefore, only a crude measure of organic acidity in surface water.

In order to quantify the contribution of organic acidity to stream acidity, it is necessary to know the acid dissociation constants (K_a) of the organic acids in the stream. Like carbonic acid ($pK_a = 6.3$), organic acids with relatively high pK_a (5.0 - 7.0) can be considered weak acids and their dissociated anions will contribute to ANC in circumneutral waters. However, organic acids with low pK_a (< 4) will behave like strong, inorganic acids (e.g., H_2SO_4, HNO_3) and depress stream pH. Measuring stream water organic K_a is a complicated task and was impractical for a synoptic survey like the NSS-I. It is possible, however, to estimate a composite stream water organic acid pK_a and thus the organic anion concentration by using the Oliver model (Oliver et al., 1983). The model is based on two empirical relationships. Oliver found that the pK_a of organic acids is related to pH and that the amount of carboxyl acidity averages about 10 μeq mg^{-1} DOC. The organic anion concentration of a sample can, therefore, be calculated from measurements of DOC and pH. The relationship between organic anions and inorganic anions in a stream water sample can be used to evaluate the effect of organic acidity on the acid/base chemistry of the stream.

Estimation of the organic anion concentration in NSS-I streams was necessary in order to classify streams that were affected by organic acidity. Organic anion concentrations were calculated from pH and DOC using the Oliver model (Oliver et al., 1983) as described above. In streams with ANC < 200 μeq L^{-1} and DOC concentrations > 2 mg L^{-1}, the organic anion concentration calculated by the Oliver model was positively correlated with the anion deficit (base cations + H^+ + NH_4^+ - SO_4^{2-} - NO_3^- - Cl^- - F^- - HCO_3^- - CO_3^{2-} - OH^-) ($r^2 = 0.64$, slope = 0.89, intercept = 23; also see Sections 4.9 and 8.6). Thus, calculation of organic anions by the Oliver model appears to yield reasonable results in low ANC streams.

Sea salt deposition has been proposed as a significant acidification mechanism in coastal surface waters. When a solution high in neutral salt (such as NaCl) passes through an acidic soil, Na^+ ions can be exchanged for H^+ ions, rendering the emerging leachate richer in H^+ and thus more acidic than the solution added to the soil (Krug and Frink, 1983). This hypothesis can be examined by plotting ANC versus Na^+:Cl^- and looking for a trend of low ANC streams with Na^+ depletions.

Sea salt in wet and dry deposition can contribute a significant amount of ions to coastal streams that do not contribute acidity and may confound a classification of streams according to probable sources of acidity. Therefore, for classification purposes, all streams within 200 km of

the coast were corrected for sea salt additions of SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, K^+ and Mg^{2+}. Seawater Cl^- contributions to mid-Atlantic streams were estimated using the equation relating stream water Cl^- to distance from the ocean, as described in subsection 6.3.5 (Figure 6-18). The other sea water ions were corrected based on their molar ratios in sea water with respect to Cl^-. In Florida (3C), there was no relation between stream Cl^- concentration and distance from the ocean. The Cl^- concentration contributed by sea water was estimated from the 1986 volume weighted concentration of Cl^- in precipitation (12.5 μeq L^{-1}) observed at the NADP/NTN site in Quincy, Florida (NADP, 1987), about 70 km from the ocean in the panhandle area of the subregion. The Cl^- concentration in precipitation was then multiplied by the evaporative concentration factor (precipitation/runoff) for subregion 3C (Geragnty et al., 1973) to determine the Cl^- concentration contributed by sea water in Florida streams. The NSS-I sites in Florida were on the average 58.5 km (SD = 24.6 km) from the ocean. The other ions affected by sea salt were corrected based on their molar ratios in sea water with respect to Cl^-.

9.3 CLASSIFICATION AND LOCATION OF ACIDIC AND LOW ANC STREAMS

In this section of the report, all streams with ANC $\leq$ 200 μeq L^{-1} have been classified according to probable source of acidity. Classification was done using the spring index data on a node-by-node basis, treating the upper and lower nodes as separate samples. The goal of the classification was to identify and remove from consideration stream nodes with substantial acid anion concentrations derived from sources other than acid deposition (mine drainage, organic acids). The acidic streams (ANC $\leq$ 0) that remain, after removing streams with other sources of acidity, constitute a high-interest subpopulation of streams whose most likely source of acidity is acid deposition. The source of acidity in the nonacidic high-interest streams (ANC 0 - 200 μeq L^{-1}) cannot be conclusively inferred from survey data. It is possible that the streams in this group have naturally low ANC. However, it is also possible that acid deposition has caused ANC reductions, because an atmospheric source can explain the strong acid anion concentrations in these high-interest low ANC streams, and other sources of acidity are unlikely. Streams affected by other sources of acidity could also be affected by acid deposition. Their chemistry, however, is likely to mask evidence of acid deposition effects. Population estimates of the number and length of reaches in each chemical classification group are presented in Sections 9.4 and 9.5.

9.3.1 Streams with Acid Mine Drainage and Substantial Watershed Sources of Sulfate

9.3.1.1 Classification--

Streams were classified as being impacted by acid mine drainage based on field observations, mapped information, and chemical screening. All 26 sites at which water samples were not collected due to high conductivity (> 500 μS cm^{-1}) were checked for the possibility of acid mine drainage. Seven of these high-conductivity nodes had pH less than 3.3 and examination of aerial photographs and topographic maps indicated the presence of strip mining activity in their watersheds. Because these nodes were not sampled for complete water chemistry, checking for other acid mine drainage chemical signatures was not possible. The available evidence does indicate that these seven nodes were being impacted by acid mine drainage and they were classified as such.

All stream nodes with index ANC values $\leq$ 0 μeq L^{-1} were screened for the presence of acid mine drainage. Acidic streams with sulfate concentrations > 300 μeq L^{-1} in the Mid-Atlantic and 200 μeq L^{-1} in the Southeast were considered possible acid mine drainage sites.

These cutoff values were chosen after examination of all site data in Table 6-7, which lists predicted stream water sulfate concentrations assuming only atmospheric sources of acidity. From this data, the best estimate of stream water sulfate concentration in the Mid-Atlantic is 158-219 μeq L^{-1} with maximum estimates of 316-413 μeq L^{-1}. A value of 300 μeq L^{-1} was chosen as a cutoff to separate streams whose sulfate comes mainly from the atmosphere from streams whose sulfate source is primarily internal (from watershed sources). Mid-Atlantic streams whose sulfate concentration is < 300 μeq L^{-1} most likely receive a majority of their sulfate, and possibly all their sulfate, from the atmosphere. Those streams with sulfate concentration > 300 μeq L^{-1} most likely receive a substantial proportion from watershed sources. However, they may also be subject to locally high sulfate deposition. A similar line of reasoning applies to the selection of 200 μeq L^{-1} as a cutoff value in Southeast streams. Predicted stream water sulfate concentrations (Table 6-7) in the Southeast (96-146 μeq L^{-1} with maximum estimates of 190-440 μeq L^{-1}) are lower than in the Mid-Atlantic, so a lower cutoff was established.

The use of these sulfate cutoff values was corroborated through examination of field comments, maps, aerial photographs, and site visits to most of the acidic reaches during the Mid-Atlantic Acid Streams Reconnaisance in the spring of 1987. In general, streams with sulfate concentrations over the cutoff value tended to have field or map evidence or chemical signatures indicating mine drainage or some other point-source perturbance (tree farm, gas well, orchard, cleared watershed), whereas streams below the cutoff value did not.

The frequency distribution of stream water sulfate concentration in nodes with ANC $\leq$ 200 μeq L^{-1} shows that most reach nodes had sulfate concentrations < 300 μeq L^{-1} or > 500 μeq L^{-1} (Figure 9-1). Of the 512 acidic, very low and low ANC nodes, only 13 had sulfate concentrations between 300 and 400 μeq L^{-1}, and 8 had values between 400 and 500 μeq L^{-1}. Another 14 nodes had sulfate concentrations between 250 and 300 μeq L^{-1}. Only 6 of these 35 nodes with intermediate sulfate concentration (250-500 μeq L^{-1}) had ANC $\leq$ 0, and an additional 6 of these nodes had ANC between 0 and 50 μeq L^{-1}. The vast majority (92%) of the acidic sample nodes (ANC $\leq$ 0 μeq L^{-1}) have sulfate concentrations > 500 μeq L^{-1} (acid mine drainage) or < 250 μeq L^{-1}. Because of the small number of nodes with intermediate sulfate concentrations, the picking of an arbitrary cutoff value did not have a great effect on the estimated population distribution of acidic and very low ANC streams likely to be affected by atmospheric deposition.

Twenty stream nodes were found to have ANC levels < 0 μeq L^{-1} and SO_4^{2-} concentrations > 300 μeq L^{-1} in the Mid-Atlantic and > 200 μeq L^{-1} in the Southeast. In 17 of these sites, there was evidence of acid mine drainage impact, such as the presence of strip mines (noted in aerial photographs, in topographic maps, or in site comments made during sampling visits). In most cases, the chemical evidence was overwhelmingly in support of acid mine drainage classification ($[SO_4^{2-}]$ > 1000 μeq L^{-1}, pH < 4, [Fe] > 100 μM, and specific conductivity > 100 μS). Stream sites with weaker chemical signatures of acid mine drainage were revisited in the spring of 1987 during the Acid Streams Reconnaissance that confirmed field evidence of acid mine drainage. Therefore, these 17 stream nodes, plus the 7 nodes not sampled due to high conductivity (with low pH, as discussed above), were classified as impacted by acid mine drainage. The other three acidic high-sulfate nodes all had high DOC concentrations (17-32 mg L^{-1}) and color values (110-163 PCU) and were located in the Mid-Atlantic Coastal Plain (3B). These three nodes are likely to be acidic due to organic acids, but their chemistry is dominated by high sulfate concentrations and they were classified as receiving substantial watershed sources of sulfate.

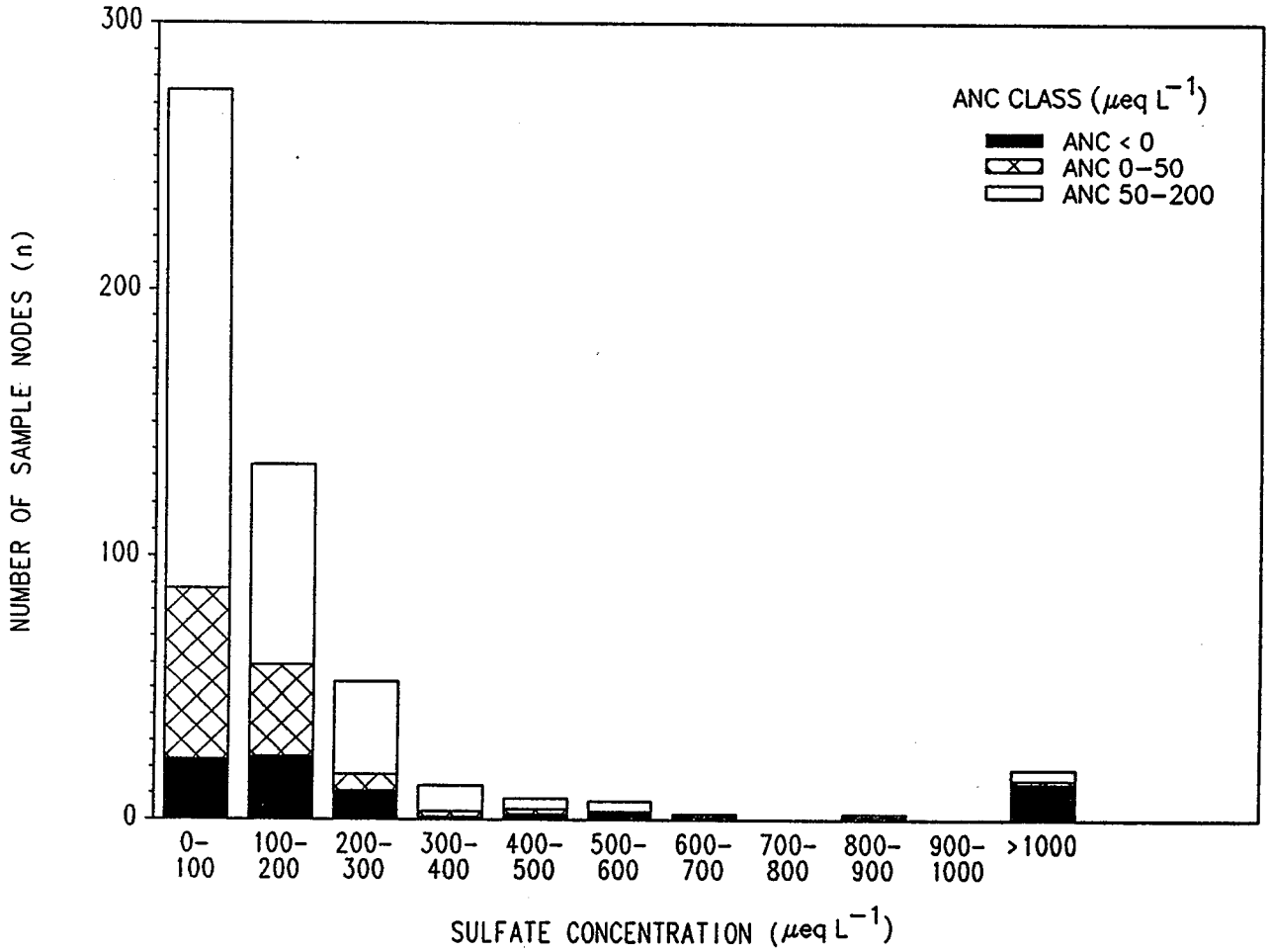


Figure 9-1. Frequency distribution (number of nodes) of spring index sulfate concentration in NSS-I stream nodes with index ANC values ≤ 200 μeq L^{-1}.

Streams with ANC between 0 and 200 μeq L^{-1} and SO_4^{2-} concentrations > 300 μeq L^{-1} in the Mid-Atlantic and > 200 μeq L^{-1} in the Southeast were classified as having substantial watershed sources of sulfate. These streams were not classified as acid mine drainage streams because they are not acidic. The ANC values are low enough to warrant concern about acid deposition, but since they receive significant amounts of sulfate from their watersheds, the potential role of acidic sulfate deposition cannot be estimated. The elevated concentrations of sulfate in these streams could be derived from mine drainage that has been neutralized by dilution with nonacidic streamflow, or by contact with alkaline weathering products from sources such as limestone (either natural or artificially added). Sulfate in these streams may also be derived from natural sulfur mineral weathering (e.g., gypsum or sulfides), or may be contributed as a result of agricultural activity or marine influences.

9.3.1.2 Location--

Reaches impacted by acid mine drainage at either their upper or lower nodes were concentrated in the Allegheny Plateau in Pennsylvania and West Virginia (Figure 9-2). One additional reach affected by acid mine drainage was observed in Tennessee. The majority of the streams with significant watershed sources of sulfate were observed in the same area as the acid mine drainage sites. The source of sulfate in these reaches is most likely sulfide or sulfate mineral weathering or neutralization of upstream acid mine drainage. The source of sulfate in the other high-sulfate reaches, mostly located in the Mid-Atlantic Coastal Plain (3B), is probably either agricultural activity or sulfate derived from weathering of marine sedimentary deposits.

The maps are provided to show the geographic location of the sites in each chemical group. No quantitative estimate of population distributions or density of streams within a geographic area should be made directly from these maps because the population weighting and site selection factors have not been taken into account. Population estimates for each chemical group are presented in Section 9.4.

9.3.1.3 Chemical Characteristics--

The weighted mean pH and ANC (4.3 and -306 μeq L^{-1}) of the stream reaches classified as being affected by acid mine drainage (Table 9-1) illustrate the severe acidity associated with this type of pollution. The mean acidity would almost certainly have been higher if chemistry had been measured at the seven sites with conductivity > 500 μS cm^{-1}. These streams have high concentrations of base cations and metals (Fe, Mn), reflecting the high rates of weathering of metallic sulfides and other minerals exposed by mining. The release of hydrogen ions during sulfide weathering further enhances the weathering of other exposed minerals, dissolving or desorbing base cations. The acid mine drainage streams contain very low concentrations of DOC, and sulfate is by far the most dominant anion (> 95% of total anions). The chemistry of the group of streams with substantial watershed sources of sulfate is similar to that in streams affected by acid mine drainage, in that sulfate is the dominant anion (> 50% of the total anions). The mean pH, however, is much higher (6.18) in the class of streams with large watershed sources of sulfate. Mean nitrate concentrations were high in this group (131 μeq L^{-1}), possibly as a result of agricultural activity. Concentrations of base cations were also high in these high sulfate streams.

ACID MINE DRAINAGE

Figure 9-2. Location of NSS-I study reaches with ANC concentrations ≤ 200 μeq L^{-1} having evidence of acid mine drainage or substantial watershed sources of sulfate at either the upper or lower node.

Table 9-1. Weighted Mean and Standard Deviation (SD) of NSS-I Spring Index Chemistry in Stream Nodes Classified as Impacted by Acid Mine Drainage and Watershed Sources of Sulfate.$

Chemical Species	Acid Mine Drainage n = 17# Mean	SD	Substantial Watershed Sources of Sulfate n = 39 Mean	SD
SO_4*	3272.46	1835.35	688.48	620.91
NO_3^-	20.34	26.43	130.79	217.18
Cl*	64.07	69.18	233.71	300.06
HCO_3^-	0.29	0.26	86.86	45.73
Organic Anions	5.28	2.22	18.80	25.20
DOC (mg L^{-1})	0.94	0.33	2.19	3.73
% Organic Anions	0.40	0.48	2.17	2.93
Color (PCU)	15.71	13.39	15.01	24.29
Sum Base Cations*	2718.88	1581.82	1192.42	729.24
SO_4^{2-}:SBC ratio	1.21	0.27	0.56	0.20
SO_4^{2-}:ANC ratio	-17.59	8.10	13.31	41.08
ANC	-305.81	341.43	112.43	66.10
pH (closed system)	4.34	0.38	6.35	0.60
Al_{tot} (μM)	99.19	63.24	5.99	6.62
Al_{ext} (μM)	100.29	62.59	1.62	3.64
$Al_{(im)}$ (μM)	72.42	59.19	0.80	2.19
Fe (μM)	102.03	132.57	2.21	6.80
Mn (μM)	43.68	32.36	1.39	2.19
Conductivity (μS cm^{-1})	377.00	198.58	140.61	79.35

$ All concentrations are expressed in μeq L^{-1}, except as noted.

* Concentrations were sea salt corrected as discussed in text.

24 nodes were classified as acid mine drainage, but 7 nodes were not sampled for water chemistry due to field exclusion criteria (pH < 3.3, conductivity > 500 μS cm^{-1}).

n = number of nodes classified in each group.

% Organic Anions = percentage of total anions that are organic.

Al_{ext} = MIBK-extractable aluminum (total monomeric).

$Al_{(im)}$ = inorganic monomeric aluminum (PCV method).

9.3.2 Streams with Organic Dominance

9.3.2.1 Classification--

To classify the streams that are likely to be acidic due to organic acids, the concentration of organic anions was compared to the concentration of sulfate and nitrate. Streams in which the organic anion concentration was greater than the sum of the nitrate and sea salt corrected sulfate concentrations were classified as organic-dominated streams. Chloride was not included in the ratio since it is not normally a major contributor to acid/base chemistry in natural waters and it is not usually associated with acid deposition. Nitrate and sulfate were compared to organic anions because they are the anions associated with acid deposition. If organic anion concentrations are larger than the concentrations of sulfate and nitrate, the stream water acidity is controlled largely by organic acids, not by additions of sulfate and nitrate associated acid deposition. For classification purposes, the class of organic-dominated streams was subdivided into three groups, acidic (ANC ≤ 0 μeq L^{-1}), very low ANC ($0 <$ ANC ≤ 50 μeq L^{-1}), and low ANC ($50 <$ ANC ≤ 200 μeq L^{-1}).

9.3.2.2 Location--

Reaches that were organic dominated at their downstream end were found only in Florida (3C) and the Mid-Atlantic Coastal Plain (3B) (Figure 9-3). Only one acidic organic-dominated lower node was observed outside Florida. Acidic reaches that were organic dominated at the upstream end (Figure 9-4) were found mainly in subregions 3C and 3B, although there was one upstream site with very low ANC in the Poconos/Catskills (1D) and one downstream site with low ANC in the Ozarks/Ouachitas (2D).

9.3.2.3 Chemical Characteristics--

The organic-dominated streams, as expected, had high weighted mean concentrations of DOC (10-50 mg L^{-1}) (Table 9-2). They also were highly colored (> 100 PCU). The acidic subgroup had low pH (4.5) and large negative values of ANC (mean = -159 μeq L^{-1}). Sulfate and nitrate concentrations were very low, and Cl^- concentrations were approximately equal to the organic anion concentrations. The high sea salt corrected Cl^- concentrations probably occurred because these sites were near the ocean; chloride may have been contributed by surface water or groundwater in contact with marine sedimentary deposits or soils inundated by sea water at some time in the past. The SO_4^{2-}:base cation ratio was uniformly low in all three ANC groups, indicating that weathering due to sulfate acidity was not an important process in these streams.

9.3.3 High-Interest Subpopulation

9.3.3.1 Classification--

After removal of organic-dominated streams, streams impacted by acid mine drainage, and streams having large watershed sulfate contributions, we are left, by process of elimination, with a high-interest subpopulation of acidic and low ANC streams. The acidic (ANC ≤ 0) and very low ANC (>0 - 50 μeq L^{-1}) stream reaches within this high-interest subpopulation are likely to have been affected by acid deposition. If strong acid anions are present in stream reaches within this group that have ANC between 50 and 200 μeq L^{-1}, the likely source of these anions is atmospheric deposition. Within the high-interest subpopulation, there is a group of streams that, while not dominated by organic anions, had organic anion contents high enough to have an important influence on stream acid/base chemistry. Therefore, those in which organic anions have some influence and those in which organic anions are virtually absent were identified.

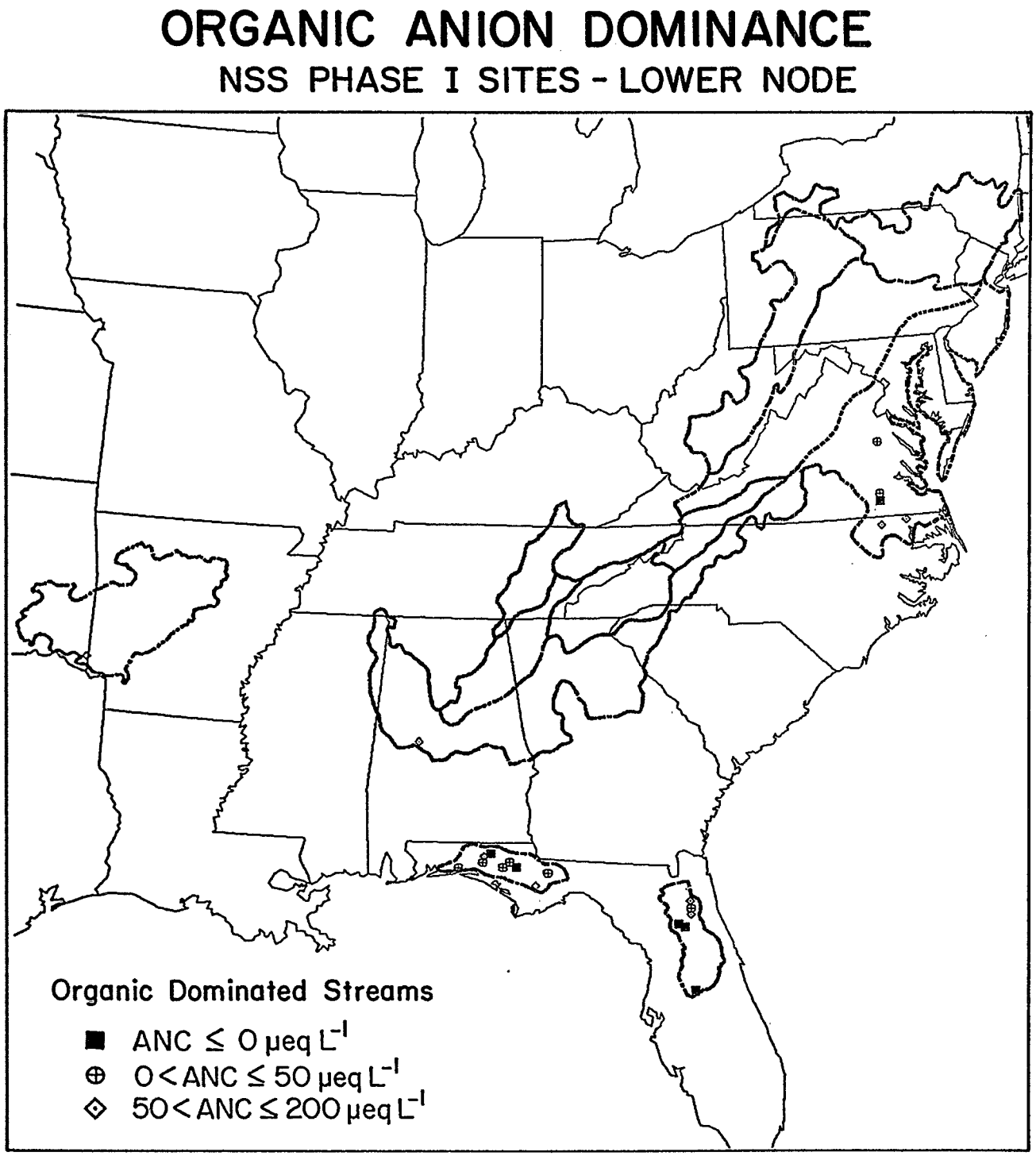


Figure 9-3. Location of NSS-I lower nodes with ANC ≤ 200 μeq L^{-1} classified as being dominated by organic anions.

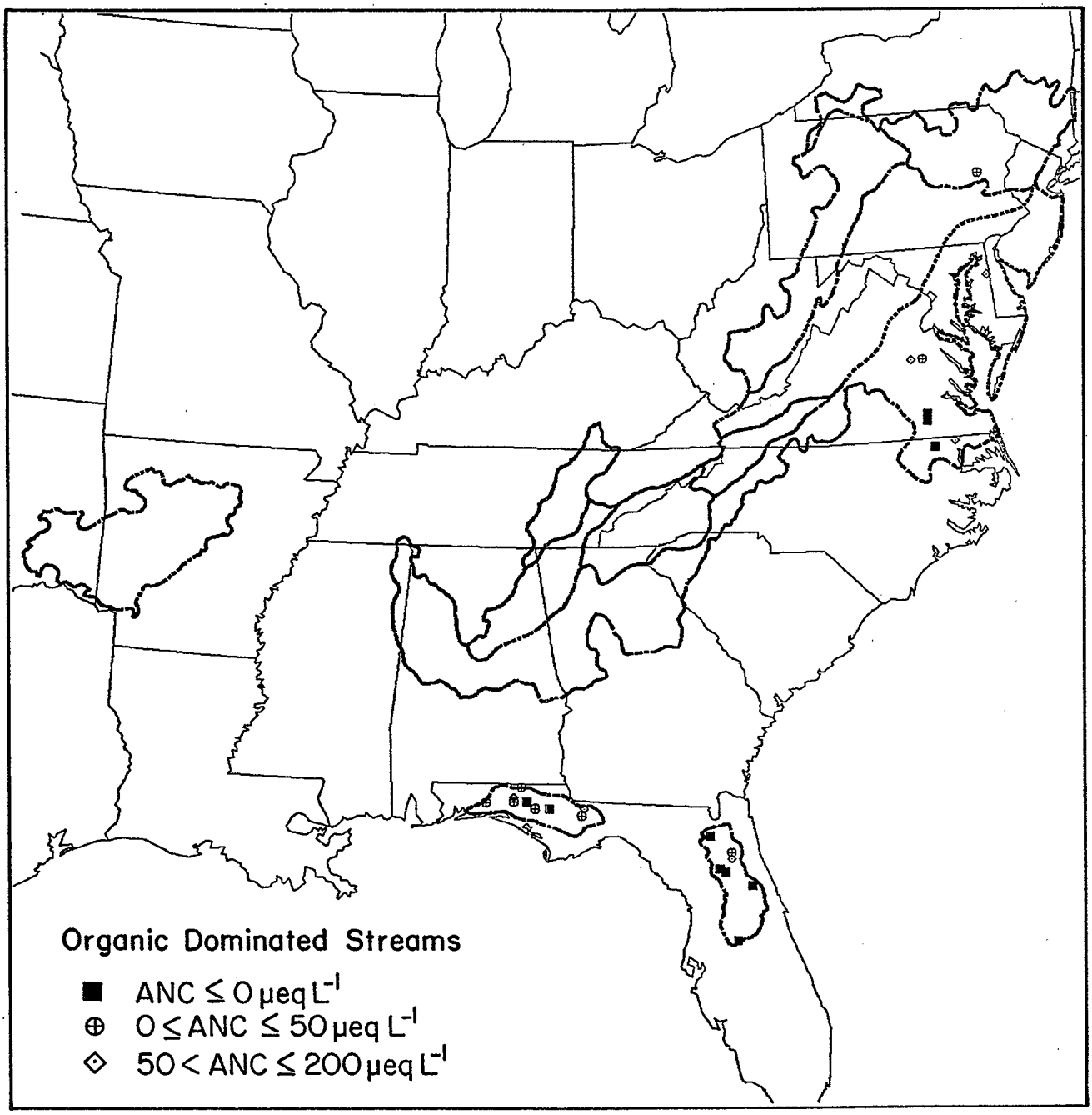


Figure 9-4. Location of NSS-I upper nodes with ANC ≤ 200 μeq L^{-1} classified as being dominated by organic anions.

Table 9-2. Weighted Mean and Standard Deviation (SD) of NSS-I Spring Index Chemistry in Organic-dominated Classified Stream Nodes$

	ORGANIC DOMINATED STREAMS					
	ANC ≤ 0		0 < ANC ≤ 50		50 < ANC ≤ 200	
Chemical	n = 16		n = 16		n = 14	
Species	Mean	SD	Mean	SD	Mean	SD
SO_4*	39.58	39.21	32.68	19.10	65.28	53.75
NO_3^-	7.31	15.75	3.31	4.29	1.53	2.71
Cl*	168.34	108.51	95.88	54.99	190.76	99.78
HCO_3^-	1.92	1.63	12.38	4.99	111.75	36.43
Organic Anions	246.89	236.55	89.93	64.16	137.80	58.20
DOC (mg L^{-1})	49.96	61.24	10.24	7.39	14.63	6.26
% Organic Anions	48.12	15.95	36.48	8.66	27.63	7.26
Color (PCU)	331.07	293.98	117.96	47.20	140.53	49.11
Sum Base Cations*	290.36	162.45	203.99	99.23	474.51	203.10
SO_4^{2-}:SBC ratio	0.15	0.11	0.15	0.08	0.13	0.07
SO_4^{2-}:ANC ratio	-2.76	2.36	2.02	1.76	0.62	0.44
ANC	-159.28	247.43	25.37	12.01	147.87	35.13
pH	4.46	0.58	5.58	0.19	6.10	0.21
Al_{tot} (μM)	19.65	9.56	12.97	8.46	29.29	16.78
Al_{ext} (μM)	8.87	5.22	3.89	3.70	5.04	4.10
$Al_{(im)}$ (μM)	4.20	3.39	1.66	1.72	1.70	1.22
Fe (μM)	14.15	7.85	6.85	5.68	16.76	12.33
Mn (μM)	0.35	0.38	0.84	0.75	2.45	2.87
Conductivity (μS cm^{-1})	76.86	67.65	28.42	9.93	54.72	22.33

$ All concentrations are expressed in μeq L^{-1} except as noted.
* Concentrations were sea salt corrected as discussed in text.

n = number of nodes classified in each group.
% Organic Anions = percentage of total anions that are organic.
Al_{ext} = MIBK-extractable aluminum (total monomeric).
$Al_{(im)}$ = inorganic monomeric aluminum (PCV method).

The organic-influenced group was defined as those streams in which organic anions comprised more than 10% of the sea salt corrected total anion sum. The value of 10% was chosen as a cutoff after examination of DOC, color, and site comment data to find streams with an organic character (moderate DOC, colored, slow moving water). The organic-influenced group represents streams likely to be affected by both acid deposition and organic acidity.

The second subgroup within the high-interest subpopulation comprises those streams in which less than 10% of the total anions were composed of organic anions. These acidic or low ANC inorganic streams represent the group of streams in which no other source of strong acid anions besides acid deposition was likely. Acidic streams in this class are very likely to have been affected by acid precipitation. For classification purposes, both the inorganic and organic-influenced class of streams were subdivided into three groups, acidic (ANC ≤ 0 μeq L^{-1}), very low ANC ($0 <$ ANC ≤ 50 μeq L^{-1}), and low ANC ($50 <$ ANC ≤ 200 μeq L^{-1}).

Streams in the acidic subgroup represent streams that are already acidic, whereas those in the very low ANC subgroup represent streams that are most sensitive to acid deposition and that, if located in geographic areas with high atmospheric acid deposition rates, may become acidic during episodes (Eshleman, in press). Streams sensitive to acid deposition are found within the low ANC (50-200 μeq L^{-1}) subgroup. Not all streams with low ANC should be considered sensitive, however, as stream water ANC is not of itself a complete indicator. Sensitivity to acid deposition effects depends also on the acid neutralizing capability of the stream watershed, which is, in turn, dependent upon such processes as sulfate adsorption and cation exchange in watershed soils.

9.3.3.2 Location--

Three of the four inorganic, acidic lower reach nodes were located in the Northern Appalachians (2Cn) (Figure 9-5). All of the acidic, organic-influenced lower reaches were found in the Mid-Atlantic Coastal Plain (3B), primarily in the New Jersey Pine Barrens. There were more acidic upper nodes (Figure 9-6) than acidic lower nodes. Inorganic, acidic upper nodes were found in the Northern Appalachians (2Cn), the Valley and Ridge (2Bn), Florida (3C), the Poconos/Catskills (1D), and the Mid-Atlantic Coastal Plain (3B). Organic-influenced, acidic upper nodes were found in subregions 1D and 3B, with one isolated site in the Southern Appalachians (2X) and two in the Florida panhandle. There were many acidic sample reaches in the New Jersey Pine Barrens, which is discussed in subsection 9.5.3.

Streams with very low ANC (between 0 and 50 μeq L^{-1}) and low ANC (between 50 and 200 μeq L^{-1}) at lower (Figure 9-7) and upper reach nodes (Figure 9-8) were found in all NSS-I subregions. All subregions except 2Bn contained at least one organic-influenced sample reach, but most were found in subregions 3C and 3B. There were more very low ANC sample reaches within the high-interest class in the Mid-Atlantic than in the Southeast. No stream reaches were observed in the Florida peninsula with ANC ≤ 200 μeq L^{-1} that were not organic dominated.

9.3.3.3 Chemical Characteristics--

Sulfate was the most abundant anion within the high-interest subpopulation of streams not influenced by organic anions (inorganic class) (Table 9-3). In the acidic subgroup, more than 75% of the mean total anion concentration was made up of sulfate. DOC concentrations were low ($<$ 2-3 mg L^{-1}) and the color value was almost always less than 30. The sum of base cations increased with increasing ANC subgroup while the SO_4^{2-}:base cation ratio decreased.

The organic-influenced streams within the high-interest subpopulation were moderately colored (29-70) and had mean DOC concentrations of 3-7 mg L^{-1} (Table 9-4), intermediate

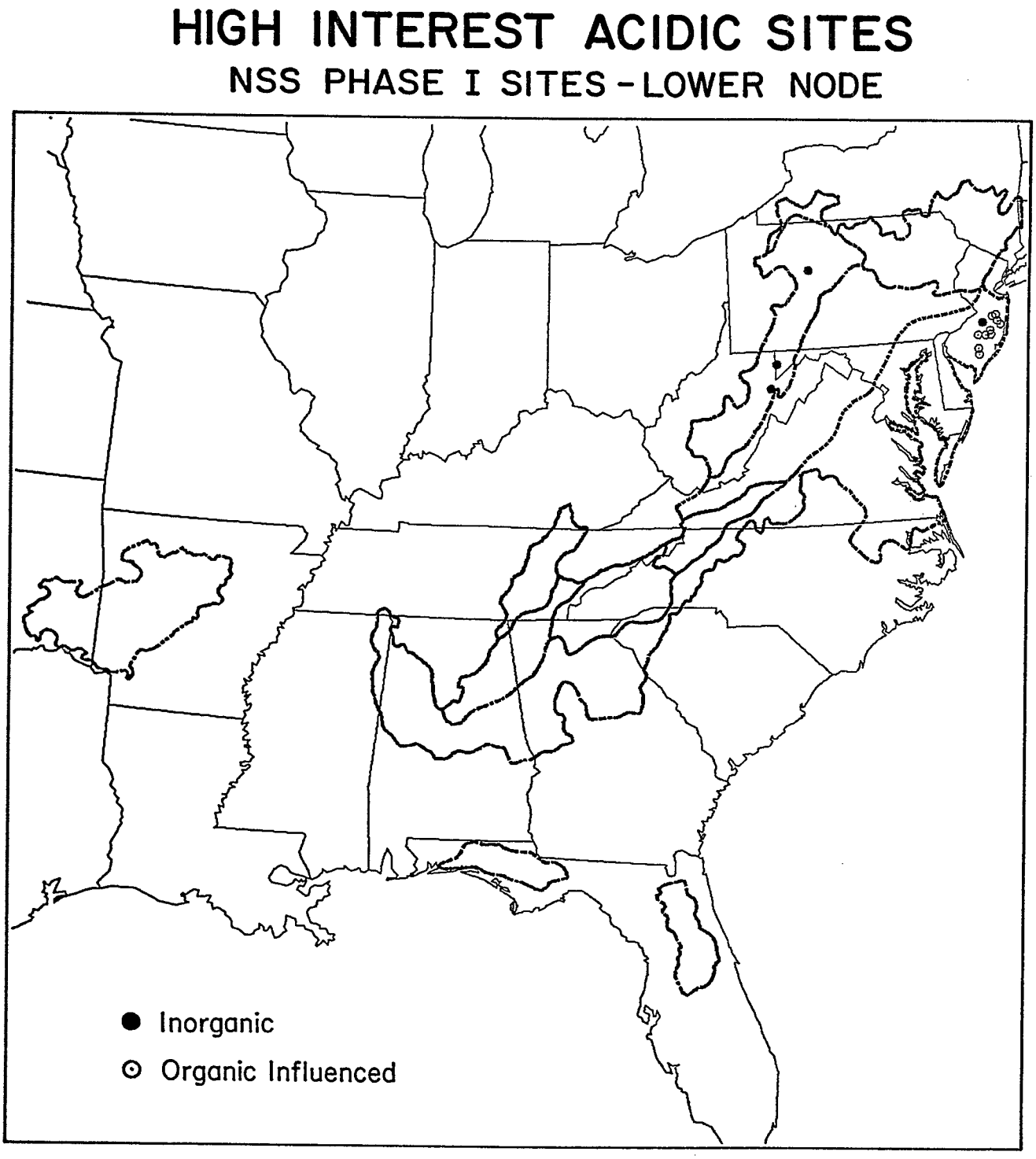


Figure 9-5. Location of the high-interest subpopulation of acidic (ANC ≤ 0 μeq L^{-1}) NSS-I lower nodes. All nodes classified as acid mine drainage and organic-dominated have been removed from the high-interest subpopulation.

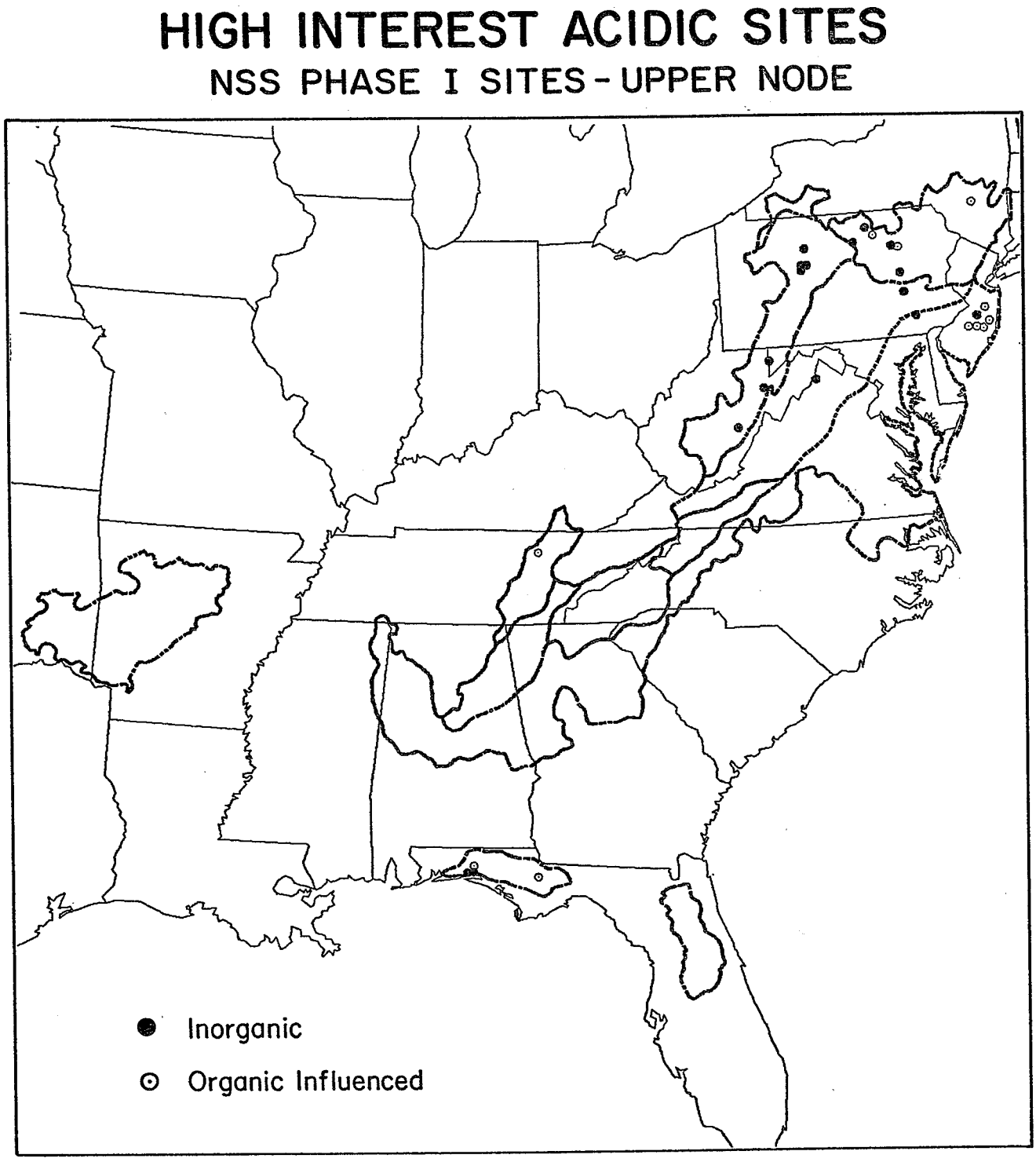


Figure 9-6. Location of the high-interest subpopulation of acidic (ANC ≤ 0 μeq L^{-1}) NSS-I upper nodes. All nodes classified as acid mine drainage and organic-dominated have been removed from the high-interest subpoplation.

HIGH INTEREST LOW ANC SITES

NSS PHASE I SITES - LOWER NODE

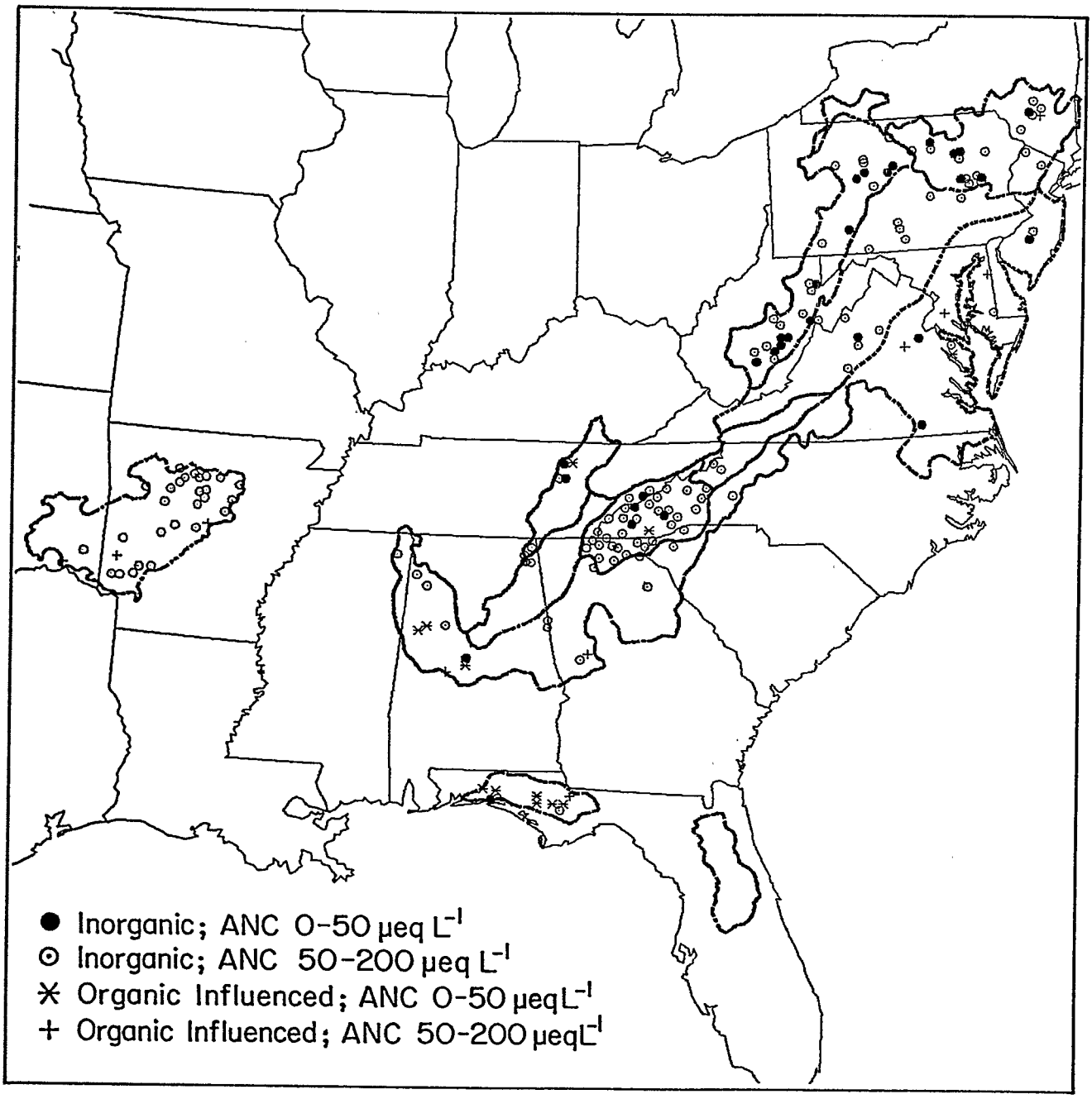


Figure 9-7. Location of the high-interest subpopulation of very low and low ANC NSS-I lower nodes. All nodes classified as having substantial watershed sources of sulfate and organic dominance have been removed from the high-interest subpopulation.

HIGH INTEREST LOW ANC SITES

NSS PHASE I SITES - UPPER NODE

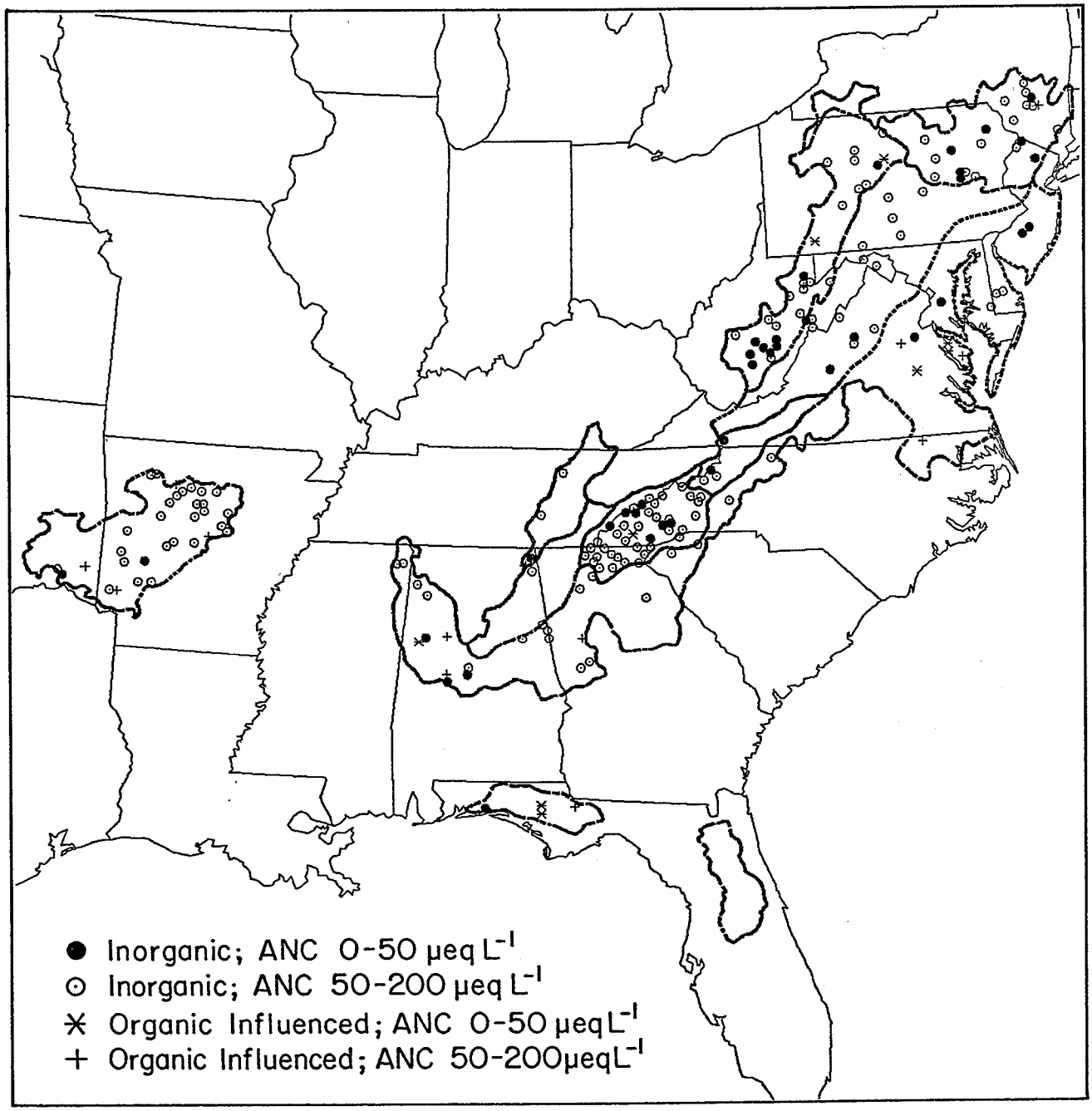


Figure 9-8. Location of the high-interest subpopulation of very low and low ANC NSS-I upper nodes. All nodes classified as having substantial watershed sources of sulfate and organic dominance have been removed from the high-interest subpopulation.

Table 9-3. Weighted Mean and Standard Deviation (SD) of NSS-I Spring Index Chemistry in Inorganic Classified Stream Nodes

	INORGANIC STREAMS					
	ANC ≤ 0		0 < ANC ≤ 50		50 < ANC ≤ 200	
Chemical	n = 21		n = 69		n = 255	
Species	Mean	SD	Mean	SD	Mean	SD
SO_4*	162.95	66.31	121.40	65.46	109.18	71.90
NO_3^-	6.90	10.19	49.01	101.78	33.82	80.55
Cl*	29.82	25.36	78.07	134.35	71.69	75.04
HCO_3^-	0.96	0.86	19.46	15.81	102.27	43.64
Organic Anions	14.70	9.22	12.84	13.28	12.96	8.12
DOC (mg L^{-1})	2.05	1.33	1.45	1.59	1.34	0.85
% Organic Anions	6.62	2.25	4.72	2.34	4.13	1.82
Color (PCU)	16.11	9.08	14.02	13.67	18.22	11.09
Sum Base Cations*	162.43	90.96	270.91	222.44	340.99	187.38
SO_4^{2-}:SBC ratio	0.96	0.35	0.52	0.20	0.31	0.16
SO_4^{2-}:ANC ratio	-15.68	15.78	12.95	26.16	1.06	0.87
ANC	-18.16	11.68	23.83	16.04	122.26	42.54
pH	4.82	0.22	5.88	0.46	6.74	0.35
Al_{tot} (μM)	11.58	5.12	4.82	4.27	6.12	9.48
Al_{ext} (μM)	8.85	4.75	1.54	1.85	0.31	0.35
$Al_{(im)}$ (μM)	6.65	4.83	0.76	1.24	0.06	0.12
Fe (μM)	1.09	1.49	0.78	1.21	1.22	2.94
Mn (μM)	1.30	0.67	0.65	0.74	0.56	1.44
Conductivity (μS cm^{-1})	34.20	13.34	35.76	29.95	38.66	23.95

$ All concentrations are expressed in μeq L^{-1} except as noted.
* Concentrations were sea salt corrected as discussed in text.

n = number of nodes classified in each group.
% Organic Anions = percentage of total anions that are organic.
Al_{ext} = MIBK-extractable aluminum (total monomeric).
$Al_{(im)}$ = inorganic monomeric aluminum (PCV method).

Table 9-4. Weighted Mean and Standard Deviation (SD) of NSS-I Spring Index Chemistry in Organic-influenced Stream Nodes

	ORGANIC INFLUENCED STREAMS					
	ANC ≤ 0		0 < ANC ≤ 50		50 < ANC ≤ 200	
Chemical	n = 21		n = 21		n = 23	
Species	Mean	SD	Mean	SD	Mean	SD
SO_4*	105.33	58.90	74.63	49.79	92.02	49.55
NO_3^-	6.72	13.84	10.02	15.03	40.46	78.37
Cl*	16.09	26.60	48.66	38.46	106.08	98.84
HCO_3^-	1.50	1.44	21.75	13.23	103.77	40.21
Organic Anions	24.01	18.28	29.35	19.27	59.63	36.84
DOC (mg L^{-1})	4.09	3.69	3.26	2.11	6.32	4.00
% Organic Anions	14.55	4.22	15.80	5.08	14.57	4.71
Color (PCU)	28.76	32.55	36.04	19.73	70.08	39.60
Sum Base Cations*	73.54	42.71	165.24	92.14	379.19	218.95
SO_4^{2-}:SBC ratio	0.84	0.42	0.37	0.16	0.25	0.11
SO_4^{2-}:ANC ratio	-4.50	9.26	2.92	7.74	1.33	2.09
ANC	-54.09	54.05	24.51	15.58	121.33	40.61
pH	4.59	0.47	5.66	0.36	6.25	0.40
Al_{tot} (μM)	8.05	6.20	11.01	9.65	17.52	19.25
Al_{ext} (μM)	6.60	6.48	2.37	2.33	1.78	1.75
$Al_{(im)}$ (μM)	4.25	3.81	0.81	0.89	0.69	0.99
Fe (μM)	4.61	4.69	2.73	2.35	9.56	14.89
Mn (μM)	1.27	2.57	1.01	0.79	2.51	2.50
Conductivity (μS cm^{-1})	40.47	25.25	24.76	10.74	47.13	28.88

$ All concentrations are expressed in μeq L^{-1} except as noted.
* Concentrations were sea salt corrected as discusssed in text.

n = number of nodes classified in each group.
% Organic Anions = percentage of total anions that are organic.
Al_{ext} = MIBK-extractable aluminum (total monomeric).
$Al_{(im)}$ = inorganic monomeric aluminum (PCV method).

between the organic-dominated and inorganic streams (Tables 9-2 and 9-3). Sulfate was the major anion in the acidic and very low ANC subgroups, whereas chloride and bicarbonate concentrations were higher than sulfate concentrations in the low ANC subgroup.

9.3.4 Discussion

The classification process described in this subsection can best be summarized with a flowchart (Figure 9-9). The end result of the classification is a group of high-interest streams for an assessment of acidic deposition effects. The criteria used to remove streams with probable acid sources other than acid deposition are summarized on the flowchart.

The differences in relative composition of anions among the stream chemical classes can be seen in trilinear plots of sulfate, nitrate, and organic anion (Figure 9-10). In each of the ANC classes, the organic-dominated stream nodes are clustered near the high organic anion tip of the triangle. Inorganic stream nodes are concentrated near the high-sulfate end of the triangle with some dispersion along the nitrate axis, all with low organic anion values. The organic-influenced stream nodes are intermediate between the organic-dominated and inorganic stream nodes.

In order to determine if neutral salt displacement of hydrogen ions was occurring in coastal areas, stream water ANC was plotted against the stream water Na^+:Cl^- ratio. If Na^+ is replacing H^+ in these watersheds, the more acidic streams (lower ANC) should have lower Na^+:Cl^- ratios, because the sodium would be removed while the chloride would remain constant (assuming chloride is conservative). In stream nodes within 50 km of the ocean, there was no relationship ($r^2 = 0.017$) between ANC and the Na^+:Cl^- ratio (Figure 9-11). The most acidic stream nodes (ANC < 0), had Na^+:Cl^- ratios greater than or equal to that found in sea water (0.86). Similar plots of ANC in coastal streams versus the ratios of the other base cations to chloride also showed little relationship (Ca^{2+}:Cl^- $r^2 = 0.297$, Mg^{2+}:Cl^- $r^2 = 0.077$, K^+:Cl^- $r^2 = 0.018$). Thus on the regional level, neutral salt hydrogen ion displacement does not appear to play a major role in stream acidification. There were many streams with Na^+:Cl^- greater than 0.86, indicating internal watershed sources of sodium.

Fish populations are very susceptible to high concentrations of aluminum, particularly inorganic monomeric aluminum ($Al_{(im)}$) (subsection 6.3.2). The $Al_{(im)}$ concentrations were much higher in NSS-I streams with ANC ≤ 0 μeq L^{-1} compared to low ANC streams (Figure 9-12) due to aluminum mobilization in the acidic water. In streams with ANC ≤ 200 μeq L^{-1}, all of the inorganic, 85% of the organic-influenced, and roughly 50% of the organic-dominated streams had $Al_{(im)}$ concentrations below 0.05 mg L^{-1}, a level generally considered a threshold concentration above which various fish species experience reductions in growth and survival (Figure 9-12). The inorganic, acidic stream group, those most likely to have been affected by acid deposition, had high $Al_{(im)}$ concentrations. About 75% of the streams in this group had $Al_{(im)}$ concentrations within the range of concentrations thought to cause damage to fish populations. Acidic streams with organic influence and dominance had lower $Al_{(im)}$ concentrations than the inorganic streams but the median concentrations were still within the range of toxic concentrations.

9.4 POPULATION ESTIMATES OF THE PROBABLE SOURCES OF ACIDITY

The NSS-I statistical design permits an estimation of the number of stream reaches in each subregion within each chemical classification group (Section 2.4; Overton, 1987). The population estimates for stream reaches classified as having acid mine drainage and substantial watershed sources of sulfate are presented in Table 9-5. The majority of these high-sulfate streams are

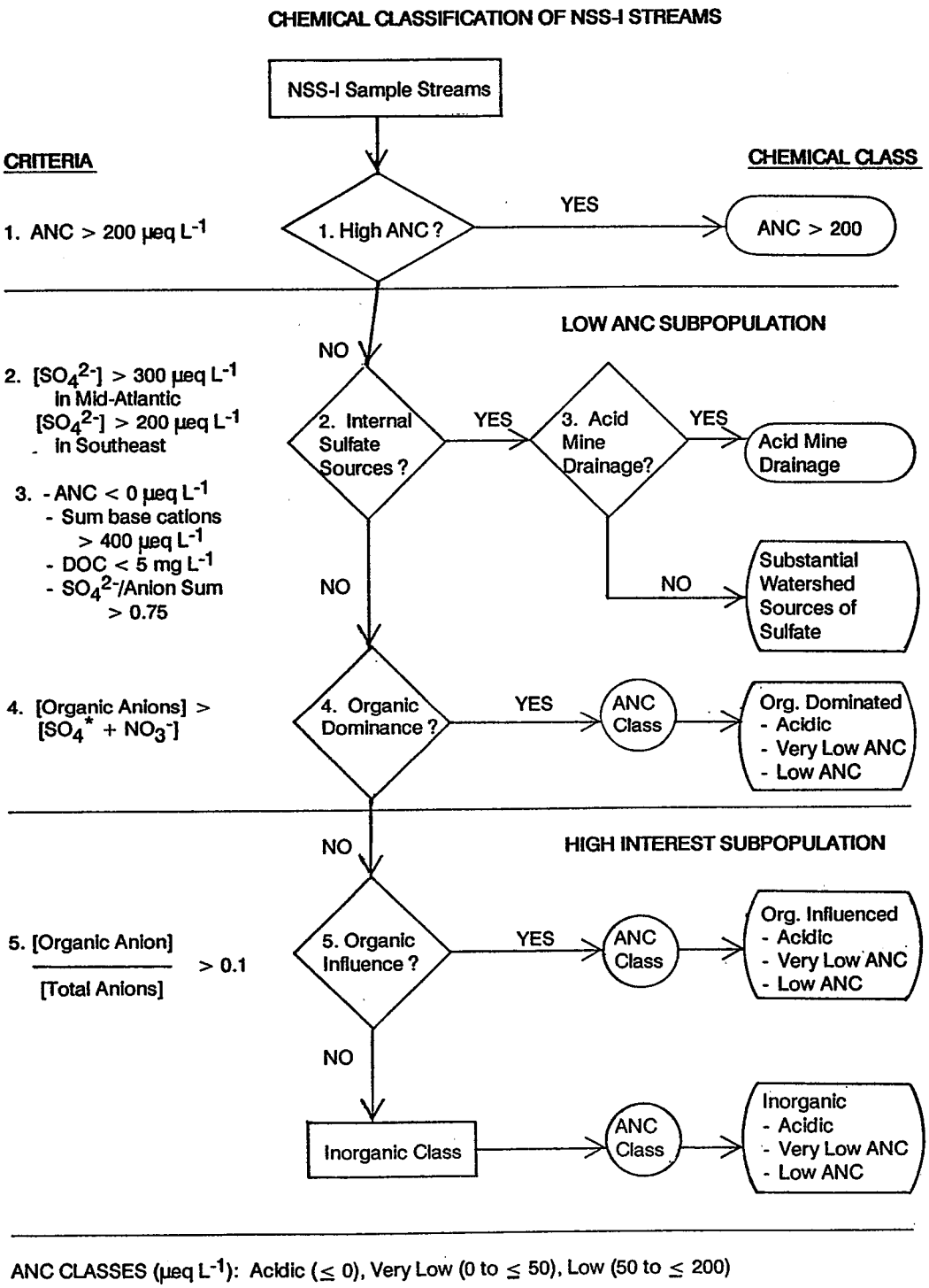


Figure 9-9. Chemical classification flowchart.

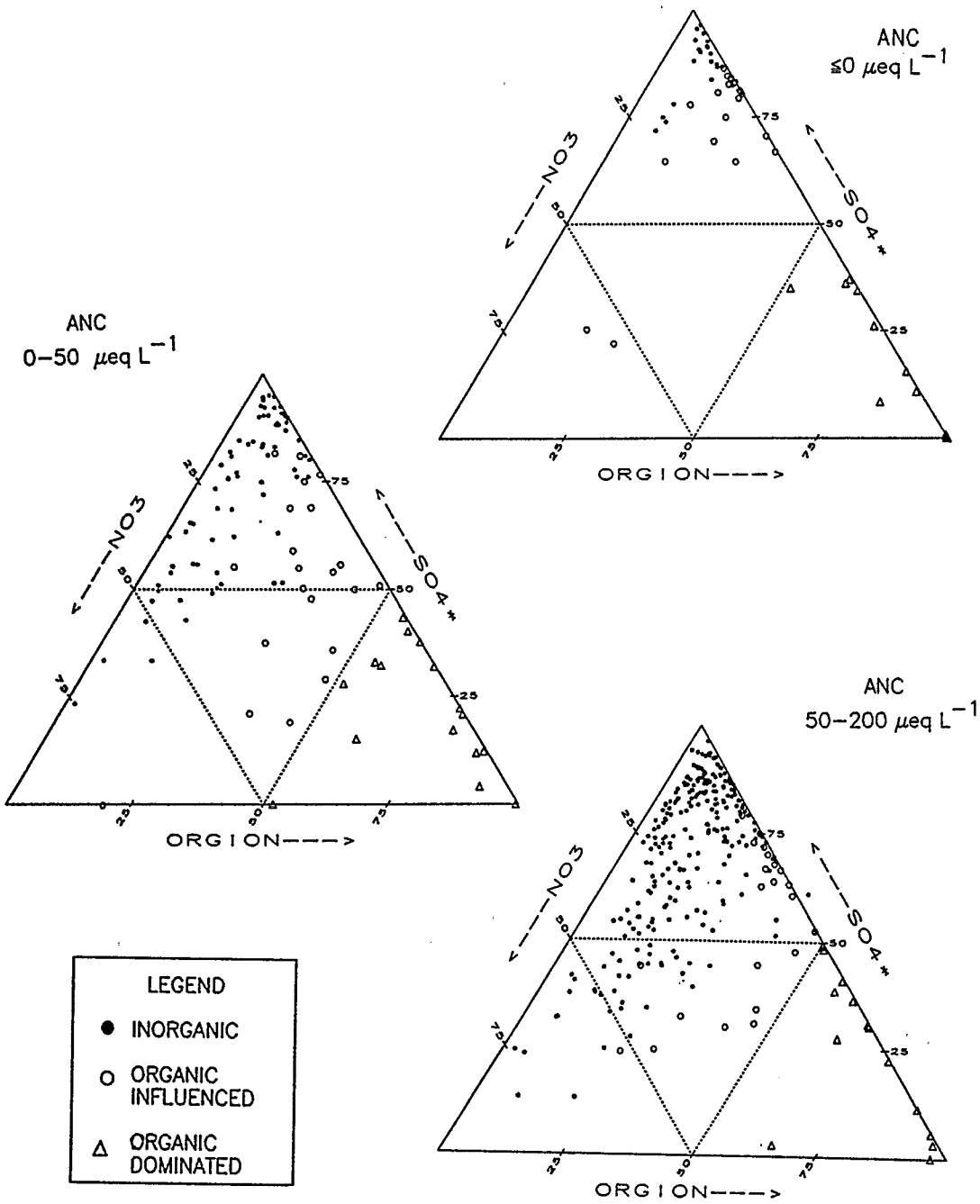


Figure 9-10. **Trilinear plots for SO_4^*, NO_3^-, and organic anions showing the different anionic makeup of inorganic, organic-influenced, and organic-dominated NSS-I nodes in three different ANC classes.**

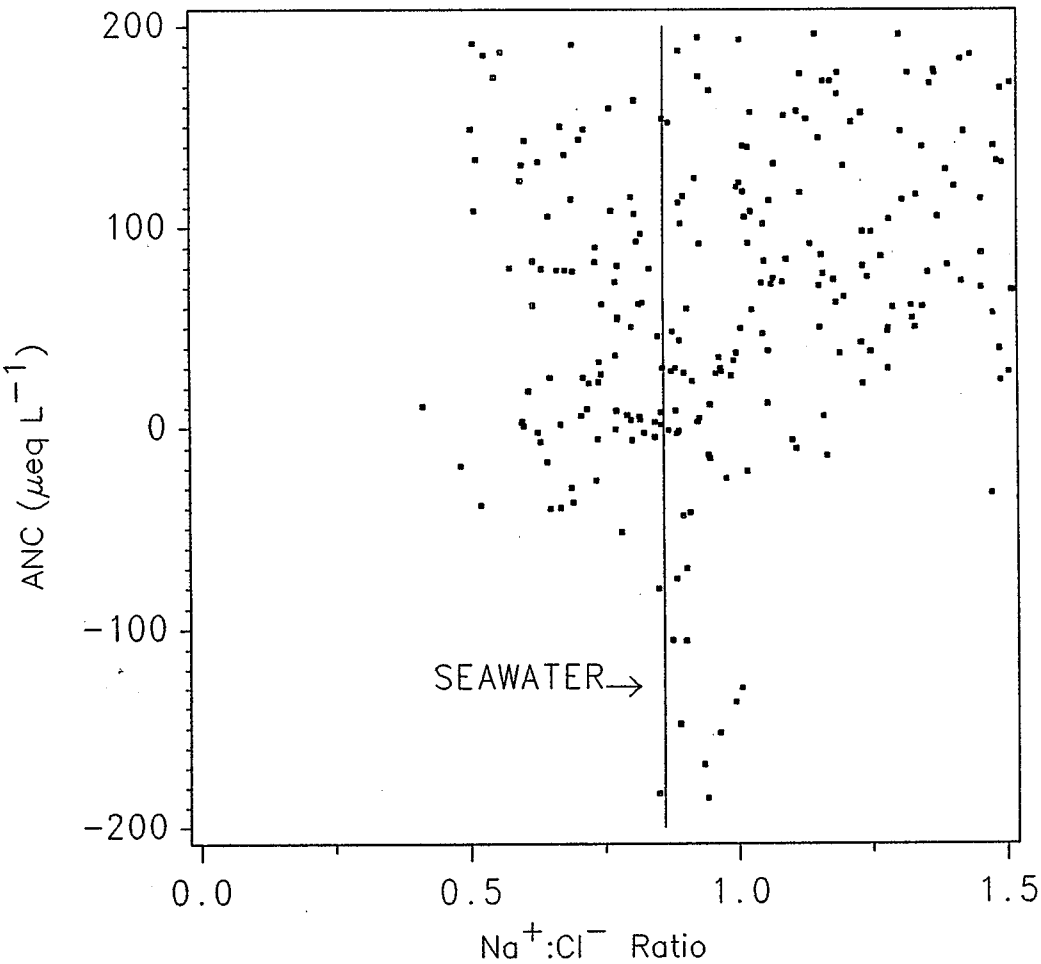


Figure 9-11. Scatterplot showing the relationship between stream water ANC (μeq L^{-1}) and stream water Na^+:Cl^- molar ratio in NSS-I nodes within 50 km of the coast. The vertical line at 0.86 represents the sea water Na^+:Cl^- ratio.

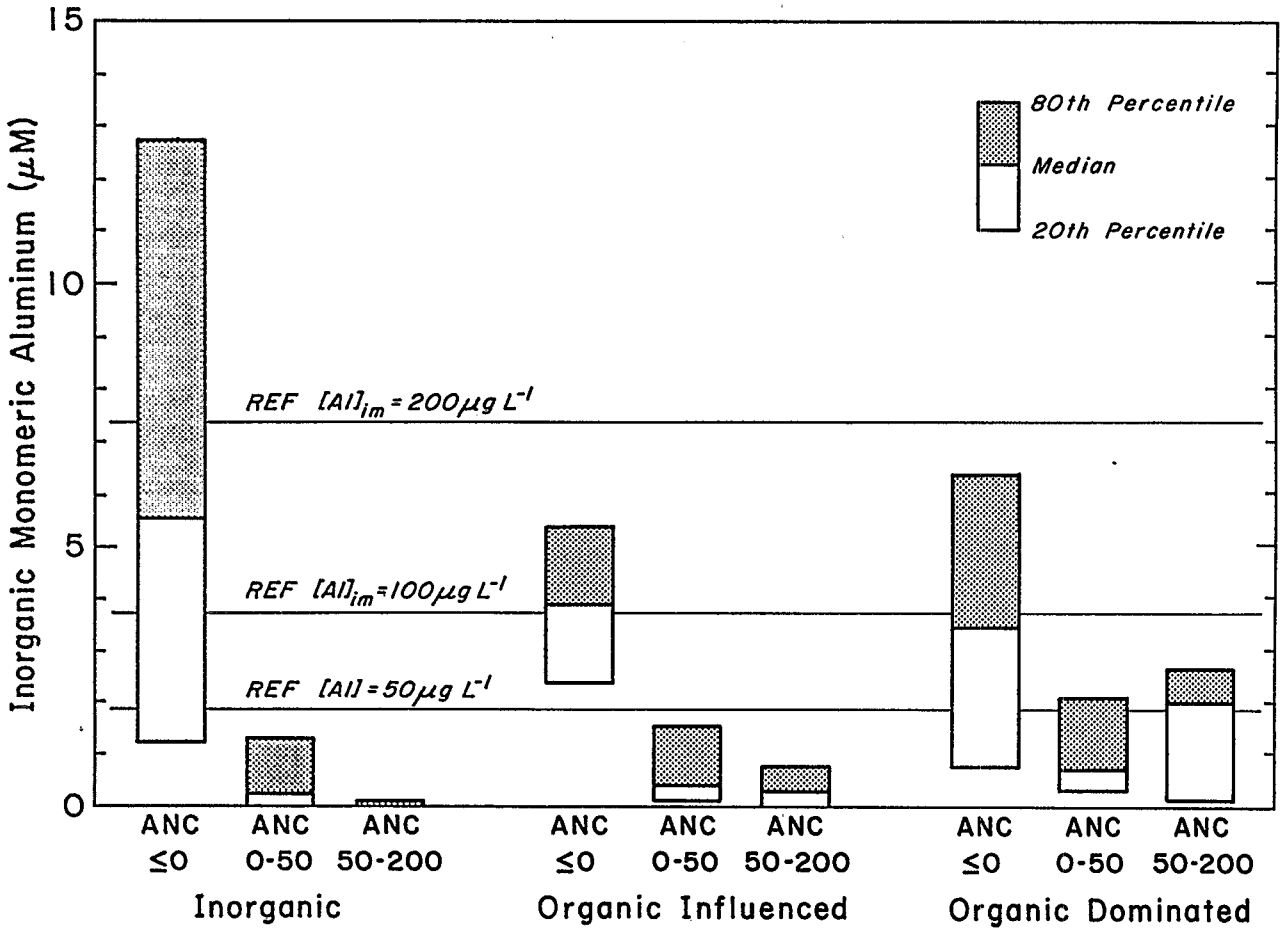


Figure 9-12. Median, 20th percentile, and 80th percentile of inorganic monomeric aluminum concentrations (μM) in inorganic, organic-influenced, and organic-dominated chemical classes. The three reference lines refer to concentration levels at which aluminum is reported to have adverse effects on fish populations.

Table 9-5. Estimated Number and Length of Stream Reaches Classified as Impacted by Acid Mine Drainage or as Having Substantial Watershed Sources of Sulfate at Either the Upper or Lower Node

ACID MINE DRAINAGE IMPACTED STREAMS

GROUP	Estimated Number of Reaches	Estimated Length (km)
SUBREGION		
Poconos/Catskills (1D)	9	126
Valley and Ridge (2Bn)	318	849
N. Appalachians (2Cn)	929	2496
S. Appalachians (2X)	121	1123
TOTAL	1377	4594
GEOGRAPHIC SITE CLASS		
Allegheny High Plateau	151	627
Allegheny Forested Plateau	296	780
Allegheny Forested/Agric. Plateau	603	2212
Glaciated Forested Plateau	9	126
Valleys of the Valley & Ridge Province	318	849
TOTAL	1377	4594

STREAMS WITH SUBSTANTIAL WATERSHED SOURCES OF SULFATE

	Estimated Number of Reaches	Estimated Length (km)
Poconos/Catskills (1D)	123	180
N. Appalachians (2Cn)	1372	3818
Valley and Ridge (2Bn)	1078	4992
Coastal Plain (3B)	1139	3409
Piedmont (3A)	158	564
S. Appalachians (2X)	225	1568
Ozarks/Ouchitas (2D)	225	1568
Total	4216	15145

The distribution of streams with substantial watershed sources of sulfate among the different geographic site classes is given in Tables 9-8 and 9-9.

found in the Northern Appalachians (2Cn). Of the estimated 9,417 reaches in the initial target population in this subregion, 929 (9.9%) were impacted by acid mine drainage at one or both nodes; 1,372 (15%) reaches had substantial watershed sources of sulfate at one or both nodes. Estimations indicate that 1,377 stream reaches, or over 4,500 km of streams in the entire NSS-I sampling area, were impacted by acid mine drainage at either upper or lower nodes, or both. Almost all the sites impacted by acid mine drainage were found in the Allegheny Plateau geographic site class. A higher number of stream reaches (4,216) have ANC $\leq$ 200 μeq L^{-1} and receive substantial contributions of sulfate from watershed sources.

It is important to keep in mind that the NSS-I subregion locations and target stream resource definitions were delineated for the purpose of assessing the status and extent of acid deposition effects. Therefore, the population estimates and maps presented in this section apply only to the streams affected by acid mine drainage within these areas and within the target reach size limitation and other inclusion criteria. The total stream resource impacted by acid mine drainage may be considerably larger.

The number of acidic, very low ANC and low ANC stream reaches, divided into inorganic, organic-influenced and organic-dominated groups for each subregion, are presented for lower nodes in Figure 9-13 and for upper nodes in Figure 9-14. No acidic lower nodes were observed in the Poconos/Catskills (1D), Valley and Ridge (2Bn), Ozarks/Ouachitas (2D), Southern Blue Ridge (2As), Southern Appalachians (2X), or Piedmont (3A). The acidic lower reaches in Florida (3C) were all organic dominated, whereas those in the Mid-Atlantic Coastal Plain (3B) were found in roughly equal amounts as inorganic, organic influenced, and organic dominated. The acidic lower reaches in subregion 2Cn were all inorganic. No acidic upper nodes were observed in subregion 2D, 2As, or 3A. The vast majority of the acidic upper reaches observed in the Interior Mid-Atlantic subregions (1D, 2Bn, 2Cn) were classified as inorganic.

Almost all the reaches in Florida (3C) estimated to have low and very low ANC were affected by organic acidity. Very few reaches affected by organic acidity were estimated outside of subregions 3A, 3B, and 3C. In the Ozarks/Ouachitas (2D), very few reaches had ANC $\leq$ 50 μeq L^{-1}, but almost 3,000 upper and lower reaches were estimated to have ANC between 50 and 200 μeq L^{-1}. The pattern observed in lower reach nodes in subregions 2Bn and 2As was similar to that in 2D.

In the combined NSS-I subregions, an estimated 565 downstream nodes (1.0% of the target population) and more than three times as many upstream nodes (1,812, or 3.2%) were acidic and classified as inorganic, indicating that the most probable source of acidity was acid deposition. Another 168 (0.3%) lower and 375 (0.7%) upper nodes were organic-influenced acidic streams, with at least a portion of their acidity potentially derived from organic acids. There were 4,159 downstream nodes (7.3%) with very low ANC estimated in the high-interest subpopulation; 3,070 were inorganic and 1,089 were organic influenced. In contrast, 5,975 upstream nodes (10.5%) had very low ANC (4,815 inorganic, 1,160 organic influenced). Over 13,000 upstream and downstream reach nodes (23-25%) were classified as inorganic, with low ANC. A smaller number of low ANC reaches (1,305 lower nodes, 1,704 upper nodes) were classified as organic influenced.

9.4.1 Interpolated Length Estimates

Chemistry at upper and lower ends of stream reaches with one or both nodes in the high-interest subpopulation was linearly interpolated to estimate the stream length having less than specified pH and ANC reference values. The NSS-I population expansion algorithm and the interpolated reach lengths were used to estimate the length of streams having less than reference values for the target population. Hydrogen ion concentration was used to linearly

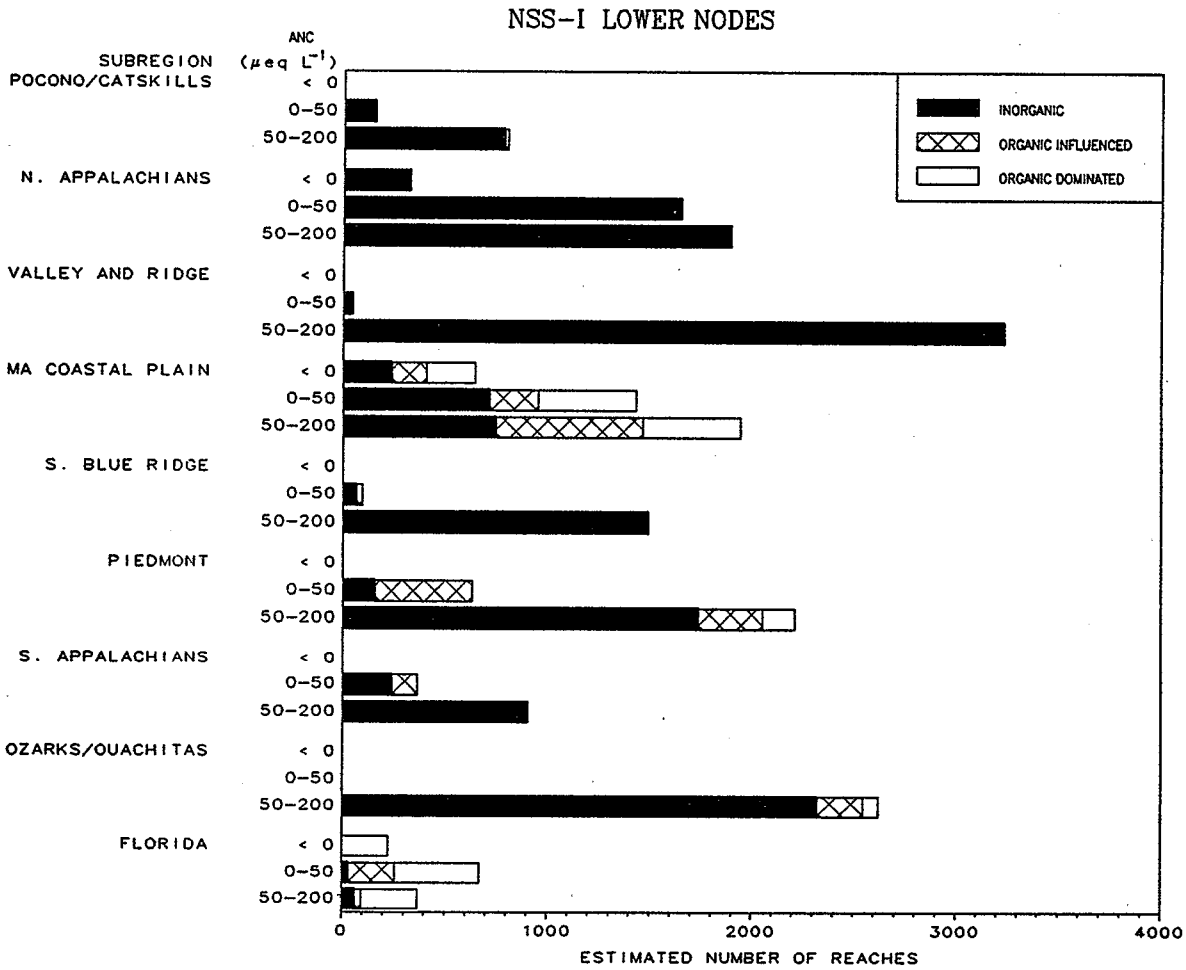


Figure 9-13. Population estimates of the number of downstream reach nodes in each NSS-I subregion found in inorganic, organic-influenced, and organic-dominated chemical classes.

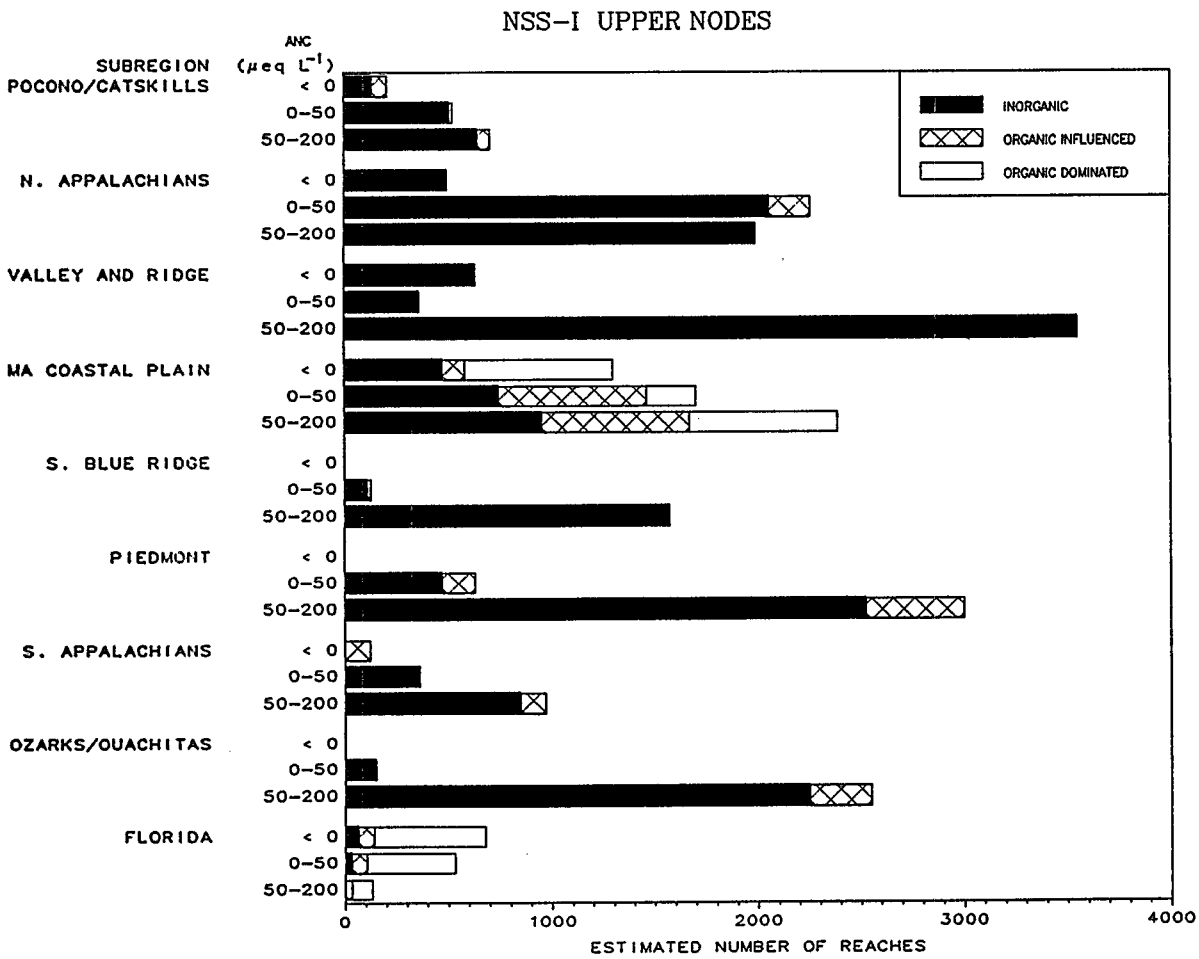


Figure 9-14. Population estimates of the number of upstream reach nodes in each NSS-I subregion found in inorganic, organic-influenced, and organic-dominated chemical classes.

interpolate pH. In cases where the alternate node of an inorganic or organic-influenced node was noninterest (affected by acid mine drainage, tidal influences, etc.), impacted by watershed sulfate sources, or dominated by organic anions, one-half of the reach was assumed to have the high-interest chemistry. This assumption was necessary because the ANC and pH of the alternate node could not be used in the interpolation, since its chemistry did not place it in the high-interest subpopulation. If one node was classified as inorganic and the other as organic influenced, and the chemistry of both nodes was below the reference value, then the reach length was classified as half inorganic and half organic influenced. If one node was above the reference value and the other below the reference value, the entire interpolated reach length was classified the same as the node below the reference value.

The estimated combined length of acidic (ANC ≤ 0) stream reaches within the high-interest subpopulation was 4,455 km (Table 9-6). Of this length, 73% was classified in the inorganic group. These inorganic acid streams were found primarily in the interior subregions of the Mid-Atlantic Region (1D, 2Bn, and 2Cn), in the New Jersey Pine Barrens in subregion 3B, and in a small length in Florida (3C). An estimated 19,945 km of streams had ANC ≤ 50 μeq L^{-1} and were classified in the high-interest subpopulation. Seventy-one percent of these streams were classified as inorganic.

The estimated combined length of stream reaches with pH ≤ 5.0 within the high-interest subpopulation was 4,145 km (Table 9-7). No sites with pH < 5.0 classified as being in the high-interest subpopulation were observed in the southeastern United States. An estimated 13,642 km of streams had pH < 5.5. A greater length of streams had pH < 5.5 in the Mid-Atlantic than the Southeast.

Estimates of acidic stream length (pH ≤ 5.0, ANC ≤ 0) based on the first NSS-I sample (in the Mid-Atlantic) were somewhat higher than estimates based on the index value (Table 9-6), due to a trend of increasing spring baseflow ANC. For ANC ≤ 50 μeq L^{-1}, ANC ≤ 200 μeq L^{-1}, pH ≤ 5.5, and pH ≤ 6.0, the estimated stream lengths based on first visit and index values were very similar.

9.5 GEOGRAPHIC DISTRIBUTION OF STREAM CHEMICAL GROUPINGS

In order to examine the relationships between probable sources of stream water acidity and geographic characteristics, stream node chemical classifications were categorized by geographic site classification (Section 5.5). Using the NSS-I population expansion algorithm, the number of stream reaches in each chemical class was estimated for each geographic site class. These estimated numbers are reported for both downstream (Table 9-8) and upstream (Table 9-9) reach nodes. The percentage of acidic (ANC ≤ 0 μeq L^{-1}) and very low ANC (0-50 μeq L^{-1}) downstream (Table 9-10) and upstream reach nodes (Table 9-11) within the refined target population of each geographic site class were also estimated. The geographic distribution of acid mine drainage sites, which are not in the refined target population, was presented in Table 9-5.

It should be emphasized that the number of reaches reported in Tables 9-8 and 9-9 are estimates, based on roughly 450 stream reach samples and calculated using the NSS-I probability sampling framework (Section 2.4). In some cases, the population estimate is based on only one sampled reach or a very few sampled reaches belonging to a particular chemical and geographic site class combination. While these estimates should be interpreted with caution, they represent a statistical best estimate of the number of stream reaches within specific combinations of geographical and chemical class. Standard errors associated with these population estimates are detailed in Appendix D. The number of streams (n) actually sampled in the refined target population within each geographic site class is listed in Tables 9-10 (lower nodes) and 9-11

Table 9-6. Interpolated Length (km) Estimates of Streams in the High-Interest Subpopulation with ANC Less than Reference Values

	ANC ≤ 0 μeq L^{-1}		
Region	Inorganic	Organic Influenced	Total
Interior Mid-Atlantic	1984 (2607)	382 (390)	2366 (2997)
Mid-Atlantic Coastal Plain	1246 (3292)	660 (1009)	1906 (4301)
Interior Southeast	-	121	121
Florida	13	49	62
Total	3243 (5912)	1212 (1569)	4455 (7481)

	ANC ≤ 50 μeq L^{-1}		
Region	Inorganic	Organic Influenced	Total
Interior Mid-Atlantic	6925 (8686)	454 (433)	7379 (9119)
Mid-Atlantic Coastal Plain	5173 (5218)	2217 (2336)	7390 (7554)
Interior Southeast	3000	1070	4070
Florida	790	416	1206
Total	15,888 (17,694)	4157 (4255)	20,045 (21,949)

	ANC ≤ 200 μeq L^{-1}		
Region	Inorganic	Organic Influenced	Total
Interior Mid-Atlantic	26,042 (27447)	509 (558)	26,551 (28,005)
Mid-Atlantic Coastal Plain	7938 (7972)	5782 (5902)	13,720 (13,874)
Interior Southeast	33,706	6298	40,004
Florida	499	936	1435
Total	68,185 (69,624)	13,525 (13,694)	81,710 (83,318)

Values in parentheses give the estimated length using data from the first sampling visit rather than the spring index value. Sites in the Southeast were only visited once.

Table 9-7. Interpolated Length (km) Estimates of Streams in the High-Interest Subpopulation with pH Less than Reference Values

	pH ≤ 5.0		
Region	Inorganic	Organic Influenced	Total
Interior Mid-Atlantic	1782 (1933)	426 (434)	2208 (2367)
Mid-Atlantic Coastal Plain	1241 (2401)	696 (1009)	1937 (3410)
Interior Southeast	-	-	-
Florida	-	-	-
Total	3023 (4334)	1122 (1443)	4145 (5777)

	pH ≤ 5.5		
Region	Inorganic	Organic Influenced	Total
Interior Mid-Atlantic	3961 (4093)	495 (514)	4456 (4607)
Mid-Atlantic Coastal Plain	6154 (6319)	1439 (1414)	7593 (7733)
Interior Southeast	411	317	728
Florida	314	551	865
Total	10,840 (11,137)	2802 (2796)	13,642 (13,933)

	pH ≤ 6.0		
Region	Inorganic	Organic Influenced	Total
Interior Mid-Atlantic	6394 (6732)	780 (726)	7174 (7458)
Mid-Atlantic Coastal Plain	8057 (7766)	5806 (5201)	13,863 (12,967)
Interior Southeast	3601	1917	5518
Florida	491	790	1281
Total	18,543 (18,590)	9293 (8634)	27,836 (27,224)

Values in parentheses give the estimated length using data from the first sampling visit instead of the spring index value. Sites in the Southeast were only visited once.

Table 9-8. Estimated Number of Target Reach Lower Nodes in Each Geographic Site Class Present in Stream Chemical Classes

Geographic Site Class	$\hat{N}$#	INORGANIC ANC ≤ 0	INORGANIC ANC 0-50	INORGANIC ANC 50-200	ORGANIC INFLUENCED ANC ≤ 0	ORGANIC INFLUENCED ANC 0-50	ORGANIC INFLUENCED ANC 50-200
Allegheny Plateau							
High Plateau	218	36	25	158	-	-	-
Forested Plateau	4,178	291	1320	760	-	-	-
Forested Agric. Plat.	3,547	-	-	833	-	-	-
NE Mid-Atlantic							
Pocono/Catskill Mts.	351	-	2	229	-	-	-
Glaciated Agric. Plat.	866	-	-	119	-	-	-
Glaciated Forested Plat.	209	-	80	119	-	-	-
Valley and Ridge Province							
Ridges	4,359	-	427	1,012	-	-	-
Valleys	11,809	-	-	2,370	-	-	16
Arkansas/Oklahoma							
Boston Mts.	873	-	-	723	-	-	-
Ouachita Mts.	1,126	-	-	375	-	-	150
Arkansas R. Valley	1,365	-	-	773	-	-	-
Piedmont Province							
Piedmont	9,258	-	-	1,108	-	-	397
Piedmont Lowlands	2,297	-	-	-	7	-	-
S. Appalachian Highlands							
Blue Ridge Mts.	2,962	-	67	2,053	-	28	-
Cumberland Plateau	1,307	-	243	821	-	121	-
French Broad R. Valley	64	-	-	-	-	-	-
Coastal Plain							
Eastern Mid-Atlantic	2,036	-	239	239	-	-	239
Western Mid-Atlantic	6,133	-	478	478	-	239	239
New Jersey Pine Barrens	432	239	-	32	161	-	-
Eastern Gulf	1,580	-	158	474	-	474	158
Western Gulf	753	-	-	453	-	-	75
Florida							
Panhandle Upland	687	-	32	32	-	227	32
Peninsula Upland	442	-	-	-	-	-	-
Panhandle Swamp	264	-	-	32	-	-	-
Peninsula Swamp	163	-	-	-	-	-	-
NSS-I TOTALS	57,277	565	3,070	13,194	168	1,089	1,305

$\hat{N}$ represents the estimated number of reaches in each geographic site class.
See Figure 9-9 for a flow chart depicting the chemical classification procedure.

Table 9-8. Estimated Number of Target Reach Lower Nodes in Each Geographic Site Class Present in Stream Chemical Classes (Continued)

Geographic Site Class	$\hat{N}$#	ORGANIC DOMINATED ANC ≤ 0	ANC 0-50	ANC 50-200	Watershed sulfate sources	ANC > 200
Allegheny Plateau						
High Plateau	218	-	-	-	-	-
Forested Plateau	4,178	-	-	-	767	1,040
Forested Agric. Plat.	3,547	-	-	-	600	2,114
NE Mid-Atlantic						
Pocono/Catskill Mts.	351	-	-	-	-	119
Glaciated Agric. Plat.	866	-	-	-	-	746
Glaciated Forested Plat.	209	-	-	-	-	10
Valley and Ridge Province						
Ridges	4,359	-	-	-	636	2,284
Valleys	11,809	-	-	-	318	9,106
Arkansas/Oklahoma						
Boston Mts.	873	-	-	-	-	150
Ouachita Mts.	1,126	-	-	-	75	525
Arkansas R. Valley	1,365	-	-	-	-	591
Piedmont Province						
Piedmont	9,258	-	-	-	-	7,754
Piedmont Lowlands	2,297	-	-	-	-	2,290
S. Appalachian Highlands						
Blue Ridge Mts.	2,962	-	-	-	-	814
Cumberland Plateau	1,307	-	-	-	121	-
French Broad R. Valley	64	-	-	-	-	64
Coastal Plain						
Eastern Mid-Atlantic	2,036	-	-	-	365	955
Western Mid-Atlantic	6,133	239	478	478	239	3,267
New Jersey Pine Barrens	432	-	-	-	-	-
Eastern Gulf	1,580	-	-	158	158	-
Western Gulf	753	-	-	75	-	150
Florida						
Panhandle Upland	687	-	203	32	-	129
Peninsula Upland	442	-	208	170	-	64
Panhandle Swamp	264	129	-	35	-	67
Peninsula Swamp	163	96	-	35	-	32
NSS-I TOTALS	57,277	464	889	983	3,277	32,272

$\hat{N}$ represents the estimated number of reaches in each geographic site class.
See Figure 9-9 for a flow chart depicting the chemical classification procedure.

Table 9-9. Estimated Number of Target Reach Upper Nodes in Each Geographic Site Class Present in Stream Chemical Classes

Geographic Site Class	$\hat{N}$#	INORGANIC ANC ≤ 0	INORGANIC ANC 0-50	INORGANIC ANC 50-200	ORGANIC INFLUENCED ANC ≤ 0	ORGANIC INFLUENCED ANC 0-50	ORGANIC INFLUENCED ANC 50-200
Allegheny Plateau							
High Plateau	221	63	-	158	-	-	-
Forested Plateau	4,327	436	1,464	589	-	29	-
Forested Agric. Plat.	3,448	-	291	955	-	168	-
NE Mid-Atlantic							
Pocono/Catskill Mts.	351	-	140	209	2	-	-
Glaciated Agric. Plat.	818	-	-	60	-	-	-
Glaciated Forested Plat.	266	77	60	60	69	-	-
Valley and Ridge Province							
Ridges	7,190	695	1,044	2,119	-	-	60
Valleys	8,342	-	60	1,970	-	-	-
Arkansas/Oklahoma							
Boston Mts.	873	-	-	648	-	-	75
Ouachita Mts.	1,126	-	75	525	-	-	150
Arkansas R. Valley	1,452	-	-	773	-	-	-
Piedmont Province							
Piedmont	8,940	-	-	1,739	-	-	397
Piedmont Lowlands	2,290	239	-	-	-	-	-
S. Appalachian Highlands							
Blue Ridge Mts.	2,962	-	231	2,134	-	17	-
Cumberland Plateau	1,307	-	121	364	121	-	279
French Broad R. Valley	64	-	-	-	-	-	-
Coastal Plain							
Eastern Mid-Atlantic	2,036	-	239	716	-	-	-
Western Mid-Atlantic	6,133	-	478	239	-	716	478
New Jersey Pine Barrens	436	239	32	-	107	-	-
Eastern Gulf	1,580	-	474	790	-	158	158
Western Gulf	753	-	75	302	-	-	75
Florida							
Panhandle Upland	623	64	32	-	75	71	32
Peninsula Upland	492	-	-	-	-	-	-
Panhandle Swamp	117	-	-	-	-	-	-
Peninsula Swamp	495	-	-	-	-	-	-
NSS-I TOTALS	56,642	1,812	4,815	14,353	375	1,160	1,704

$\hat{N}$ represents the estimated number of reaches in each geographic site class.
See Figure 9-9 for a flow chart depicting the chemical classification procedure.

Table 9-9. Estimated Number of Target Reach Upper Nodes in Each Geographic Site Class Present in Stream Chemical Classes (Continued)

Geographic Site Class	$\hat{N}$#	ORGANIC DOMINATED ANC ≤ 0	ANC 0-50	ANC 50-200	Watershed sulfate sources	ANC > 200
Allegheny Plateau						
High Plateau	221	-	-	-	-	-
Forested Plateau	4,327	-	-	-	769	1,040
Forested Agric. Plat.	3,448	-	-	-	167	1,867
NE Mid-Atlantic						
Pocono/Catskill Mts.	351	-	-	-	-	-
Glaciated Agric. Plat.	818	-	-	-	-	758
Glaciated Forested Plat.	266	-	-	-	-	-
Valley and Ridge Province						
Ridges	7,190	-	15	-	443	2,813
Valleys	8,342	-	-	-	123	6,189
Arkansas/Oklahoma						
Boston Mts.	873	-	-	-	-	150
Ouachita Mts.	1,126	-	-	-	75	300
Arkansas R. Valley	1,452	-	-	-	75	604
Piedmont Province						
Piedmont	8,940	-	-	-	-	6,804
Piedmont Lowlands	2,290	-	-	-	-	2,051
S. Appalachian Highlands						
Blue Ridge Mts.	2,962	-	-	-	-	579
Cumberland Plateau	1,307	-	-	-	-	421
French Broad R. Valley	64	-	-	-	-	64
Coastal Plain						
Eastern Mid-Atlantic	2,036	-	-	239	365	478
Western Mid-Atlantic	6,133	716	239	478	478	2,312
New Jersey Pine Barrens	436	-	-	-	58	-
Eastern Gulf	1,580	-	-	-	-	-
Western Gulf	753	-	-	-	-	300
Florida						
Panhandle Upland	623	-	221	64	-	64
Peninsula Upland	492	-	208	-	-	284
Panhandle Swamp	117	78	-	-	-	39
Peninsula Swamp	495	460	-	35	-	-
NSS-I TOTALS	56,642	1,255	683	815	2,551	27,118

$\hat{N}$ represents the estimated number of reaches in each geographic site class.
See Figure 9-9 for a flow chart depicting the chemical classification procedure.

Table 9-10. Estimated Percentage of Target Stream Reach Lower Nodes in Each Geographic Site Class in Acidic and Very Low ANC Chemical Classes

Geographic Site Class	n$	$\hat{N}$#	Inorganic ANC ≤ 0	Inorganic ANC 0-50	Organic Influenced ANC ≤ 0	Organic Influenced ANC 0-50	Organic Dominated ANC ≤ 0	Organic Dominated ANC 0-50
Allegheny Plateau								
High Plateau	6	218	16.3	11.4	-	-	-	-
Forested Plateau	27	4,178	7.0	31.6	-	-	-	-
Forested Agric. Plat.	26	3,547	-	-	-	-	-	-
NE Mid-Atlantic								
Pocono/Catskill Mts.	8	351	-	0.7	-	-	-	-
Glaciated Agric. Plat.	15	866	-	-	-	-	-	-
Glaciated Forested Plat.	6	209	-	38.1	-	-	-	-
Valley and Ridge Province								
Ridges	19	4,359	-	9.8	-	-	-	-
Valleys	72	11,809	-	-	-	-	-	-
Arkansas/Oklahoma								
Boston Mts.	10	873	-	-	-	-	-	-
Ouachita Mts.	15	1,126	-	-	-	-	-	-
Arkansas R. Valley	14	1,365	-	-	-	-	-	-
Piedmont Province								
Piedmont	50	9,258	-	-	-	-	-	-
Piedmont Lowlands	9	2,297	-	-	0.3	-	-	-
S. Appalachian Highlands								
Blue Ridge Mts.	56	2,962	-	2.3	-	1.0	-	-
Cumberland Plateau	10	1,307	-	18.6	-	9.3	-	-
French Broad R. Valley	4	64	-	-	-	-	-	-
Coastal Plain								
Eastern Mid-Atlantic	9	2,036	-	11.7	-	-	-	-
Western Mid-Atlantic	25	6,133	-	7.8	-	3.9	3.9	7.8
New Jersey Pine Barrens	11	432	55.3	-	37.3	-	-	-
Eastern Gulf	10	1,580	-	10.0	-	30.0	-	-
Western Gulf	9	753	-	-	-	-	-	-
Florida								
Panhandle Upland	19	687	-	4.7	-	33.0	-	29.6
Peninsula Upland	4	442	-	-	-	-	-	47.0
Panhandle Swamp	6	264	-	-	-	-	49.0	-
Peninsula Swamp	5	163	-	-	-	-	59.0	-
NSS-I Totals	445	57,277	1.0	5.4	0.3	1.9	0.8	1.6

$\hat{N}$# is the estimated number of target reaches within each geographic site class.
n$ is the number of target stream nodes sampled within each geographic site class.

Table 9-11. Estimated Percentage of Target Stream Reach Upper Nodes in Each Geographic Site Class in Acidic and Very Low ANC Chemical Classes

Geographic Site Class	n$	N̂#	Inorganic ≤ 0	Inorganic 0-50	Organic Influenced ≤ 0	Organic Influenced 0-50	Organic Dominated ≤ 0	Organic Dominated 0-50
Allegheny Plateau								
High Plateau	7	221	28.4	-	-	-	-	-
Forested Plateau	29	4,327	10.1	33.8	-	0.7	-	-
Forested Agric. Plat.	28	3,448	-	8.4	-	4.9	-	-
NE Mid-Atlantic								
Pocono/Catskill Mts.	8	351	-	39.9	0.7	-	-	-
Glaciated Agric. Plat.	16	818	-	-	-	-	-	-
Glaciated Forested Plat.	7	266	28.9	22.5	26.1	-	-	-
Valley and Ridge Province								
Ridges	37	7,190	9.7	14.5	-	-	-	0.2
Valleys	52	8,342	-	0.7	-	-	-	-
Arkansas/Oklahoma								
Boston Mts.	10	873	-	-	-	-	-	-
Ouachita Mts.	15	1,126	-	6.7	-	-	-	-
Arkansas R. Valley	15	1,452	-	-	-	-	-	-
Piedmont Province								
Piedmont	49	8,940	-	-	-	-	-	-
Piedmont Lowlands	8	2,290	10.4	-	-	-	-	-
S. Appalachian Highlands								
Blue Ridge Mts.	56	2,962	-	7.8	-	0.6	-	-
Cumberland Plateau	10	1,307	-	9.3	9.3	-	-	-
French Broad R. Valley	4	64	-	-	-	-	-	-
Coastal Plain								
Eastern Mid-Atlantic	9	2,036	-	11.7	-	-	-	-
Western Mid-Atlantic	25	6,133	-	7.8	-	11.7	11.7	3.9
New Jersey Pine Barrens	11	436	54.8	7.4	24.5	-	-	-
Eastern Gulf	10	1,580	-	30.0	-	10.0	-	-
Western Gulf	9	753	-	10.0	-	-	-	-
Florida								
Panhandle Upland	17	623	10.3	5.1	12.1	11.3	-	35.5
Peninsula Upland	5	492	-	-	-	-	-	42.2
Panhandle Swamp	3	117	-	-	-	-	66.5	-
Peninsula Swamp	6	495	-	-	-	-	93.0	-
NSS-I Totals	446	56,642	3.2	8.5	0.7	2.0	2.2	1.2

N̂# is the estimated number of target reaches in each geographic region.
n$ is the number of target stream nodes sampled within each geographic site class.

(upper nodes). It would be erroneous to ignore weighted estimates in Tables 9-8 and 9-9 by inferring population characteristics based on the distribution of stream sample numbers without weighting, because the stream target population was not uniformly sampled. The weighting factor takes into account the difference in sampling inclusion probabilities (including ANC stratification) among the stream samples.

9.5.1 Streams with Watershed Sulfate Sources

Streams with ANC $\leq$ 200 μeq L^{-1} and substantial watershed sources of sulfate were found mainly in the Allegheny Plateau, the Ouachita Mountains, the Valley and Ridge Province, and the agricultural regions in the Coastal Plain. These high-sulfate sites made up 5.7% of the lower node target population and 4.5% of the upper node target population.

9.5.2 Streams with Chemistry Dominated by Organics

Except for an estimated 15 upstream reach nodes in the ridges of the Valley and Ridge Province, all organic-dominated streams were found in coastal areas--Florida, and the Mid-Atlantic and Gulf Coastal Plains. Organic acidic (ANC $\leq$ 0 μeq L^{-1}) stream reaches were found primarily along the western Mid-Atlantic Coastal Plain and in large numbers at lowland swampy sites in both the Florida panhandle and peninsula. It was estimated that over 50% of the lower nodes and 88% of the upper nodes of these swampy reaches in Florida were organic acidic. Very low and low ANC ($\leq$ 200 μeq L^{-1}), organic-dominated reaches were found in the relatively higher elevation Florida upland and Mid-Atlantic and Gulf Coastal Plain sites.

9.5.3 High-Interest Subpopulation (Inorganic and Organic-Influenced Streams)

In the high-interest subpopulation, acidic lower nodes (an estimated 733 reaches, 1.3% of the target population) were observed only in the Allegheny Plateau, the New Jersey Pine Barrens, and the Piedmont Lowlands. Acidic high-interest upper nodes in the target population (2,187 reaches, 3.9%) were observed in the Allegheny Plateau, the Pine Barrens, the forested Glacial Plateau in northeast Pennsylvania, the Poconos/Catskills, the ridges of the Valley and Ridge Province, the uplands of the Florida panhandle, the Cumberland Plateau, and the Piedmont Lowlands.

9.5.3.1 Allegheny Plateau, Northeast Mid-Atlantic, and Valley and Ridge Geographic Sites--

In addition to a large number of acid mine drainage streams, the Allegheny Plateau was estimated to have a large number of inorganic, acidic reaches (327 lower nodes (4.1%), and 499 upper nodes (6.2%)). In the Allegheny Plateau, acidic high-interest sites were found only on the High Plateau and the Forested Plateau. On the Forested Plateau, 1,611 (39%) lower nodes and 1,929 (45%) upper nodes had ANC values < 50 μeq L^{-1}. No acidic sites were found on the Plateau in areas of mixed forest and agriculture.

In the Valley and Ridge Province geographic site class (within subregions 1D, 2Bn, 2Cn, 2As and 2X), only upper nodes on the ridges were acidic. Of the 7,190 estimated upper node target sites on ridges, an estimated 695 (9.7%) reaches were acidic, 1,044 (15%) reaches had spring index ANC concentrations between 0 and 50 μeq L^{-1}, and another 2,179 (30%) reaches had ANC between 50 and 200 μeq L^{-1}. Valley sites had almost no sites with ANC < 50 μeq L^{-1} (only 60 upper reach nodes), whereas there were 2,386 (20%) lower nodes and 1,970 (24%) upper nodes at Valley sites with ANC between 50 and 200 μeq L^{-1}.

In the Glacial Plateau, as in the Allegheny Plateau, there were more acidic and low ANC reaches in forested drainages than in those with mixed forest and agricultural land use. No reaches with ANC $\leq$ 50 μeq L^{-1} were observed in the agricultural part of the Glacial Plateau and only an estimated 119 lower nodes (14%) and 60 upper nodes (7%) had ANC between 50 and 200 μeq L^{-1}. All of the reaches (except 10 downstream reach nodes) in the forested section of the Glacial Plateau had ANC $\leq$ 200 μeq L^{-1}. Over half of the estimated 266 upper nodes in this geographic site class were acidic (77 nodes were inorganic and 69 were organic influenced). All of the estimated 351 upper nodes and 231 of the lower nodes (65.8%) in the Pocono/Catskill Mountains had ANC $\leq$ 200 μeq L^{-1}. However, very few reaches had ANC < 50 μeq L^{-1} (an estimated 142 upper nodes and 2 lower nodes).

Very few of the estimated 25,537 lower nodes and 24,963 upper nodes in the interior section of the Mid-Atlantic (Allegheny Plateau, Glaciated Plateau, Valley and Ridge, and Pocono/Catskill Mountains) were organic influenced (16 lower nodes and 328 upper nodes). The organic-influenced stream reaches present were usually located in valleys or in low gradient headwaters atop plateaus.

9.5.3.2 Florida, Arkansas/Oklahoma, Piedmont, and Southern Appalachian Highland Geographic Sites--

The only Southeast geographic site class in which acidic streams not influenced by organics were observed was in Florida. These estimated 64 inorganic acidic reaches were located in upstream nodes of upland sites in the Florida panhandle. Between 20% and 30% of upstream and downstream nodes in upland drainages in the Florida panhandle were classed as organic-influenced reaches with ANC below 50 μeq L^{-1}.

In Arkansas and Oklahoma, no acidic sites were observed and only 75 upper nodes were estimated to have ANC between 0 and 50 μeq L^{-1}. All three geographic site classes in this area, however, were dominated by streams in the low ANC class (50-200 μeq L^{-1}). Of the 3,364 lower nodes and 3,451 upper nodes in this area, 63% of the lower nodes and 60% of the upper nodes were in the low ANC class, mostly in the inorganic group.

There were no reaches with ANC < 50 μeq L^{-1} observed in the Piedmont, but there were an estimated 1,505 (16%) lower nodes and 2,136 (24%) upper nodes with ANC between 50 and 200 μeq L^{-1}. The Piedmont geographic site class extends from southeastern Pennsylvania in the north to Mississippi in the south and is not entirely within the Southeast Screening area. Except for 121 inorganic, acidic upper reach nodes and 7 organic-influenced lower nodes, there were no reaches with ANC $\leq$ 200 μeq L^{-1} in the Piedmont Lowlands. The estimate of 121 acidic reaches resulted from 1 upper node sampled in a forested ridge in southeastern Pennsylvania. The land use pattern for this node was atypical for the Piedmont Lowlands. The estimate of 7 organic-influenced acidic downstream reaches resulted from 1 lower node sampled that was just outside the New Jersey Pine Barrens. The upper node of the reach was in the Pine Barrens.

The majority of the estimated 4,269 upstream and downstream nodes in the Blue Ridge Mountains and Cumberland Plateau were in the 50-200 μeq L^{-1} ANC class (2,874 lower nodes and 2,777 upper nodes). A small number of streams in this area (149 lower nodes and 417 upper nodes) were organic influenced. All of the estimated 64 reaches in the French Broad River Valley of North Carolina had ANC > 200 μeq L^{-1}.

9.5.3.3 Coastal Plain Geographic Sites--

In the New Jersey Pine Barrens, 93% of the estimated 432 lower nodes and 79% of the 436 upper nodes were acidic. Of these acidic nodes, 239 (55% of target population) upper and lower reach nodes were inorganic, whereas 107 (25%) of the upper reach nodes and 161 (37%) of the

lower reach nodes were classified as organic-influenced, but not organic-dominated, acidic reaches. The fact that there was a greater number of acidic lower reach nodes than upper nodes is probably due to organic acid influence. The water at the lower nodes has been in contact with organic sources longer and thus could have leached out more organic acids. The remaining nodes in the Pine Barrens all had ANC $\leq$ 200 μeq L^{-1}. Contrary to expectations, no reaches were observed in the Pine Barrens where organic anions clearly dominated sulfate and nitrate, even though Pine Barrens reaches had high DOC concentrations (mean = 7.96 mg L^{-1}, SD = 6.88) and color (mean = 54, SD = 43). This is in marked contrast to findings in Florida, where a clear majority of reaches in the target population were dominated by acidic and very low ANC reaches with high DOC concentrations and very low concentrations of sulfate and nitrate. These findings are to be expected, given the considerably higher atmospheric sulfate deposition rates in the Pine Barrens (2.5-3.0 g m^{-2} yr^{-1}) compared to Florida (< 1.8 g m^{-2} yr^{-1}) (Section 2, Figure 2-2).

Johnson (1979a,b) has noted an annual drop of 0.2-0.5 pH units in the long-term record of two streams in the Pine Barrens and suggested that it was due to an observed decrease in precipitation pH. Morgan (1984) disagreed with Johnson's assessment and concluded that any long-term trend in these data could be divided into several short-term trends, each explainable by natural causes, and none of which was entirely consistent with an acid deposition hypothesis. In addition, aquatic flora and fauna communities characteristic of very low pH waters have long existed in the Pine Barrens (since at least 1900), as evidenced by historic descriptions of flora and fauna characteristic of acidic environments (Forman, 1979; Morgan, 1984). Almost all the historic pH data (1950 - present) from the Pine Barrens have shown that the normal pH of the waters in this area is between 4.0 and 5.5. Although it appears likely that much of the acidity in the streams in the Pine Barrens is of natural origin, it is possible that acid deposition may currently be causing decreases in already low stream ANC and may have acidified some stream systems.

No inorganic, acidic reaches were observed in the Mid-Atlantic and Gulf Coastal Plain sites (an estimated 10,502 upper and lower nodes). However, a large number of reaches influenced, but not dominated by organic acids (1,424 lower and 1,585 upper reach nodes) were estimated in this area. One-fourth to one-third of the stream reaches in the Coastal Plain (excluding the Pine Barrens) were inorganic, with ANC $\leq$ 200 μeq L^{-1} (2,519 lower nodes, 3,313 upper nodes).

9.6 CLASSIFICATION OF SPECIAL INTEREST SITES

The 36 NSS-I special interest sites (Section 2.6, Table 2-4) were classified geographically and chemically as described in Section 9.3 using spring index data (see flowchart in Figure 9-9). The vast majority of the special interest streams (Table 9-12) had ANC below 200 μeq L^{-1} (31 of the 36 streams). Most of the streams (21) were classified as inorganic. Almost all of these inorganic streams were located in forested, mountainous, or ridge top areas.

The special interest site in the New Jersey Pine Barrens (McDonalds Branch) was classified as organic-influenced acidic, as were many of the NSS-I streams sampled there. All of the organic-influenced streams with ANC between 0 and 200 μeq L^{-1} were found in the Southeast, mainly in the Blue Ridge Mountains. In spite of the fact that the DOC concentration in all of these streams was less than 1 mg L^{-1}, the concentration of the inorganic ions was so low (sulfate = 14-40 μeq L^{-1}) that the streams were classified as organic influenced. It should be remembered, however, that the system decision limit for DOC samples was 0.45 mg L^{-1} (Table 4-1). Also, DOC measurements at concentrations below 2 mg L^{-1} had a %RSD of 20% - 25% (Table 4-3). Thus, it is possible that there is almost no DOC present in these streams and

Table 9-12. Chemical and Geographical Classification of Special Interest Site Streams Sampled during NSS-I. (Index chemistry is given in units of $\mu eq\ L^{-1}$ except for DOC, which is given in $mg\ L^{-1}$.)

Stream Name	Reach ID	Geographic Class	Index Chemistry ANC	SO_4^{2-}	pH	DOC
INORGANIC CLASS, ANC ≤ 0 $\mu eq\ L^{-1}$						
E. Branch Neversink	1D030912	Catskill/Pocono Mts.	-7.3	124.3	5.0	1.88
Mill Run	2B047919	Ridges of Valley & Ridge	-20.7	233.2	4.7	2.39
Cole Run	2C041914	Forested Allegheny Plateau	-30.4	186.6	4.8	1.00
INORGANIC CLASS, ANC 0-50 $\mu eq\ L^{-1}$						
Biscuit Brook	1D030910	Catskill/Pocono Mts.	31.6	141.9	6.4	1.51
Tillman Brook	1D030926	Ridges of Valley & Ridge	41.0	221.7	6.5	2.21
Cosby Creek	2A07891	Blue Ridge Mts.	37.0	50.7	6.7	0.38
Detweiler Run	2B036903	Ridges of Valley & Ridge	1.7	149.8	5.5	0.80
White Oak Run	2B047916	Blue Ridge Mts.	18.9	81.5	6.2	0.55
Deep Run	2B047917	Blue Ridge Mts.	3.0	99.8	5.7	0.88
N. Fork Bens Creek	2C035913	Forested Allegheny Plateau	7.1	195.2	5.8	0.49
Fernow Control	2C041901	Forested Allegheny Plateau	18.2	92.6	6.0	0.60
N. Fork Saline R.	2D083927	Ouachita Mts.	16.0	59.8	6.2	0.45
INORGANIC CLASS, ANC 50-200 $\mu eq\ L^{-1}$						
High Falls Creek	1D030911	Catskill/Pocono Mts.	101.8	141.5	6.9	1.76
Van Campens Brook	1D030924	Ridges of Valley & Ridge	129.8	238.8	7.1	1.15
Green Brook	1D030925	Glaciated Forested Plateau	124.0	247.0	6.7	2.04
Leading Ridge #1	2B036904	Ridges of Valley & Ridge	171.0	177.5	6.9	1.04
Laurel Run	2B036905	Ridges of Valley & Ridge	51.4	160.6	6.5	0.87
N. Fork Dry Run	2B047918	Blue Ridge Mts.	51.3	101.0	6.6	0.52
Old Rag Run	2B047920	Blue Ridge Mts.	61.1	37.0	6.6	0.63
E. Fork Saline R.	2D083928	Ouachita Mts.	57.5	55.9	6.6	0.00
Pequea Creek	3B042921	Piedmont	97.4	191.1	6.7	0.85
ORGANIC INFLUENCED CLASS, ANC ≤ 0 $\mu eq\ L^{-1}$						
McDonalds Branch	3B043909	NJ Pine Barrens	-101.0	176.0	4.0	6.22
ORGANIC INFLUENCED CLASS, ANC 0-50 $\mu eq\ L^{-1}$						
Pinnacle Branch	2A07896	Blue Ridge Mts.	47.1	22.3	6.8	0.44
Chester Creek	2A08891	Blue Ridge Mts.	41.2	15.2	6.7	0.42
Camp Branch	2C077923	Cumberland Plateau	14.9	39.6	5.2	0.98

Table 9-12. Chemical and Geographical Classification of Special Interest Site Streams Sampled during NSS-I. Index chemistry is given in units of $\mu eq\ L^{-1}$ except for DOC, which is given in $mg\ L^{-1}$. (Continued)

Stream Name	Reach ID	Geographic Class	Index Chemistry ANC	SO_4^{2-}	pH	DOC
ORGANIC INFLUENCED CLASS, ANC 50-200 $\mu eq\ L^{-1}$						
Twenty-mile Creek	2A07892	Blue Ridge Mts.	61.6	19.5	6.8	0.81
Jarrett Creek	2A07893	Blue Ridge Mts.	86.7	13.8	6.9	0.55
Shope Fork/Gauge 8	2A07894	Blue Ridge Mts.	76.3	14.0	6.9	0.55
Moses Creek	2A07895	Blue Ridge Mts.	134.0	21.1	7.2	0.77
ACID MINE DRAINAGE IMPACTED						
N. Br. Quemahoning	2C035915	Forested Allegheny Plateau	-51.4	298.4	4.5	0.72
SUBSTANTIAL WATERSHED SOURCES OF SULFATE CLASS						
Bacon Ridge	3B042908	West MA Coastal Plain	183.4	425.7	6.5	1.92
ANC > 200 $\mu eq\ L^{-1}$ CLASS						
Hunting Creek	2B042922	Blue Ridge Mts.	332.6	122.2	7.4	1.86
Mill Run Trib	2B047929	Ridges of Valley & Ridge	468.1	147.5	7.4	1.18
Elk Lick Run	2C041902	Forested Allegheny Plateau	325.1	178.7	7.5	0.69
Magothy River	3B042907	West MA Coastal Plain	224.6	430.2	6.6	3.08
Lyons Creek	3B048906	West MA Coastal Plain	255.3	589.8	6.9	2.55

MA = Mid-Atlantic

they should be in the inorganic class. It should be emphasized that streams in this organic-influenced group are still in the high-interest subpopulation of streams. The organic anion proportion is high enough, however, to potentially have some effect on acid/base chemistry.

The North Branch of the Quemahoning was classified as impacted by acid mine drainage, even though its index SO_4^{2-} concentration (298 μeq L^{-1}) was just below the 300 μeq L^{-1} cutoff. This classification was made after evidence of acid mine drainage was found on a field visit during the 1987 Acid Stream Reconnaisance. The acid mine drainage, however, was not severe. The headwaters of this stream are fairly pristine. It is possible that the NSS-I sample was taken downstream of a site where other research is taking place and picked up acid mine drainage effects.

Examination of the special interest site data is in its beginning phase. It is of special interest because some of these streams may be selected for future long-term monitoring of trends and effects of acid deposition. Thus it is important to find out how these special interest site streams compare with the streams selected through a randomized systematic sample.

SECTION 10
EVIDENCE OF ACIDIFICATION

10.1 OVERVIEW

The National Stream Survey - Phase I (NSS-I) was designed primarily to determine the status and extent (number, length) of streams in subregions of the mid-Atlantic and southeastern United States that are presently acidic or that may be at risk as a result of acidic deposition. Other important issues about the effects of acidic deposition, however, include the extent to which the chemical status of streams has already been altered by acidic deposition and the relationship between current deposition rates and surface water quality among the subregions.

The only direct way to conclusively demonstrate surface water acidification is through historical data on water quality. Because of a lack of such data for the target population of interest, a second approach for assessing whether surface waters have been acidified involves indirect methods using chemical models to infer changes in water quality. In this section, we use this approach to assess whether streams in the various subregions may have been acidified. In addition, we have examined the relationship between sulfate deposition and surface water chemistry in streams in the different subregions to assess whether observations are consistent with a hypothesis that atmospheric deposition has influenced stream water chemistry. It is important to note that the results presented (e.g., ANC deficits and relationships between surface water sulfate and deposition rates) are not, in themselves, conclusive evidence for acidification. They are to be compared with other information that may also support or refute a hypothesis of surface water acidification by atmospheric deposition.

10.2 ION BALANCE AND ANC RELATIONSHIPS

Henriksen (1979, 1980, 1982) has argued that the acidification of surface waters by acidic deposition can be described as a continuous process analogous to the titration of a bicarbonate solution with sulfuric acid. The bicarbonate is produced through the weathering of primary minerals in the watershed by carbonic acid generated in soil respiration, and the atmosphere is a source of the acid through precipitation and dry deposition.

Except where the ANC has been completely titrated (ANC ≤ 0), a determination of whether streams have been acidified (decline in ANC due to titration) is constrained by the lack of historical information on ANC under pristine conditions (low deposition rates of strong mineral acids). Almer et al. (1978), Dickson (1980), and Henriksen (1982), however, have shown that oligotrophic surface waters in areas with low acidic deposition rates, and with no geological source of sulfate contain approximately equivalent amounts of alkalinity and nonmarine calcium plus magnesium. This one-to-one ratio of bicarbonate alkalinity to nonmarine divalent base cations is a result of the fact that calcium, magnesium, and bicarbonate typically make up most of the total ion content in bicarbonate dominated waters. It also implies that approximately one equivalent of divalent base cation is released to solution for every equivalent of alkalinity produced in the process of carbonic acid weathering.

Based on this relationship, Henriksen (1979, 1980) argued that acidification of surface waters due to inputs of strong mineral acids could be estimated by examining the relationship between the nonmarine calcium plus magnesium and the alkalinity or ANC. In areas where sulfate was the major acid anion in precipitation and where little sulfur was supplied by weathering, Henriksen and others have shown that the difference (in equivalents) between the

divalent base cations and alkalinity was directly proportional to the nonmarine sulfate concentration. The so-called ANC deficit, defined as the difference between the nonmarine base cation equivalents and the alkalinity or ANC, was assumed to provide a quantititive measure of acidification. This assertion, however, was based on the assumption that the ANC deficit is caused entirely by a titration of the ANC and that the base cation concentration has remained constant over time. Although this assumption may be nearly correct in some waters (e.g., in poorly buffered streams of low ionic strength), there are indications that base cation concentrations in some streams may not remain constant over time (Reuss and Johnson, 1986; Cresser and Edwards, 1987).

As pointed out by Kramer and Tessier (1982) and Reuss et al. (1986), these relationships among base cations, sulfate, and ANC support the Henricksen model only in the sense that they demonstrate the validity of the charge balance principle; that is, the present ion composition would occur regardless of whether surface waters reached their present chemical condition because of titration by a strong mineral acid, increased leaching of base cations, or some combination of both. Reuss et al. (1986) concluded that it did not seem possible using this approach to assess whether the ANC deficit was due to acidification (reduced ANC) or increased base cation export.

To separate the effect of titration from that of increased base cation leaching on the ANC deficit, Henriksen (1982) introduced the so-called F-factor, which is defined as the fraction of nonmarine sulfate that is accompanied by change in base cations, leaving ANC unaffected. The remainder of the sulfate presumably goes to titrate the ANC. F is thus defined as:

$$F = \frac{\Delta\ [\text{sum of base cations}]}{\Delta\ [SO_4^{2-}]}$$

Thus, when F = 0, all the sulfate goes to titrate the alkalinity, and when F = 1, all the sulfate goes to increase the export of base cations through increased weathering and cation exchange; the ANC remains constant.

The relationship between nonmarine base cations [$Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}$] and ANC was examined for each of the NSS-I subregions to determine if there was evidence of acidification or increased base cation leaching. An F-factor of zero was applied, so that the deficits represent the maximum change in ANC resulting from a hypothesized strong acid titration. As Figure 10-1 shows, all the subregions have some streams with an ANC deficit (ANC less than the sum of nonmarine base cations), as demonstrated by the data points plotting below the line, implying stream acidification (natural or anthropogenic), increased base cation export, the presence of neutral salts (e.g., NaCl, $CaSO_4$), or some combination of these. Base cations have been reduced by an amount proportional to their chloride ratio in sea water, based on their stream water [Cl^-], in an attempt to adjust for neutral salt additions from sea salt deposition or road salting.

Subregions in which streams have the largest ANC deficit are the Northern Appalachians (2Cn), Poconos/Catskills (1D), Mid-Atlantic Coastal Plain (3B), and the Valley and Ridge (2Bn). Almost all the streams in the target population in these subregions plot below the one-to-one line, indicating that an ANC deficit exists in almost the entire stream population of interest in these subregions (Figure 10-1).

In contrast, most of the streams in the Southern Blue Ridge (2As), Ozarks/Ouachitas (2D), Piedmont (3A), Southern Appalachians (2X), and Florida (3C) fall on or closer to the line of equality, indicating a lower ANC deficit, and therefore, either less stream acidification or lower increases in base cation export in these subregions. The lower ANC deficits in streams in these subregions in the southeastern United States is generally consistent with the greater sulfate

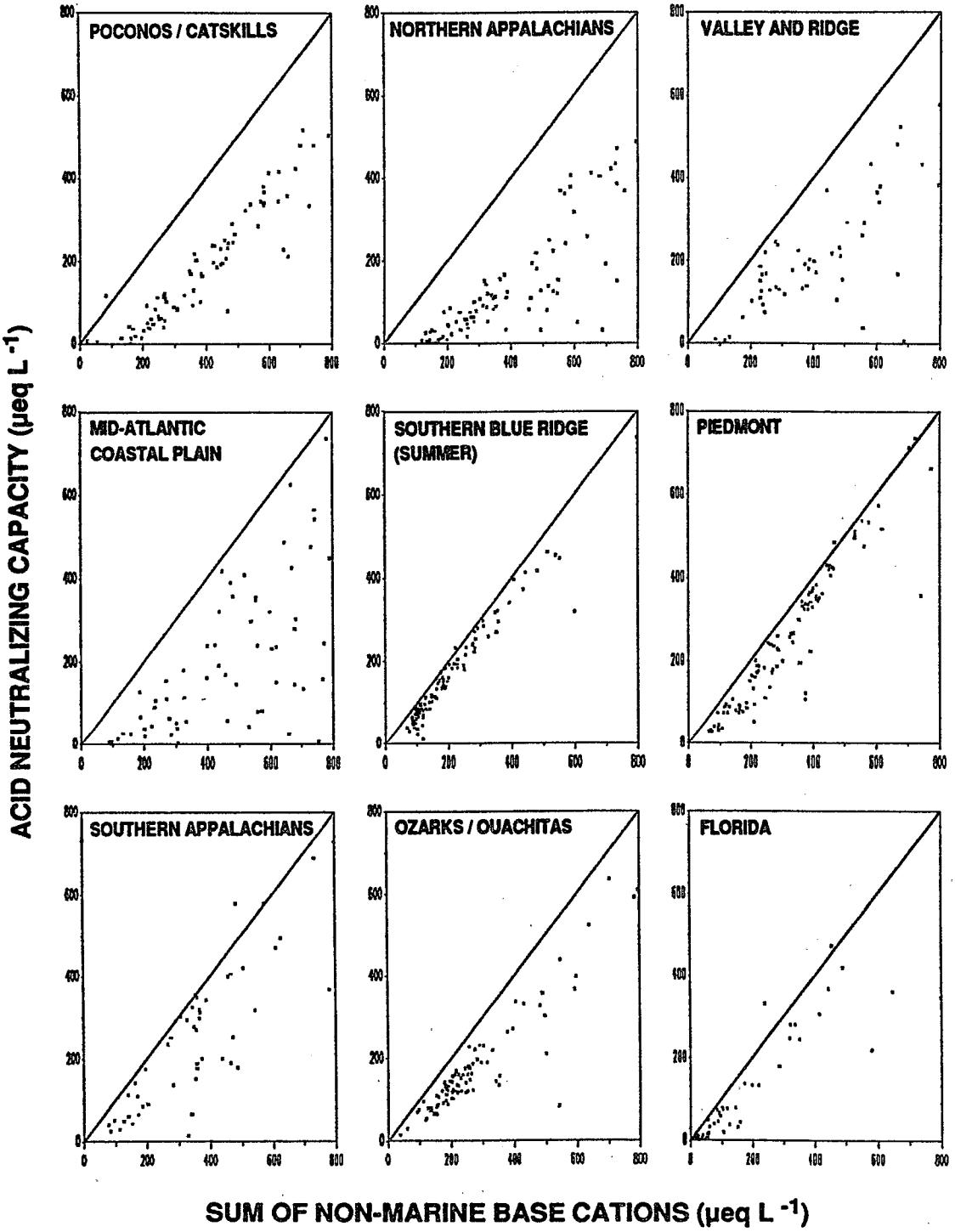


Figure 10-1. ANC of stream water vs. the nonmarine base cation concentration in stream water in NSS-I subregions.

adsorption capacity of soils in the southeastern United States. Because the acidic anion must be mobile in soils for surface waters to be acidified by acidic deposition or for sulfate to cause an increase in base cation leaching, adsorption of atmospherically deposited sulfate by soils effectively precludes these processes from occurring, even though the streams may have a low ANC.

Because a sea salt correction was used in estimating the nonmarine component of base cations in stream water (by assuming that all of the chloride present is from sea salt deposition), there is some uncertainty associated with the estimated contribution of weathering to base cations in stream water. If some of the chloride present is from internal (i.e., watershed) sources, the contribution of weathering will be underestimated. However, this portion of base cations is associated neither with bicarbonate nor with an acid source of anions, so the deficit generated by including these base cations would have overestimated the ANC deficit potentially reflecting stream acidification. A conservative approach for sea salt correction was used in this analysis in order not to overestimate the ANC deficit. The chloride-distance envelope approach for sea salt correction (used in subsections 6.3.5, Figure 6-18) was not used because it took the perspective of not overestimating the sea salt correction factors (minimum estimate of sea salt correction).

As previously stated, an ANC deficit alone does not prove that surface water acidification has occurred. It does, however, suggest either that some of the ANC has been titrated or that the export of base cations has increased without a corresponding increase in the ANC. If the latter occurs, it reflects soil acidification resulting from the exchange of protons for strong base cations in the soil, a source of neutral salts (e.g., $CaSO_4$) not accounted for by sea salt correction, and/or increased weathering of base cations.

The exact causes of anion deficits are unknown, but they include natural or anthropogenic sources of mineral acids that increase the leaching of base cations or depress the ANC, strong organic acids which have the same effect, or some combination of both. To determine whether sulfate alone could account for the apparent ANC deficit in the various subregions, ANC plus nonmarine sulfate was regressed against the sum of nonmarine base cations (Figure 10-2). This figure shows that with the exception of the Mid-Atlantic Coastal Plain (3B) and Florida (3C), streams in most of the subregions plotted on or near to the one-to-one line when sulfate was added to the ANC. This indicates that sulfate is the major anion that contributes to the ANC deficit in these subregions. To assess whether other mineral acid anions and organic acids could account for the calculated ANC deficit of streams in each subregion, the deficit was regressed against sulfate, nitrate, chloride, and DOC, the latter variable serving as a surrogate of strong organic acid anions. Only SO_4^{2-} was corrected for sea salt inputs.

Results of these step-wise linear regressions are shown in Table 10-1. The high partial coefficient of determination (r^2) for sulfate in most subregions shows that sulfate alone can account for most of the variation in the anion deficit among streams in these subregions. In the Mid-Atlantic region, for example, sulfate accounts for > 75% of the variation in the ANC deficit in almost all of the subregions. The only exception is the Mid-Atlantic Coastal Plain (3B) where nitrate is associated with more of the variation in the ANC deficit than is sulfate. This result is consistent with results of the standardized regression analysis showing that nitrate was associated with a portion of the variation in ANC among streams in the Mid-Atlantic Coastal Plain. Whether the effect of nitrate on the ANC deficits in this subregion are due to nitric acid inputs from the atmosphere or to inputs of nitrate as either a neutral salt or ammonia that was applied as fertilizer and was subsequently nitrified is unknown.

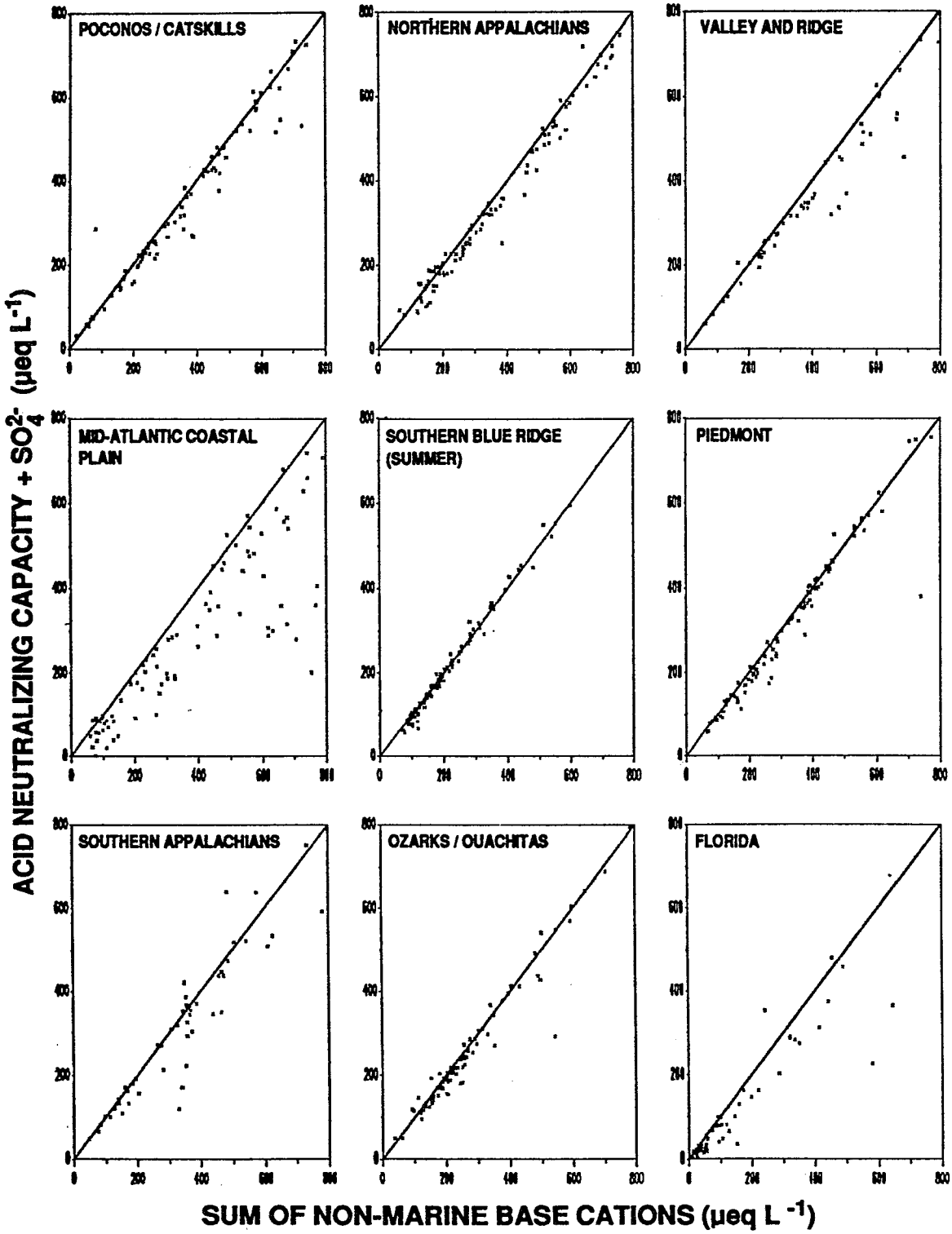


Figure 10-2. ANC plus SO_4^{2-} concentration versus the nonmarine base cation concentration in stream water in NSS-I subregions.

In the Southeast subregions, sulfate also explains a large percentage of the variation in the ANC deficit among streams. The only exceptions are at the upper nodes of reaches in the Piedmont (3A) and in Florida (3C). In both of these subregions, sulfate alone explains ≤ 15% of the variation in the ANC deficit. The results for Florida are consistent with the results of the standardized regression analysis, which showed that dissolved organic carbon was associated with a major portion of the variation in ANC among the upper reach nodes in this subregion. In the upper reach nodes of the Piedmont (3A), sulfate and nitrate are the only two anions that are associated with a significant fraction of the variation in the ANC deficit. However, together they account for only 20% of the variation. The reason for the large residual error in the regression model is unknown but may be due to analytical errors in the measurement of ANC, base cations, and sulfate. Because the ANC deficit in most of the streams in this subregion is relatively small, analytical errors could account for the large residual error in the regression model.

In summary, analysis from the charge balance/ANC deficit model show that many streams in the target population have sea water corrected base cation concentrations greater than their ANC (i.e., an ANC deficit). Such deficits can indicate acidification of stream water, increased leaching of base cations from the surrounding watershed due to inputs of strong acids, or sources of strong mineral acid anions in association with base cations as neutral salts. Sulfate alone explains most (> 50%) of the variation in the ANC deficit among streams in all of the subregions except at the upper reach nodes in subregions 3C and 3A and at the upper and lower reach nodes in subregion 3B. In Florida (3C), organic acids appear to account for most (81%) of the variation in the deficit among streams, whereas in the Mid-Atlantic Coastal Plain (3B), nitrate accounts for most of the deficit (70 and 73% at the lower and upper nodes, respectively). Additional analysis of these data is warranted to refine our quantitative understanding of potential watershed contributions of neutral salts and the effect of various acid anions on the ANC deficit when different F-factors are assumed.

10.3 ATMOSPHERIC SULFATE DEPOSITION AND STREAM WATER CHEMISTRY

To examine the relationship between stream water sulfate concentration and sulfate deposition in streams potentially sensitive to acid deposition, a representative sulfate concentration was calculated for each reach (average of upper and lower node index value) after deleting nodes that had either ANC > 200 μeq L^{-1} or SO_4^{2-} > 400 μeq L^{-1}, or both. Reaches with the highest sulfate concentrations were found in the areas of highest wet sulfate deposition (Figure 10-3). A large fraction of the sample streams that had wet sulfate deposition rates > 3 g m^{-2} yr^{-1} had stream water sulfate concentrations > 200 μeq L^{-1}. With few exceptions, the rest of the sample streams in this area had sulfate concentrations > 100 μeq L^{-1}. In areas that had deposition rates < 2.5 g m^{-2} yr^{-1}, most of the streams had sulfate concentrations < 100 μeq L^{-1}. The streams in this area with sulfate concentrations > 100 μeq L^{-1} were mainly found near the coast, where they may have been influenced by agriculture, sulfate from groundwater, or weathering of old marine deposits. To further reduce the possible influence of watershed sulfate sources on this analysis, we confined the analysis to upstream nodes. There was a strong positive relationship (r = +0.88) between the median upstream reach node sulfate concentration and the median annual average total (wet and dry) sulfate deposition from 1980 to 1984 (deposition rates taken from Wampler and Olsen, 1987, and Dennis and Seilkop, 1987) in each subregion (Figure 10-4). Although a large range of stream water sulfate concentrations was observed within most subregions, the regional pattern observed in subregion medians is

Table 10-1. Fraction (r^2) of the Variation in the Estimated ANC Deficit in Stream Water that Can be Accounted for by Sulfate, Nitrate, Chloride, and DOC, and the Partial Regression Coefficient (b) for Each Relationship

Subregion (Node)	SO_4^{2-}		NO_3^-		Cl^-		DOC		Overall Model$
	r^2	b	r^2	b	r^2	b	r^2	b	R^2
Pocono/Catskills (L)	0.81	1.12	0.13	1.08		ns*	0.005	11.05	0.95
Pocono/Catskills (U)	0.77	1.19	0.19	1.15		ns		ns	0.96
N. Appalachians (L)	0.99	1.02	0.002	1.36	0.003	1.02		ns	>0.99
N. Appalachians (U)	0.84	1.09	0.005	0.90		ns		ns	0.99
Valley and Ridge (L)	0.84	1.06	0.14	0.94	0.001	0.04		ns	0.98
Valley and Ridge (U)	0.86	1.40	0.12	0.81		ns	0.001	-6.82	0.99
Coastal Plain (L)	0.23	1.34	0.70	1.34	0.003	0.05	0.03	6.59	0.96
Coastal Plain (U)	0.21	1.04	0.73	1.19		ns		ns	0.94
Southern Blue R. (L)	0.94	0.97	0.03	0.62	0.002	-0.04		ns	0.97
Southern Blue R. (U)	0.53	0.84	0.16	0.78	0.11	-0.18		ns	0.79
Piedmont (L)	0.84	0.98	0.04	0.97		ns		ns	0.88
Piedmont (U)	0.15	0.69	0.05	0.71		ns		ns	0.20
S. Appalachians (L)	0.99	1.02	0.003	1.19		ns		ns	0.99
S. Appalachians (U)	0.98	1.05	0.012	1.13		ns	0.001	7.65	>0.99
Ozarks/Ouachitas (L)	0.97	1.00	0.007	0.92	0.002	-0.08		ns	0.98
Ozarks/Ouachitas (U)	0.76	0.92	0.15	0.97	0.007	-0.15	0.04	5.23	0.95
Florida (L)	0.61	1.14	0.02	0.39	0.27	0.81	0.02	3.05	0.93
Florida (U)	0.10	0.56		ns	0.01	0.24	0.81	4.42	0.93

* ns = partial regression coefficient (b) not significantly different from zero ($P > 0.15$).
$ R^2 is the coefficient of multiple determination when all four independent variables are included in the regression model.

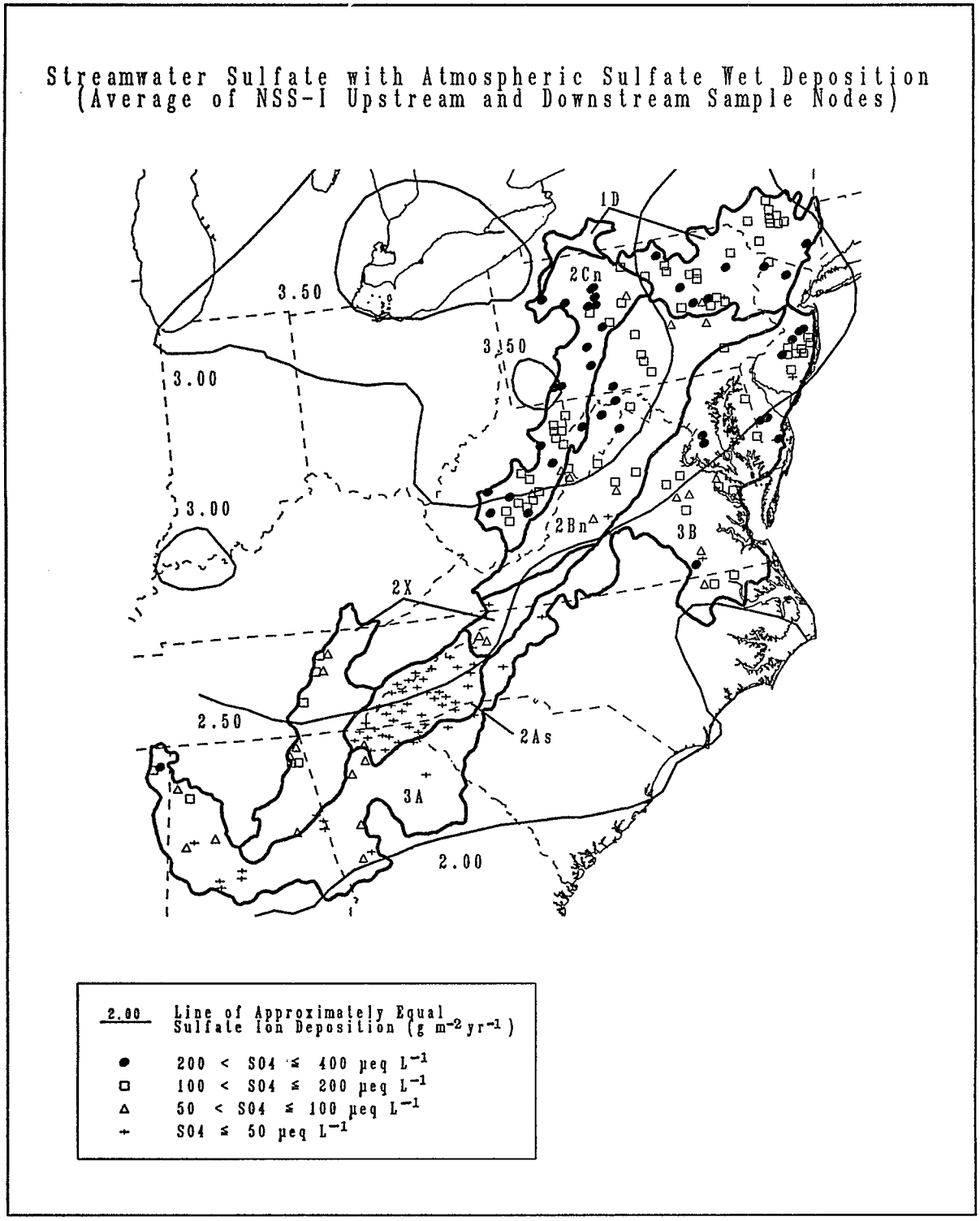


Figure 10-3. Map of reach average sulfate concentration (μeq L^{-1}) in streams after excluding stream nodes with ANC > 200 μeq L^{-1} and/or SO_4^{2-} > 400 μeq L^{-1} in the eastern United States overlayed with isopleths of the 1980-1984 annual average wet sulfate deposition. Sulfate wet deposition rates taken from Wampler and Olsen, (1987).

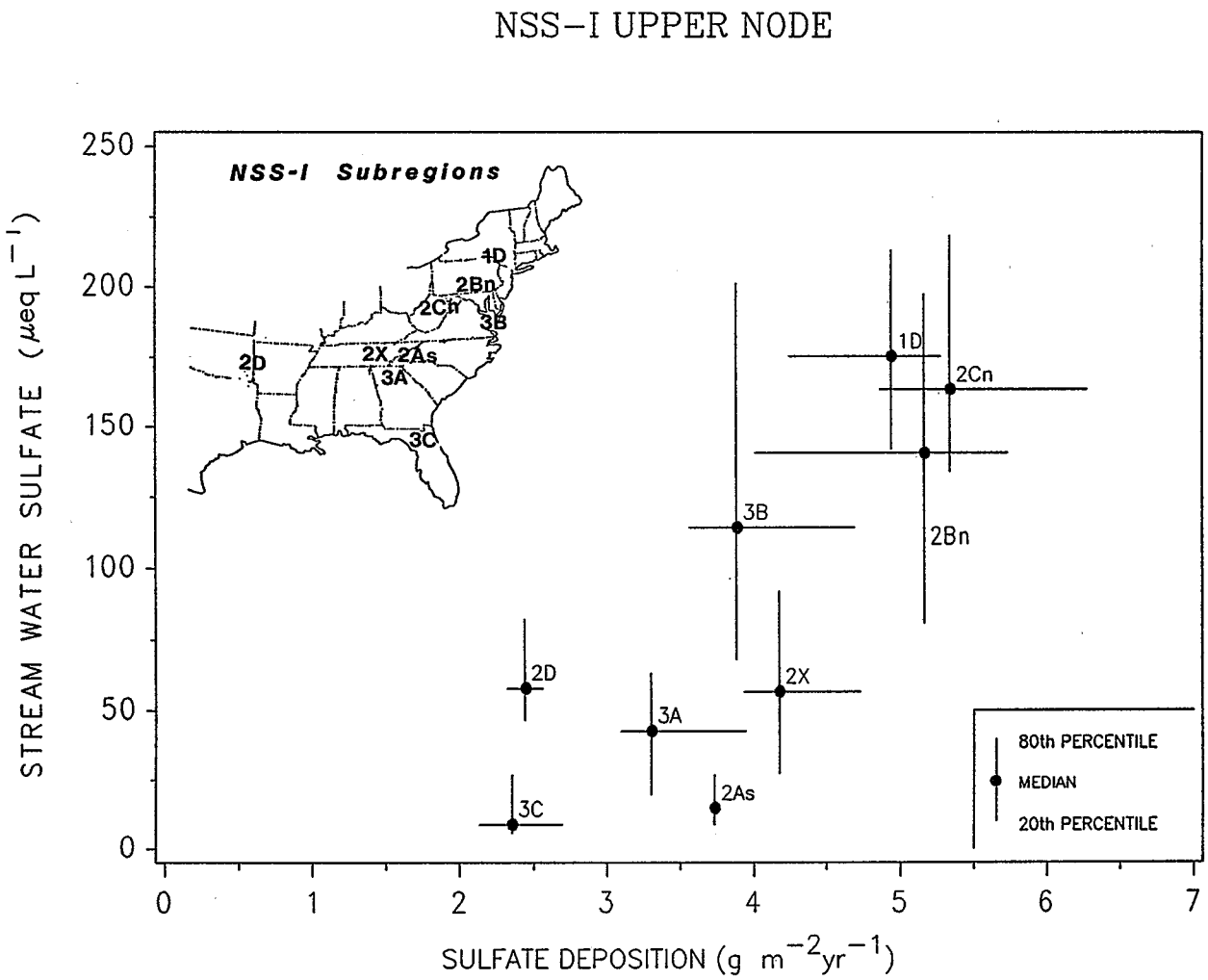


Figure 10-4. Relationship between 1980 to 1984 median annual wet and dry sulfate deposition and median stream water sulfate concentration in stream reach upper nodes with ANC ≤ 200 μeq L^{-1} and SO_4^{2-} < 400 μeq L^{-1} in the nine NSS-I subregions. Deposition rates taken from Wampler and Olsen (1987) and Dennis and Seilkop (1987).

consistent with the hypothesis that atmospheric sulfate deposition is an important factor controlling sulfate concentration in the subpopulation of low ANC streams.

Sullivan et al. (1988) reported that lake water sulfate concentrations, when expressed as subregion median values, were highly correlated with median estimated deposition rates in a probability sample of eastern and western lakes from the National Lake Survey (Linthurst et al., 1986; Landers et al., 1987). Sullivan and his colleagues observed that lakes in the Southern Blue Ridge had lower sulfate concentrations than expected, supporting observations by Galloway et al. (1983) and Rochelle and Church (1987) that sulfur retention (principally sulfate adsorption in soils) is high in many southeastern watersheds. To compare stream results with those of Sullivan et al. (1988), we have combined NSS-I data with data from the National Lake Survey (Linthurst et al., 1986; Landers et al., 1987) to produce a plot of median surface water sulfate versus wet sulfate deposition in low ANC regions of the United States (Figure 10-4). Streams in the Mid-Atlantic subregions (1D, 2Cn, 2Bn, 3B) and the Ozarks/Ouachitas (2D) fall closely in line with eastern and upper midwest lakes in a positive, approximately linear trend. As also observed by Sullivan et al. (1988) for Southern Blue Ridge lakes, Figure 10-5 shows that streams in this area had lower than expected SO_4^{2-} in relation to deposition. In addition, streams in the Piedmont (3A) and Southern Appalachian (2X) subregions also fell below those predicted by the roughly linear trend. These observations further support those of Galloway et al. (1983) and Rochelle and Church (1987) regarding sulfur retention in southeastern watersheds.

Florida streams (NSS-I Subregion 3C) had median sulfate concentrations considerably lower than those reported for Florida lakes (NLS-I Subregion 3B). Linthurst et al. (1986) observed a large amount of heterogeneity in Florida lakes, and reported that extremely high sulfate concentrations in some Florida lakes appear to be associated with an influx of sulfur-rich groundwater from the Floridan Aquifer. These lakes are typically found in parts of the central Florida peninsula not contained within the NSS-I Florida Subregion 3C (Eilers, pers. comm. 1987).

There was no obvious relationship between median stream water ANC and the median estimated sulfate deposition rates for the nine NSS-I subregions. This lack of a clear relationship was observed also for eastern and western lakes by Sullivan et al. (1988) and supports conclusions given in Section 8 that most of the regional variation in stream water ANC is probably due to pre-existing differences in base cation supply from weathering sources.

To further examine the relationship between atmospheric sulfate deposition and stream water acidity, the locations of low ANC ($\leq 200\ \mu eq\ L^{-1}$) upstream reach nodes were plotted on a map of the eastern United States and then overlayed with isopleths of atomospheric wet sulfate deposition rates (Figure 10-6). Sample sites affected by acid mine drainage, substantial watershed sources of sulfate, and organic anion dominance were excluded from the plot. Most of the acidic and low ANC upper reach nodes observed in the NSS-I were in areas of high sulfate deposition ($> 3.0\ g\ m^{-2}\ yr^{-1}$). Very few of the remaining acidic stream reaches were observed in areas with deposition rates less than $2.5\ g\ m^{-2}\ yr^{-1}$.

It would be a mistake, however, on the basis of these findings, to interpret $2.5\ g\ m^{-2}\ yr^{-1}$ as an acceptable target loading simply because of the absence of inorganic, acidic streams. Many of the NSS-I areas with deposition rates below $2.5\ g\ m^{-2}\ yr^{-1}$ are known to be areas where deep, well-weathered soils are highly retentive of sulfate (Galloway et al., 1983; Rochelle and Church, 1987). In such areas, stream water sulfate and ANC would not be expected to be in steady state with regard to acid deposition. Although more common in the Mid-Atlantic (where there is higher deposition), low and very low ANC sites were also observed in the Interior Southeast.

Causal inferences cannot be made based on these survey data alone. Whereas the data are consistent with a hypothesis of an atmospheric source of acidification, other processes could also

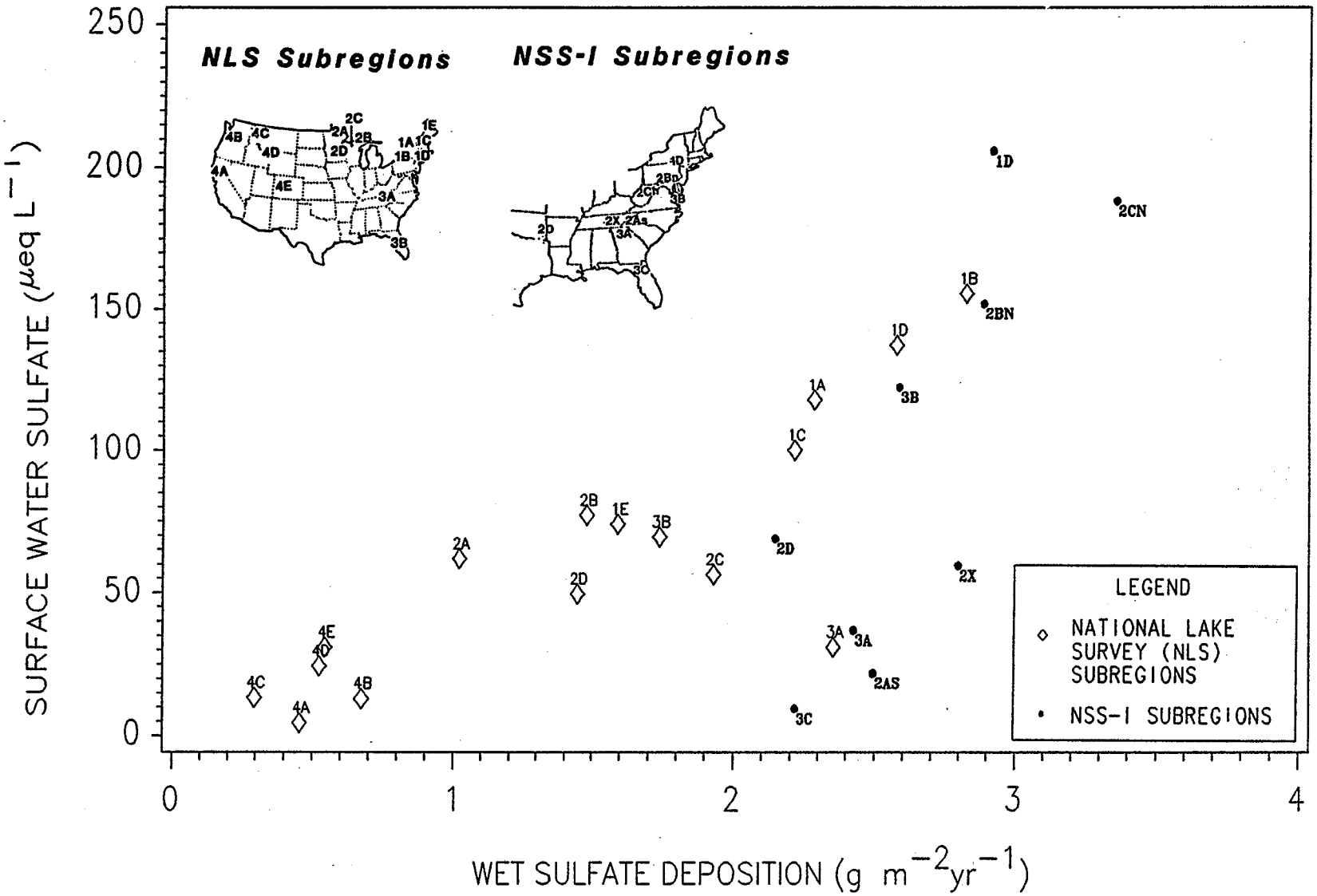


Figure 10-5. Relationship between median wet sulfate deposition (1980-1984) and median sulfate concentration in surface waters with SO_4^{2-} < 400 μeq L^{-1} in National Lake Survey and NSS-I (upstream reach ends) subregions. Sulfate wet deposition rates taken from Wampler and Olsen (1987).

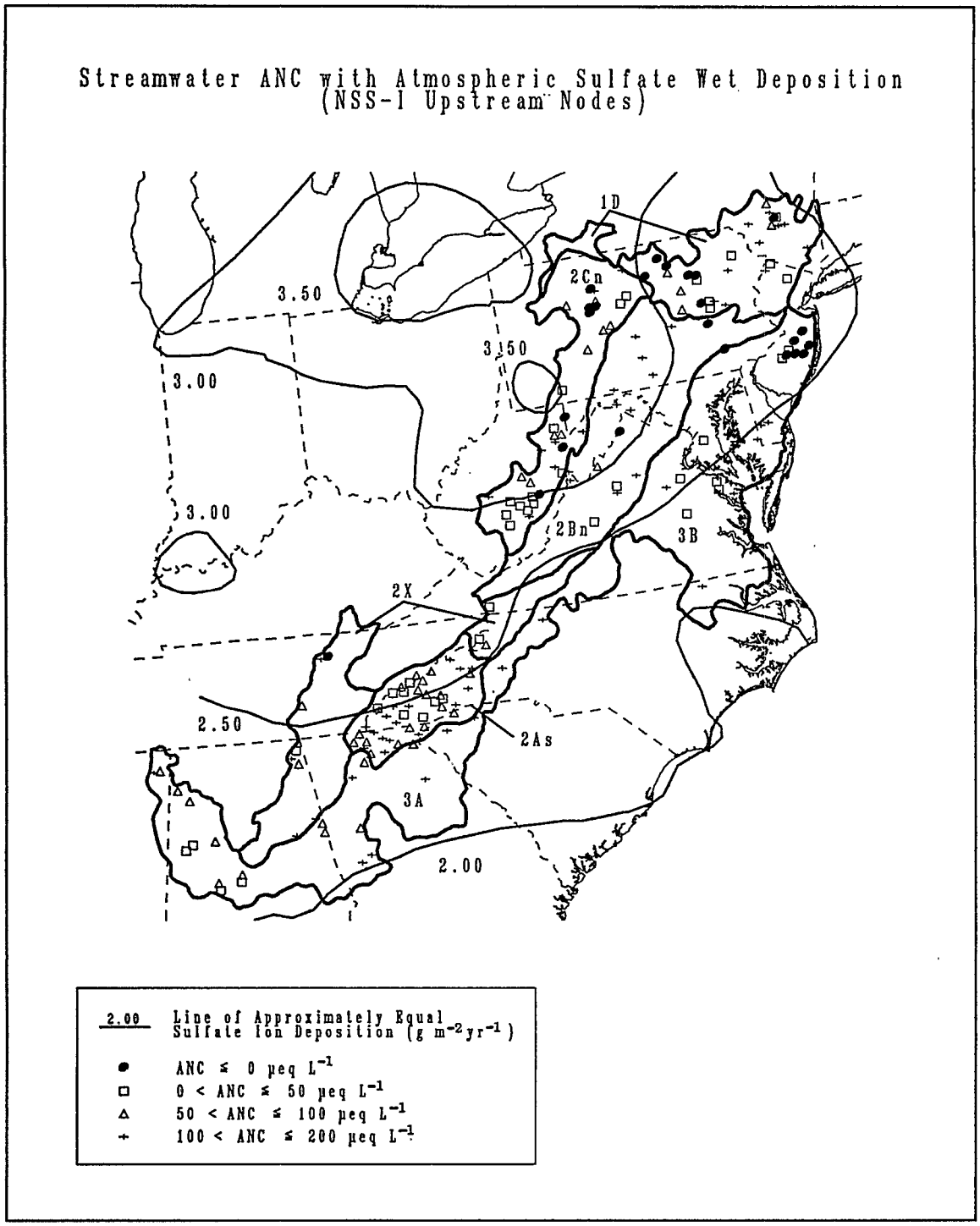


Figure 10-6. Map of upstream node spring index ANC concentration (μeq L^{-1}) in streams with ANC $\leq$ 200 μeq L^{-1} in the eastern United States overlayed with isopleths of the 1980 to 1984 annual average wet sulfate deposition (g m^{-2} yr^{-1}). All streams classified in the acid mine drainage, substantial watershed sources of sulfate, or organic-dominated groups were excluded from the map. Sulfate wet deposition rates taken from Wampler and Olsen (1987).

cause the observed patterns. For example, the same pattern in surface water sulfate could be produced by regional differences in export of sulfate derived from geologic sources in the absence of sulfate deposition. This explanation is unlikely in data that exclude streams and lakes with $[SO_4^{2-}]$ greater than 400 μeq L^{-1}. Furthermore, one would have to evoke unsupportable assumptions of high deposition sulfate retention in northeastern and mid-Atlantic watersheds to account for the sulfate received by these sites in atmospheric deposition. An alternative explanation is that the observed sulfate pattern results entirely from differences in sulfate retention by watersheds. This explanation, however, is also consistent with a hypothesis of regional surface water or watershed soil acidification. The geographic patterns in sulfur retention and their relationship to watershed characteristics is an important part of ongoing EPA studies in the Direct/Delayed Response Project (DDRP)

SECTION 11
SUMMARY AND CONCLUSIONS

11.1 BACKGROUND

National Stream Survey - Phase I (NSS-I) field activities were conducted in the mid-Atlantic and southeastern United States in the spring of 1986 by the U.S. Environmental Protection Agency (EPA) as part of the National Surface Water Survey (NSWS). The first phase of the NSWS was designed to determine the present chemical status of surface waters in regions of the United States containing a majority of streams and lakes considered to be at risk as a result of acidic deposition. The NSS-I was conducted as part of the National Acid Precipitation Assessment Program (NAPAP). Like the previous EPA NSWS activities (Eastern and Western Lake Surveys), it contributes directly to one of NAPAP's principal objectives: the quantification of the extent, location, and characteristics of acidic and potentially sensitive streams and lakes in the United States.

The NSS-I was conducted in four Mid-Atlantic and five Southeast subregions of the United States, identified on the basis of similar physiographic characteristics:

- <u>Mid-Atlantic (MA) Region</u>

  - Interior Mid-Atlantic (IMA) Subregions
    -- Poconos/Catskills (1D)
    -- Northern Appalachians (2Cn)
    -- Valley and Ridge (2Bn)

  - Mid-Atlantic Coastal Plain Subregion (3B)

- <u>Southeast (SE) Region</u>

  - Interior Southeast (ISE) Subregions
    -- Southern Blue Ridge (2As) - Pilot Survey in 1985
    -- Piedmont (3A)
    -- Southern Appalachians (2X)
    -- Ozarks/Ouachitas (2D)

  - Florida Subregion (3C)

NSS-I field activities to date have not included areas of the Northeast, Upper Midwest, and West. Though these regions are expected to contain low ANC or acidic streams potentially sensitive to acidic deposition, they also contain numerous lakes that were sampled as part of EPA's Eastern and Western Lake Surveys. Furthermore, NSS-I field activities thus far have not included synoptic stream chemistry sampling in parts of the South Atlantic and Gulf Coastal Plains expected to contain predominantly low ANC surface waters--but where deposition rates are comparatively lower than in most of the Survey area, and where organic acidity is expected to play an important role. Field activities in the Florida subregion test the utility of NSS-I logistical and design protocols in lowland stream networks of the Southeastern Coastal Plain.

11.2 OBJECTIVES

The objectives of the NSS-I in the Mid-Atlantic and Southeast were to:

- Determine the percentage, extent (number, length, and drainage area), location, and chemical characteristics of streams in the Mid-Atlantic and Southeast regions that are presently acidic, or that have low acid neutralizing capacity (ANC) and thus might become acidic in the future.

- Identify streams representative of important classes in each region that might be selected for more intensive study or long-term monitoring.

11.3 DESIGN

Within the NSS-I subregions, the stream resource of interest (the "target" resource) was identified as those streams that have drainage areas less than 155 square kilometers (60 square miles), but that are large enough to be represented as blue lines on 1:250,000-scale U.S. Geological Survey (USGS) topographic maps.

The NSS-I sampled stream reaches defined as segments of the stream network, as represented by blue lines on the 1:250,000-scale maps. These segments, or reaches, were identified as the mapped blue-line segments between two tributary confluences. Sampling points on each of these reaches were just above the downstream point of confluence (lower node) and just below the upstream point of confluence (upper node). The upper node of a reach represented as a headwater was defined as the farthest upstream extent of the mapped blue line representation.

A two-stage sampling procedure was used to obtain a randomized, systematic sample of approximately 500 reaches with good spatial distribution over each of the nine NSS-I subregions (50 to 80 reaches per subregion). Reaches were excluded if they were too large (drainage area > 155 km^2) or were located within metropolitan areas. The target population was further refined as a result of field visits and data analysis to exclude tidal influences and such perturberances as acid mine drainage.

The NSS-I used index values based on one or the average of two or three baseflow measurements to describe the chemical status of each stream sampled. This index value was measured during the spring season between snowmelt and leafout (approximately March 15 to May 15) and excluded storm episodes. The choice of the spring index sampling period involved a trade-off between minimizing within-season and episodic chemical variability and maximizing the probability of sampling chemical conditions potentially limiting for aquatic organisms.

11.4 SELECTED RESULTS

11.4.1 Regional Chemical Characteristics

Proportions of the target stream reach population with spring index ANC $\leq$ 200 μeq L^{-1} were similar in the Mid-Atlantic (MA) and Southeast (SE) regions surveyed by the NSS-I. Many published works have used 200 μeq L^{-1} ANC as a reference level below which surface waters may be considered potentially sensitive to acidification. Excluding Florida, 51% (18,542) MA reaches and 52% (9,642) of SE reaches had ANC $\leq$ 200 μeq L^{-1} at their upstream ends. After flowing an average of 3 km to their downstream ends, an estimated 41% (15,060) of MA reaches and 47% (8,682) of SE reaches were at or below this index value.

In the Mid-Atlantic Region, 7.4% (2,677) of the reaches were acidic (ANC ≤ 0 μeq L^{-1}) at their upstream ends and 3% (1,098) were acidic at their downstream ends. Estimates based on the first NSS-I sample visit alone (rather than the average of the two spring visits) were slightly higher because of a seasonal trend of increasing spring baseflow ANC. Based upon the earlier spring sample, 8.9% (3,123) of the reaches were acidic at their upper ends and 3.8% (1,339) were acidic at their downstream ends. These figures do not include reaches acidic due to acid mine drainage.

In the Interior Southeast (ISE) subregions (this excludes Florida), we estimate that less than 1% (120) of target reaches were acidic at either their upstream or downstream end. As in the Mid-Atlantic, these estimates do not include reaches acidic due to acid mine drainage.

In the Mid-Atlantic Region, an estimated 13% (4,770) of the reaches had spring baseflow pH ≤ 5.5 at their upstream ends and 5.4% (1,991) had pH at or below this level at their downstream ends. An estimated 26% (9,406) of the reaches had pH ≤ 6.0 at their upstream nodes; 10% (3,760) had pH below this reference value at their lower nodes. Again, these figures do not include reaches acidic because of acid mine drainage.

In the portions of the Interior Southeast Region surveyed by the NSS-I (this excludes Florida), 2% (347) of the reaches had pH ≤ 5.5 at their upstream ends and less than 1% had pH at or below this value at their downstream ends. An estimated 8.6% (1,605) had pH below a reference level of 6.0 at their upper nodes; 2.7% (512) had index pH levels less than this value at their lower nodes.

Among the subregions of the Mid-Atlantic Region, the NSS-I found the greatest number of acidic stream reaches in the Mid-Atlantic Coastal Plain, where 12% of the target reaches (1,334) were acidic or had pH ≤ 5.0 at their upper ends. Another 12% of these upper reach ends had pH between 5.0 and 5.5. After flowing typically 2 to 3 km to their downstream ends, 7% (772) of the reaches remained acidic (ANC ≤ 0) and had pH ≤ 5.5. In the other Mid-Atlantic subregions (Poconos/Catskills, Valley and Ridge, and Northern Appalachians), relatively few reaches were acidic at their downstream ends. Of these three subregions, only the Northern Appalachians were estimated to have reaches acidic at their downstream nodes (4%, or 326 reaches). However, between 5% and 6% (209, 636, and 499 reaches, respectively) were acidic at their upstream nodes in the Pocono/Catskill, Valley and Ridge, and Northern Appalachian subregions.

Among the Interior Southeast subregions (this excludes Florida), acidic reaches were observed only in the Southern Appalachians, where an estimated 120 reaches (2%) were acidic at their upstream ends. Though acidic stream reaches were rare in the Southeast, two Southeast subregions, the Southern Blue Ridge and the Ozarks/Ouachitas, had among the highest proportions of streams with relatively low ANC. In the Southern Blue Ridge, 84% (1,703) of target reaches had ANC ≤ 200 μeq L^{-1} at their upstream ends; in the Ozarks/Ouachitas, the proportion was 68% (2,850).

The Florida subregion stands out as a geographic area with a relatively high percentage of acidic, low ANC, and low pH streams. It is also an area where there are many highly colored streams with high concentrations of dissolved organic carbon (DOC). Population percentage estimates for the Florida subregion are not strictly comparable with those from other subregions, because the Florida sample was drawn from a more restrictive target population focused only on the portion of this state with expected ANC < 200 μeq L^{-1}, rather than 400 μeq L^{-1} (as was the criterion for all the other subregions). At the upstream ends, however, an estimated 678 (39%) of the Florida reaches were acidic (ANC ≤ 0 μeq L^{-1}); another 531 (31%) had ANC between 0 and 50 μeq L^{-1}. Smaller numbers of reaches were still acidic at their downstream ends (225, or 14%), but there remained a large number (670, or 43%) with downstream ANC betweem 0 and 50 μeq L^{-1}. Whereas the acidic reaches in the Florida peninsula were primarily high DOC, colored

water systems, some of those in the panhandle were clear or slightly colored acidic streams with very low ionic strength and very low sulfate, nitrate, and DOC concentrations. As expected, pH distributions were similar to those for ANC. At the upstream ends, an estimated 539 Florida reaches (31%) had pH $\leq$ 5.0; another 324 (19%) were between pH 5.0 and 5.5. Index pH was generally higher at the downstream ends of reaches, where an estimated 225 reaches (14%) had pH $\leq$ 5.0, and another 146 (9%) were between pH 5.0 and 5.5.

Stream water sulfate concentrations were markedly higher in the four Mid-Atlantic subregions (medians from 125 to 238 μeq L^{-1}) than in the five Southeast subregions (medians from 10 to 71 μeq L^{-1}).

11.4.2 Chemical Relationships

Standardized multiple regression analyses showed that regional variation in ANC among streams within NSS-I subregions was associated more closely with differences in base cation concentrations than with differences in concentrations of mineral acid or organic acid anions. This result suggests that watershed geochemical and hydrologic characteristics controlling the supply of mineral weathering products are very important in determining the regional patterns in stream water ANC and therefore buffering of acid inputs.

Examination of the difference between air-equilibrated and non-equilibrated pH measurements indicates that almost all NSS-I sample streams with pH > 6.0 were super-saturated with CO_2. The pH increases upon air equilibration (excess CO_2 is degassed) ranged from approximately 0.25 units to one full pH unit, indicating that carbonic acid alone has an important effect on the pH of stream waters with pH > 6.0. In all NSS-I subregions except Florida and the upper reach nodes in the Mid-Atlantic Coastal Plain, this is the majority of streams.

The only direct way to conclusively demonstrate surface water acidification is through historic data on water quality. Because of a lack of such data on a regional scale for the streams of interest in the NSS-I, a second approach for assessing whether streams in the Mid-Atlantic and Southeast have been acidified involves an indirect method of inferring past changes in ANC through an examination of present water chemistry. Previous researchers have used the ANC deficit (nonmarine base cation concentration minus ANC) as a rough measure of surface water acidification resulting from either natural or anthropogenic causes. It is important to recognize that ANC deficits, in themselves, reflect simply a presence of strong acid anions in water at the time of sampling. ANC deficits can be observed in stream water for a number of reasons: (1) they may reflect a reduction in ANC caused by the addition of a strong acid (like sulfuric acid) to the stream, as might occur with acid deposition onto a poorly buffered watershed; (2) they may reflect an increase in base cation concentration (with no change in ANC) in the stream resulting from cation exchange or accelerated weathering of watershed soils and rock (this can be due to acidic deposition); (3) they may result from an addition of base cations in neutral salts (e.g., $CaSO_4$), with no change in ANC; or finally (4) they may result from a combination of all these mechanisms. The last combination of factors is the most likely for a heterogeneous assemblage of streams subject to a wide range of influences. However, the interpretation of ANC deficits in relatively pristine streams draining watersheds underlain by metamorphic rock is not as uncertain. In these pristine streams, ANC deficits were higher in areas that receive larger amounts of acidic deposition. The lack of plausible sources of neutral salts in these streams makes it likely that the observed ANC deficits in such upland, forested streams are due to titration by strong acids or increases in base cation export, and that both mechanisms are probably associated with atmospheric acidic deposition.

In order to interpret the observed ANC deficit as a measure of the amount of historic change in ANC, one must first assume that the ANC deficits are due largely to titration by strong acids and that the base cation concentrations in streams have remained nearly constant over time. These assumptions are more likely to be correct in poorly buffered stream waters of low ionic strength. There are indications, however, that base cations may not remain constant over time in many streams. In addition, several conditions must also be met before the ANC deficit in a given stream could be interpreted as a measure of historic change in ANC due to acid deposition: (1) an atmospheric source of strong acids can be demonstrated to be of sufficient magnitude to cause the observed ANC deficit, (2) other potential sources of strong acid anions can be ruled out as unlikely (e.g., sulfide weathering, organic acidity), and (3) concentrations of acids not derived from atmospheric deposition (e.g., organics from watershed sources) have remained relatively constant over time.

Most of the NSS-I subregions have some streams with a deficit of ANC in relation to nonmarine base cations. The four Mid-Atlantic subregions (Poconos/Catskills, Northern Appalachians, Valley and Ridge, and Mid-Atlantic Coastal Plain) had the largest number of streams with a deficit of ANC in relation to base cations. However, some streams in all the NSS-I subregions show a deficit.

The observation of smaller ANC deficits in most Southeast streams, compared with those in Mid-Atlantic subregions, is generally consistent with the lower atmospheric acid deposition rates and greater sulfate adsorption capacities of soils in many parts of the southeastern United States. These results do not preclude the possibility of soil acidification leading to future stream acidification in any of the NSS-I subregions. Sulfate was the dominant strong acid anion in most acidic and low ANC streams and was in sufficient concentration to account for the observed ANC deficits in the majority of stream reaches in all subregions except Florida and the Mid-Atlantic Coastal Plain.

11.4.3 Sources of Acidity in Acidic and Low ANC streams

Potential sources of acidity were examined in a subpopulation of acidic and low ANC (≤ 200 μeq L^{-1}) streams within the NSS-I target population. Stream reaches affected by acid mine drainage, substantial watershed sources of sulfate, and organic acids were identified and excluded from this group by site visits and examination of stream chemical data. After the exclusions, a group of acidic (ANC ≤ 0) and low ANC (0 - 200 μeq L^{-1}) stream reaches remain, for which sulfate is the dominant strong acid anion. Acid deposition cannot be ruled out as the major source of acidity in this group of streams. Stream water sulfate concentrations can readily be accounted for by evaporative concentration of sulfate in wet plus dry deposition.

Within the subpopulation of acidic streams in the NSS-I target population, a group of acidic stream reaches has been identified for which atmospheric deposition is the most probable source of acidity and effects due to acid deposition cannot be ruled out. Based on interpolations between upper and lower node chemistry, this high-interest subpopulation within the group of acidic reaches had an estimated combined length of 4,455 km. Most (4,272 km) of these reaches are in the Mid-Atlantic subregions, where they comprise 4% of the total length of target stream reaches. Estimates based upon the first NSS-I sample visit alone (rather than the average of the two spring visits) were somewhat higher than 4,455 km because of a seasonal trend of increasing spring baseflow ANC. Based on the earlier spring sample, a combined length of 7,481 km of acidic stream reaches were within the high-interest subpopulation of streams for which acid deposition impacts cannot be ruled out. Again, most of these reaches are in the Mid-Atlantic subregions, where they comprise 6.6% of the total length of target stream resource.

These reaches are located primarily in the forested upland drainages and coastal areas of the Mid-Atlantic Region that experience high rates of atmospheric sulfate deposition. Specifically, most stream reaches within this group are located:

- In upland forested drainages of the Allegheny Plateau, in the ridges of the Valley and Ridge physiographic province, and in the Glaciated Plateau in northeast Pennsylvania (included in NSS-I subregions 1D, 2Bn and 2Cn). An estimated 695 (9.7%) of 7,190 reaches on ridges of the Valley and Ridge geographic area and 499 (11%) of 4,548 reaches in forested drainages of the Allegheny and Glaciated Plateaus were acidic at their upstream nodes.

- In the New Jersey Pine Barrens (within subregion 3B). Seventy-nine percent of upstream nodes and 93% of downstream nodes were in this high-interest subgroup; approximately one-third of these had chemistry influenced (> 10% of the anion sum) but not dominated by organic anions (organic anion < SO_4^{2-} + NO_3^-).

Although streams in the New Jersey Pine Barrens appear to have elevated concentrations of sulfate derived from atmospheric deposition, historic data suggest that some Pine Barrens streams have probably been acidic at least since the early 1900's. There is no reason, however, to believe that most of the upland forested reaches in the Mid-Atlantic have always been acidic.

A high-interest group of streams was identified within the subpopulation of non-acidic stream reaches with very low ANC (> 0 - ≤ 50 μeq L^{-1}) in the NSS-I target population. For these streams, organic acidity and substantial terrestrial sulfate sources are unlikely; the predominant sulfate source appears to be atmospheric deposition. Based on interpolation between upper and lower node chemistry, an estimated 15,590 km of target reach length is within this group. Approximately two-thirds of these reaches were in the Mid-Atlantic subregions, where they made up about 9.6% of the combined length of the target population. Calculations of these totals based on the earlier spring sample did not differ substantially from those based on the average from two spring visits. These very low ANC streams are located primarily on upland, forested sites of the Allegheny Plateau, Valley and Ridge Province, Blue Ridge Mountains, and Cumberland Plateau. In addition, a large number of these reaches were found in Coastal Plain areas (East and West Mid-Atlantic, New Jersey Pine Barrens, East and West Gulf Coast).

A third group of high-interest, low ANC (50-200 μeq L^{-1}) stream reaches was identified that contained sulfate as the dominant strong acid anion. As in the acidic and very low ANC groups above, reaches with likely geologic or other non-atmospheric sulfate sources, and those dominated by organic anions, were excluded. Based on upper node chemistry, an estimated 61,665 km, or 31%, of the combined length of reaches in the target population within the NSS-I survey area were in this category. Stream reaches in this group were found in all the NSS-I subregions and in virtually all geographic site classes. Approximately half the combined reach length in this category was located in the Valley and Ridge, Piedmont, and Blue Ridge geographic site classes. This comprised an estimated 35,934 km of reaches in this category in the Interior Southeast subregions (41% of the total resource). In the Interior Mid-Atlantic, 19,172 km of reaches in this category made up 28% of the target stream length.

An estimated 88% (538) of the stream reaches in a subpopulation of low elevation, swampy reaches in the panhandle and peninsula of Florida were acidic at their upstream nodes, apparently due to organic acids. In the Glaciated Plateau and Allegheny Plateau, and on ridges of the Valley and Ridge Province, stream reaches were more commonly acidic at their upstream ends than at their downstream ends.

NSS-I estimates of number or length of acidic stream resources do not include an additional estimated 1,300 reaches in Pennsylvania and West Virginia (combined length 3,500 km) and an additional 120 reaches (1,100 km in length) in the Southeast that were acidic at one or both ends due to acid mine drainage. Within the subregions surveyed by the NSS-I, acid mine drainage impacts were concentrated in the Allegheny Plateau (western Pennsylvania and West Virginia). Of the estimated 9,417 stream reaches in the initial target population (before refinement) in the Northern Appalachian subregion that were within the NSS-I target stream size range, 10% (929 reaches with a combined length of 2,276 km) were acidic due to acid mine drainage.

The distribution of sulfate concentrations in eastern United States streams with baseflow sulfate concentrations not dominated by terrestrial sulfate sources corresponds well with sulfate deposition rates. A plot of population median stream sulfate concentration in the nine NSS-I subregions versus rates of sulfate deposition shows a strong positive linear relationship. However, when data from the National Lake Survey (NLS) are added to the plot, a group of Southeast lakes and streams appears to have lower sulfate concentrations than expected, given the sulfate deposition rates in their respective subregions. These observations are consistent with other research showing substantial amounts of sulfate retention, by mechanisms such as sulfate adsorption, in watersheds of the Southeast.

SECTION 12
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SECTION 13
GLOSSARY

13.1 ABBREVIATIONS AND SYMBOLS

13.1.1 Abbreviations

AERP	-- Aquatic Effects Research Program
AL	-- analytical laboratory
AMD	-- acid mine drainage
ANC	-- acid neutralizing capacity
ANOVA	-- analysis of variance
ASTM	-- American Society for Testing and Materials
BC	-- base cations
BNC	-- base neutralizing capacity
C.I.	-- confidence interval
CDF	-- cumulative distribution function
CL	-- Confidence Limit
CRDL	-- contract required detection limit
DDRP	-- Direct/Delayed Response Project
DIC	-- dissolved inorganic carbon
DOC	-- dissolved organic carbon
DQO	-- data quality objective
ELS-I	-- Eastern Lake Survey - Phase I
ELS-II	-- Eastern Lake Survey - Phase II
EMSL-LV	-- Environmental Monitoring Systems Laboratory - Las Vegas
EPA	-- U.S. Environmental Protection Agency
ERL-C	-- Environmental Research Laboratory - Corvallis
ERP	-- Episodic Response Project
ESS	-- effective sample size
IBM	-- International Business Machines
ID	-- identification number
IMA	-- Interior Mid-Atlantic subregions (1D, 2Cn, and 2Bn)
ISE	-- Interior Southeast subregions (2As, 3A, 2X, and 2D)
L	-- stream reach lower node or liter
Lockheed-EMSCO	-- Lockheed Engineering and Management Services Company, Inc.
LTM	-- Long-term Monitoring (Project)
MA	-- Mid-Atlantic Region
MD DNR	-- State of Maryland, Department of Natural Resources
MIBK	-- methyl-isobutyl-ketone

NADP/NTN	-- National Acid Deposition Program/National Trends Network
NAPAP	-- National Acid Precipitation Assessment Program
NBS	-- National Bureau of Standards
NCC	-- National Computer Center
NLS	-- National Lake Survey
NRDC	-- Natural Resources Defense Council
NSS-I	-- National Stream Survey - Phase I
NSWS	-- National Surface Water Survey
NTU	-- nephelometric turbidity unit
ORNL	-- Oak Ridge National Laboratory
PCA	-- Principal Component Analysis
PCU	-- platinum cobalt units (for water color measurement)
PCV	-- Pyrocatechol violet
PL	-- processing laboratory
QA	-- quality assurance
QC	-- quality control
QCCS	-- quality control check solution
RSD	-- relative standard deviation
SAOA	-- strong acid organic anions
SAS	-- Statistical Analysis System
SBC	-- sum of base cations
SBR	-- Southern Blue Ridge
SD	-- standard deviation
SDL	-- system decision limit
SE	-- Southeast Region or standard error
TIME	-- Temporal Integrated Monitoring of Ecosystems (Project)
TVA	-- Tennessee Valley Authority
U	-- stream reach upper node
UCB	-- upper 95% confidence bound
USDA	-- U.S. Department of Agriculture
USFS	-- U.S. Forest Service
USGS	-- U.S. Geological Survey
USU	-- Utah State University
WAOA	-- weak acid organic anions
YSI	-- Yellow Springs Instruments

13.1.2 Symbols

$\hat{A}$	-- total area of direct watershed
a_1	-- direct drainage area
a_2	-- drainage area of upstream node for nonheadwater reaches
a_3	-- headwater drainage area of upstream node
Al	-- aluminum
Al_{ext}	-- MIBK-extractable aluminum (total monomeric)
$Al_{(im)}$	-- inorganic monomeric aluminum
Alk	-- carbonate alkalinity
b_i	-- regression coefficient
b_i'	-- standardized regression coefficient
Ca^{2+}	-- calcium
Cl^-	-- chloride
cm	-- centimeter
CO_2	-- carbon dioxide
CO_3^{2-}	-- carbonate
$\hat{D}$	-- total discharge index
F^-	-- fluoride
Fe	-- iron
$Fe(OH)_3$	-- ferric hydroxide
FeS_2	-- pyrite (ferrous sulfide)
F(x)	-- cumulative distribution function
H^+	-- hydrogen ion
ha	-- hectare
HCO_3^-	-- bicarbonate
HNO_3	-- nitric acid
H_2CO_3	-- carbonic acid
H_2O	-- water
H_2SO_4	-- sulfuric acid
K_a	-- acid dissociation constant
K^+	-- potassium
kg	-- kilogram
km	-- kilometer
$\hat{L}$	-- total length of target reaches
m	-- meter or slope of regression line
MAX	-- maximum value of x
M_c	-- molar conductivity
mg	-- milligram
mg L^{-1}	-- miligrams per liter, unit of concentration

Mg^{2+}	-- magnesium
mi	-- mile
MIN	-- minimum value of x
mL	-- milliliter
Mn	-- manganese
n	-- number of samples
$\hat{N}$	-- total number of target reaches
Na^+	-- sodium
NaCl	-- sodium chloride
NH_4^+	-- ammonium
NO_3^-	-- nitrate
n.s.	-- not significant
OH^-	-- hydroxide
O_2	-- oxygen
p	-- significance level
pCO_2	-- partial pressure of CO_2
pH	-- the negative logarithm of the hydrogen ion molar concentration
pK_a	-- negative logarithm (base 10) of acid dissociation constant
Q_{20}	-- population 20th percentile, 1st quintile
Q_{80}	-- population 80th percentile, 4th quintile
r	-- Pearson's correlation coefficient
$RCOO^-$	-- organic anion
r^2	-- coefficient of determination
R^2	-- coefficient of multiple determination
$\hat{S}$	-- total stream surface area
SiO_2	-- silicon dioxide
SO_4^{2-}	-- sulfate
$\hat{V}$	-- estimated variance
w	-- weight or expansion factor
°C	-- degrees Celsius
Δ	-- delta: denotes an increment of change
π	-- reach inclusion probability
$\mu eq\ L^{-1}$	-- microequivalents per liter, unit of concentration
$\mu g\ L^{-1}$	-- micrograms per liter, unit of concentration
$\mu S\ cm^{-1}$	-- micro-Siemens per centimeter, unit of electrical conductance
μM	-- micromole per liter, unit of concentration
1D	-- Poconos/Catskills subregion
2As	-- Southern Blue Ridge subregion (NSS Pilot Survey)

2Bn	-- Valley and Ridge subregion
2Cn	-- Northern Appalachians subregion
2D	-- Ozarks/Ouachitas subregion
2X	-- Southern Appalachians subregion
3A	-- Piedmont subregion
3B	-- Mid-Atlantic Coastal Plain subregion
3C	-- Florida subregion

13.2 DEFINITIONS

ACID MINE DRAINAGE - runoff with high concentrations of metals, sulfate and acidity resulting from the oxidation of sulfide minerals that have been exposed to air and water (usually from mining activities). Considered a NONINTEREST attribute for calculating NSS-I population estimates.

ACID NEUTRALIZING CAPACITY - the total acid-combining capacity of a water sample determined by titration with a strong acid. Acid neutralizing capacity includes ALKALINITY (carbonate species) as well as other basic species (e.g., borates, dissociated ORGANIC ACIDS, alumino-hydroxy complexes).

ACIDIC DEPOSITION - rain, snow, or dry fallout containing high concentrations of sulfuric acid, nitric acid, or hydrochloric acid, usually produced by atmospheric transformation of the by-products of fossil fuel combustion (power plants, smelters, autos, etc.); precipitation with a pH less than 5.0 is generally considered to be unnaturally acidic.

ACIDIC STREAM - for this report, a stream with ACID NEUTRALIZING CAPACITY less than or equal to 0 μeq L^{-1}.

ACIDIFICATION - any temporary or permanent loss of ACID NEUTRALIZING CAPACITY.

ACCURACY - the closeness of a measured value to the true value of an ANALYTE.

AIR-EQUILIBRATED - a sample ALIQUOT that has been brought to equilibrium with standard air (300 ppm CO_2) before analysis; used with some pH and DISSOLVED INORGANIC CARBON measurements.

ALIQUOT - a subsample of a 4-L water sample processed in a specific manner for chemical analysis at a later time.

ALKALINITY - the titratable base of a sample consisting of hydroxide, carbonate, and bicarbonate ions, i.e., the equivalents of acid required to neutralize the basic carbonate components.

ALKALINITY MAP CLASS - a geographic area defined by the expected ALKALINITY of a majority of SURFACE WATERS (does not necessarily reflect measured alkalinity); used in the NSWS probability sampling design. (See LOW ANC STRATUM.)

AMONG-BATCH PRECISION - the estimate of PRECISION that includes the effects of different laboratories and day-to-day (BATCH-to-BATCH) differences.

ANALYTICAL LABORATORY - in this report, a laboratory under contract with the U.S. Environmental Protection Agency to analyze water samples shipped from the PROCESSING LABORATORIES.

ANALYTE - a chemical species that is measured in a water sample.

ANC DEFICIT - the difference in concentration between the sum of the nonmarine base cations and ANC.

ANION - a negatively charged ion.

ANION-CATION BALANCE - an assessment of the total charge of positive ions (CATIONS) compared to the total charge of negative ions (ANIONS).

ANION DEFICIT - the concentration in $\mu eq\ L^{-1}$ of measured CATIONS minus measured ANIONS.

AUDIT - an on-site evaluation of field sampling or laboratory activities to verify that standardized protocols are being followed.

AUDIT SAMPLE - a standardized water sample submitted to laboratories to check overall performance in sample analysis. See FIELD AUDIT SAMPLE and LABORATORY AUDIT SAMPLE.

BASE CATION - a nonprotolytic cation that does not affect ACID NEUTRALIZING CAPACITY; in the NSS-I, consists of calcium, magnesium, sodium, and potassium.

BATCH - A group of samples (including QUALITY CONTROL samples) processed and analyzed together at the PROCESSING LABORATORY; associated with a unique batch ID code.

BEDROCK - solid rock exposed at or underlying the land surface.

BIAS - the systematic difference between the measurements or estimations and the true values.

BLANK - a sample of REAGENT GRADE WATER analyzed as a QUALITY ASSURANCE/ QUALITY CONTROL sample in the NSS-I. See FIELD BLANK SAMPLE, LABORATORY BLANK SAMPLE, and PROCESSING LABORATORY BLANK.

BLUE LINE REACH - a REACH appearing as a BLUE LINE on a 1:250,000-scale USGS topographic map.

BUFFERING CAPACITY - the quantity of ACID or BASE that can be added to a water sample with little change in pH.

CALCULATED CONDUCTANCE - the sum of the theoretical specific conductances of all measured ions in a sample.

CALIBRATION BLANK - a solution used in standardizing or checking the calibration of analytical instruments; also used to determine instrument detection limits.

CATCHMENT - see WATERSHED.

CATION - a positively charged ion.

CATION EXCHANGE - a reversible process occurring in soil in which acidic CATIONS (e.g., hydrogen ions) are adsorbed and BASE CATIONS are released.

CHELATOR - a class of compounds, organic and inorganic, that can bind metal ions and change their biological availability.

CIRCUMNEUTRAL - close to neutrality with respect to pH (pH = 7).

CLOSED SYSTEM - method of measurement in which a water sample is collected and analyzed for pH and DISSOLVED INORGANIC CARBON without exposure to the atmosphere.

CLUSTER ANALYSIS - a multivariate classification technique for identifying similar (or dissimilar) groups of observations.

COMPARABILITY - a measure of data quality that assesses the similarity within and among data sets.

COMPLETENESS - a measure of data quality that is the quantity of acceptable data actually collected relative to the total quantity for which collection was attempted.

CONDUCTANCE - a measure of the electrical conductance (the reciprocal of the electrical resistance) of a water sample; proportional to the total ionic concentration.

CONTRACT REQUIRED DETECTION LIMIT - for each chemical variable, the highest INSTRUMENT DETECTION LIMIT allowable in the ANALYTICAL LABORATORY contract.

CUBITAINER - a 3.8 L container made of semirigid polyethylene used to transport field samples (routine, duplicate, blank) from the stream site to the processing laboratory.

CUMULATIVE DISTRIBUTION FUNCTION - a function, F(x), such that for any reference value X, F(x) is the estimated proportion of streams in the population having a value $x \leq X$.

DATA QUALIFIER - see FLAG and TAG.

DATA QUALITY OBJECTIVES - ACCURACY, DETECTABILITY, and PRECISION limits desired by data users, established prior to the beginning of a sampling effort. Also includes goals for COMPLETENESS, COMPARABILITY, and REPRESENTATIVENESS.

DATA SET 1 - set of files containing RAW data.

DATA SET 2 - set of files containing VERIFIED data.

DATA SET 3 - set of files containing VALIDATED data.

DATA SET 4 - set of files containing final, enhanced data; missing values or errors in the VALIDATED data set were replaced by substitution values, duplicate values were averaged, and negative measurements (except ACID NEUTRALIZING CAPACITY) were set equal to zero.

DETECTABILITY - the capacity of an instrument or method to determine a measured value for an ANALYTE above background levels. See INSTRUMENT DETECTION LIMIT and SYSTEM DECISION LIMIT.

DISSOLVED INORGANIC CARBON - a measure of the dissolved carbon dioxide, carbonic acid, bicarbonate and carbonate anions in a water sample; comprises the major part of ACID NEUTRALIZING CAPACITY in a stream.

DISSOLVED ORGANIC CARBON - a measure of the organic (noninorganic) fraction of carbon in a water sample that is dissolved or unfilterable (0.45 μm pore size in the NSS-I).

DOWNSTREAM REACH NODE - see LOWER NODE.

DUPLICATE STREAM SAMPLE - see FIELD DUPLICATE SAMPLE.

EFFECTIVE SAMPLE SIZE (n') - the number of grid points examined within each STRATUM to obtain the Stage II sample reaches to be visited in the field.

ELECTRONEUTRALITY - having no electric charge.

EPISODE - A short-term change in stream pH and ANC during storm flows or snowmelt runoff; considered a NONINTEREST attribute for calculating NSS-I population estimates.

EQUIVALENT - unit of ionic concentration; the quantity of a substance that either gains or loses one mole of protons or electrons.

EXTRACTABLE ALUMINUM - an operationally defined aluminum fraction determined using a MIBK extraction.

FIELD AUDIT SAMPLE - a standardized water sample submitted to PROCESSING LABORATORIES to check overall performance in sample analysis by both PROCESSING and ANALYTICAL LABORATORIES.

FIELD BLANK SAMPLE - a sample of REAGENT GRADE WATER prepared at the stream site by field crews; these samples were analyzed by both PROCESSING and ANALYTICAL LABORATORIES.

FIELD DUPLICATE SAMPLE - an additional water sample collected at stream side immediately after a ROUTINE SAMPLE in accordance with standardized protocols.

FLAG - qualifier of a data value; used to identify specific notes or observations made during the VERIFICATION and VALIDATION procedures.

FRAME - a structural representation of a population providing a sampling capability.

FRAME POPULATION - in the NSS-I, the set of BLUE LINE STREAM segments appearing on a 1:250,000-scale USGS topographic map within a designated region of interest.

GEOGRAPHIC SITE CLASS - a post sampling stratification of the NSS-I TARGET POPULATION according to a combination of physio-geographic attributes and land use patterns that is not constricted by SUBREGION boundaries.

GRADIENT - the ratio between the elevation difference and length distance between the UPPER and LOWER NODE of a REACH.

GRAN ANALYSIS - a mathematical procedure used to determine the equivalence points of a titration curve for ACID and BASE NEUTRALIZING CAPACITY.

HEADWATER REACH - map scale dependent, the uppermost reach of a stream drainage network (i.e., a reach with a STRAHLER ORDER and SHREVE ORDER equal to 1).

HOLDING TIME - the time elapsed between sample collection and analysis.

HYDROLOGIC FLOW PATHS - the distribution and circulation of water on the surface of the land, in the soil, and underlying rocks within a watershed.

IN SITU - referring to measurements collected within the water column at a stream.

INCLUSION PROBABILITY - the chance of a stream being selected for sampling.

INDEX PERIOD - see SPRING BASEFLOW INDEX PERIOD.

INDEX VALUE - the average of one to three samples collected at a stream NODE during the SPRING BASEFLOW INDEX PERIOD, used to represent chemical conditions in the stream.

INITIAL DIC - a measurement of DISSOLVED INORGANIC CARBON made on an ALIQUOT immediately before it is titrated for ACID NEUTRALIZING CAPACITY.

INORGANIC MONOMERIC ALUMINUM - an operationally defined aluminum fraction determined in the NSS-I as the difference in concentration between TOTAL MONOMERIC ALUMINUM and ORGANIC ALUMINUM (PCV technique).

INSTRUMENT DETECTION LIMIT - a value calculated from LABORATORY BLANK SAMPLES that indicates the minimum concentration (with 95% confidence) that can be distinguished from blank samples by the instrument(s) used.

INTERLABORATORY BIAS - systematic differences in performance between laboratories estimated from analysis of the same type of AUDIT SAMPLES.

INVERSE DISTRIBUTION FUNCTION - a function, 1-F(x), such that for any reference value X, 1-F(x) is the estimated number of streams in the population having a value $x \geq X$.

ION BALANCE - see ANION-CATION BALANCE.

IONIC STRENGTH - a measure of the interionic effect resulting from the electrical attraction and repulsion between various ions; can be calculated from the measured concentrations of ANIONS and CATIONS.

LABILE ALUMINUM - see INORGANIC MONOMERIC ALUMINUM.

LABORATORY BLANK SAMPLE - a sample of REAGENT GRADE WATER prepared and analyzed by ANALYTICAL LABORATORIES.

LABORATORY DUPLICATE SAMPLE - a split sample prepared and analyzed at the ANALYTICAL LABORATORIES.

LONG-TERM MONITORING PROGRAM - an ongoing program sponsored by the U.S. Environmental Protection Agency that monitors the chemistry of selected lakes and streams at least three times per year, designed to detect long-term trends in chemistry.

LOW ANC STRATUM - a subset of sample reaches within the STAGE I SAMPLE representing those having an ANC less than 50 μeq L^{-1} based on expected alkalinity maps.

LOWER NODE - the downstream NODE of a stream REACH.

MAP POPULATION - in the NSS-I, the blue-line representation of streams depicted on 1:250,000-scale U.S. Geological Survey TOPOGRAPHIC MAPS.

MEAN SQUARE ERROR - a measure of accuracy, usually variance plus square of BIAS.

MEDIAN (M) - the value of x such that F(x) or G(x) = 0.5; the 50th percentile.

METHOD LEVEL PRECISION - PRECISION associated with the analysis of PROCESSING and ANALYTICAL LABORATORY DUPLICATE SAMPLES.

MINERAL WEATHERING - dissolution of rocks and minerals by erosive forces.

NATURAL AUDIT SAMPLE - an AUDIT SAMPLE collected from a surface waters having known ion concentrations similar to those expected in sample streams.

NODE - the points identifying either an upstream or downstream end of a REACH. In the NSS-I, The point above or below the confluence of two streams.

NONINTEREST REACHES - a set of REACHES excluded during the refinement of the TARGET POPULATION after field visitation due to some external influence (tidal effects, acid mine drainage, dry stream channel, etc.). Data from these reaches were excluded in the calculation of NSS-I population estimates.

NONTARGET REACHES - a set of REACHES not in the focus of the NSS-I objectives (urban areas, swamps, large rivers, etc.); excluded from the NSS-I TARGET POPULATION before field visitation.

NTU - nephelometric turbidity unit; a measure of light scattered by a solution of suspended materials.

OLIVER MODEL - a set of empirical equations used to calculate ORGANIC ANION concentrations from DOC and pH.

OPEN SYSTEM - a measurement of pH or DISSOLVED INORGANIC CARBON obtained from a sample that was exposed to the atmosphere during collection and/or measurement.

ORGANIC ACIDS - organic compounds possessing an acidic functional group; includes fulvic and humic acids.

ORGANIC ALUMINUM - an operationally defined aluminum fraction determined by colorimetry (PCV technique) after passing the sample through a strong cation exchange column.

ORGANIC ANION - an organic molecule with a negative net ionic charge.

OUTLIERS - observations not typical of the population from which the sample is drawn.

PERCENT ION BALANCE - percent difference between the anion deficit and the total ionic equivalents [(sum cations - sum anions)/(sum of cations + sum of anions) * 100)].

PERCENT RELATIVE STANDARD DEVIATION (% RSD) - the STANDARD DEVIATION divided by the mean, then multiplied by 100.

pH - the negative logarithm of the hydrogen ion activity. The pH scale runs from one (most acidic) to fourteen (most alkaline); the difference of one pH unit indicates a ten fold change in hydrogen ion activity.

PLATINUM COBALT UNIT - measure of the color of a water sample defined by a potassium hexachloroplatinate and cobalt chloride standard color series.

POPULATION ESTIMATE - a statistical estimate of the numbers (or length, watershed area) of stream reaches within a specified population or subpopulation of interest.

PRECISION - a measure of the capacity of a method to provide reproducible measurements of a particular ANALYTE (often represented by variance).

PROBABILITY SAMPLE - a sample in which each unit (stream reach, in this case) has a known probability of being selected.

PROCESSING LABORATORY - laboratory in which sample processing (preservation, separation into ALIQUOTS, and analysis of selected chemical variables) was performed before shipping of water samples to the ANALYTICAL LABORATORY.

PROCESSING LABORATORY BLANK - a REAGENT GRADE WATER sample prepared at the PROCESSING LABORATORY, but analyzed at an ANALYTICAL LABORATORY.

PROCESSING LABORATORY DUPLICATE - a SPLIT SAMPLE prepared in the PROCESSING LABORATORY.

PROTOLYTE - an analyte that reacts with either H^+ or OH^- in solution.

QUALITY ASSURANCE - steps taken to ensure that a study is adequately planned and implemented to provide data of the highest quality, and that adequate information is provided to determine the quality of the data base resulting from the study.

QUALITY CONTROL - steps taken during sample collection and analysis to ensure that the data quality meets the minimum standards established by the QUALITY ASSURANCE plan.

QUALITY CONTROL CHECK SOLUTION - a sample of known concentration used to verify continued calibration of an instrument.

QUINTILE - any of the four values (Q_1, Q_2, Q_3, Q_4) that divide a population distribution into five equal classes, each representing 20% of the population; used to provide additional values to compare among populations of streams.

RAW DATA SET - the initial data set (DATA SET 1) that has received a cursory review to confirm that data are provided in proper format and are complete and legible.

REACH - segments of the stream network represented as blue lines on 1:250,000-scale USGS maps. Each REACH (segment) is defined as the length of stream between two blue-line confluences. In the NSS-I, stream reaches were the sampling unit. See HEADWATER REACH.

REAGENT BLANK - a LABORATORY BLANK SAMPLE that contained all the reagents required to prepare a sample for analysis.

REAGENT GRADE WATER - deionized water used for BLANK samples that had measured CONDUCTANCE less than 1 $\mu S\ cm^{-1}$.

REFERENCE VALUE (X_c) - a concentration of interest for a given chemical variable.

REFINED TARGET POPULATION - a subset of the TARGET POPULATION that remains after removing NONINTEREST REACHES (post-sampling field and chemical exclusions).

REGION - for this report, a major area of the conterminous United States where a substantial number of streams with ALKALINITY less than 400 μeq L^{-1} can be found.

REPRESENTATIVENESS - a measure of data quality; the degree to which sample data accurately and precisely reflect the characteristics of a population.

ROOT MEAN SQUARE ERROR - the square root of the MEAN SQUARE ERROR.

ROUTINE SAMPLE - a water sample collected using standardized protocols at a stream sample site and analyzed for all NSS-I chemical and physical variables.

SAMPLE ID - each water sample collected during a visit to NSS-I REACH is identified by a unique sample identification code, a number used to distinguish every sample from another.

SAS - Statistical Analysis System, Inc. (Cary, NC). A statistical data file manipulation and data analysis software package.

SHREVE ORDER - a map scale dependent system devised by Shreve (1966), for ranking streams according to their positions within the larger stream drainage network. The Shreve order of a stream is equal to the number of fingertip tributaries (headwaters) within the drainage area upstream from the point of reference on the stream.

SITE INCLUSION CRITERIA - see SITE RULES.

SITE RULES - the set of rules used to categorize REACHES or other features identified by grid points into various TARGET or NONTARGET categories.

SPECIAL INTEREST SITE - in this Survey, a non-randomly selected stream that is not part of the PROBABILITY SAMPLE; selection was based on quality and amount of data available or involvement in other research programs.

SPLIT SAMPLE - a subsample of a field BATCH sample that was sent to a laboratory other than an ANALYTICAL LABORATORY for analysis.

SPRING BASEFLOW INDEX PERIOD - a period of the year when streams are expected to exhibit chemical characteristics most closely linked to acidic deposition. The time period between snowmelt and leafout (March 15 to May 15 in the NSS-I) when NSS-I stream REACHES were visited coinciding with expected periods of highest geochemical and assessment interest (i.e., low seasonal pH and sensitive life stages of biota).

STAGE I SAMPLE - the set of TARGET POPULATION, BLUE LINE STREAM REACHES selected from 1:250,000 USGS topographic maps using a rectangular dot grid sampling frame (1 point per 64 mi^2) and which met the SITE INCLUSION CRITERIA.

STAGE II SAMPLE - the set of stream reaches visited in the field, selected (using a randomized systematic sampling procedure) from the STAGE I SAMPLE.

STAGE III SAMPLING - the procedures by which field observations and chemical measurements were taken on STAGE II sample reaches.

STANDARD ERROR - the square root of the variance of a statistic.

STRAHLER ORDER - a map scale dependent system devised by Strahler (1957) for ranking streams on the basis of their position within the stream drainage network. Within this ordering system, tributaries at the head of the drainage network are designated as first-order stream segments. Two first-order segments join to form a second-order stream segment; two second-order streams join to form a third-order segment, and so on.

STRATIFICATION FACTORS - factors used to define STRATA before stream selection; the factors used in the NSS-I were SUBREGION and ANC STRATUM. See STRATUM.

STRATIFIED DESIGN - a statistical design in which the population is divided into strata, and a sample selected from each STRATUM.

STRATUM - in the NSS-I, sampling strata were designated as region and expected alkalinity map class (greater than or less than 50 μeq L^{-1}).

STREAM ID - a unique nine-character identification code given to each stream sampling site (NODE). It contains four fields indicating the NSS-I subregion code, the 1:250,000-scale map ID, the grid point identification code, and the node identifier. Stream ID 3B041016L designates a lower node of the 16th grid point on the 1:250,000-scale map 041 in subregion 3B.

SUBPOPULATION - any defined subset of the TARGET POPULATION.

SUBREGIONS - areas within the NSS-I study area that are similar in water quality, PHYSIOGRAPHY, vegetation, climate, and soil; used as a STRATIFICATION FACTOR in NSS-I design.

SURFACE WATER - for this report, streams and lakes.

SYNOPTIC - relating to or displaying conditions as they exist over a broad area.

SYNTHETIC AUDIT SAMPLE - an AUDIT SAMPLE prepared by diluting solutions of known chemical composition.

SYSTEM DECISION LIMIT - a value calculated from FIELD BLANK data that indicates the minimum concentration (with 95% confidence) that can be distinguished from background levels.

SYSTEM LEVEL PRECISION - PRECISION associated with the sample collection, transport, processing, preservation, shipment, analysis, and data reporting of FIELD DUPLICATE SAMPLES.

SYSTEMATIC ERROR - a consistent error introduced in the measuring process. Such error commonly results in biased estimations.

SYSTEMATIC RANDOM SAMPLING - a sampling technique in which the units in the population are ordered and the sample selected in a systematic probabilistic manner (see Section 2.4).

TAG - code on a data point that is added at the time of collection or analysis to qualify the data.

TARGET POPULATION - a subset of the FRAME POPULATION conforming to the specified criteria established for conduct of the NSS-I (see SITE INCLUSION CRITERIA).

TOTAL ALUMINUM - in the NSS-I, the total aluminum (measured by atomic absorption spectroscopy) in an unfiltered, acidified sample.

TOTAL MONOMERIC ALUMINUM - an operationally defined aluminum fraction determined by colorimetry (PCV technique).

TRILINEAR DIAGRAM - a diagram showing three components; for this report, these diagrams were used to examine the ratios of major CATIONS and ANIONS (synonymous with ternary diagrams).

TRUE COLOR - the color of water that has been filtered or centrifuged to remove particles that may impart an apparent color; true color ranges from clear (0 PCU) to blackish-brown (> 500 PCU).

TURBIDITY - a measure of light scattering by suspended particles in an unfiltered water sample.

UPPER CONFIDENCE BOUND (95%) - a value such that one is 95% confident that the true value is below this bound.

UPPER NODE - the upstream NODE of a stream REACH.

UPSTREAM REACH NODE - see UPPER NODE.

VALIDATION - process by which data are evaluated for quality with reference to the intended data use; includes identification of OUTLIERS and evaluation of potential SYSTEMATIC ERROR.

VERIFICATION - process of ascertaining the quality of the data in accordance with the minimum standards established by the QUALITY ASSURANCE plan.

WATERSHED - the land area contributing to the flow of a stream at a given point. Topographically defined in the NSS-I as the drainage area contained within a drainage divide above a specified point on a stream.

WEATHERING - see MINERAL WEATHERING.

WEIGHT - the inverse of a sample stream's INCLUSION PROBABILITY; each sample stream represents this number of streams in the target population.

APPENDIX A
DATA QUALITY ASSESSMENT TABLES

The following eight data tables present additional QA data that was not presented in Section 4. These tables contain information on the data quality objectives, instrument detection limits, system decision limits, and accuracy estimates for each of the two analytical laboratories, along with method, system, and among-batch precision estimates for all of the NSS-I chemical variables. The last table (Table A-8) summarizes the QA results with respect to detectability, accuracy, and precision for all NSS-I chemical variables. These tables were taken from the NSS-I Quality Assurance Report (Cougan et al., 1988) and interested readers should refer to that document for additional information, explanations, and interpretation.

Table A-1. Analytical Data Quality Objectives for Detectability, Precision, and Accuracy for the NSS-I

Variable (units)	Detection limit objective (units)	Within-laboratory precision (%RSD)[a]	Within-laboratory accuracy (%)
FIELD SITE			
pH, field	--	--	±0.1[b]
Specific conductance (μS cm^{-1})	--	--	5
Dissolved oxygen (mg L^{-1})	--	--	5
PROCESSING LABORATORY			
Aluminum (mg L^{-1})			
Total monomeric (PCV)	0.01	10 (>0.01 mg L^{-1}) 20 (≤0.01 mg L^{-1})	10 (>0.01 mg L^{-1}) 20 (≤0.01 mg L^{-1})
Nonexchangeable monomeric (PCV)	0.01	10 (>0.01 mg L^{-1}) 20 (≤0.01 mg L^{-1})	10 (>0.01 mg L^{-1}) 20 (≤0.01 mg L^{-1})
Specific conductance (μS cm^{-1})	c	3	5
pH, closed system	-	0.1[b]	±0.1[b]
Dissolved inorganic carbon, closed system (mg L^{-1})	0.05	10	10
True color (PCU)	0	5[b]	--
Turbidity (NTU)	2	10	10

Table A-1. (continued)

Variable (units)	Detection limit objective (units)	Within-laboratory precision (%RSD)[a]	Within-laboratory accuracy (%)
ANALYTICAL LABORATORY			
Acid neutralizing capacity (μeq L^{-1})	d	10	10
Aluminum (mg L^{-1})			
Total extractable (MIBK)	0.005	10 (>0.01 mg L^{-1}) 20 (≤0.01 mg L^{-1})	10 (>0.01 mg L^{-1}) 20 (≤0.01 mg L^{-1})
Total	0.005	10 (>0.01 mg L^{-1}) 20 (≤0.01 mg L^{-1})	10 (>0.01 mg L^{-1}) 20 (≤0.01 mg L^{-1})
Ammonium (mg L^{-1})	0.01	5	10
Base-neutralizing capacity (μeq L^{-1})	d	10	10
Calcium (mg L^{-1})	0.01	5	10
Chloride (mg L^{-1})	0.01	5	10
Specific conductance (μS cm^{-1})	c	2	5
Dissolved inorganic carbon (mg L^{-1})			
Initial	0.05	10	10
Air equilibrated	0.05	10	10
Dissolved organic carbon (mg L^{-1})	0.1	5 (>5.0 mg L^{-1}) 10 (≤5.0 mg L^{-1})	10
Fluoride, total dissolved (mg L^{-1})	0.005	5	10
Iron (mg L^{-1})	0.01	10	10

Table A-1. (continued)

Variable (units)	Detection limit objective (units)	Within-laboratory precision (%RSD)[a]	Within-laboratory accuracy (%)
Magnesium (mg L^{-1})	0.01	5	10
Manganese (mg L^{-1})	0.01	10	10
Nitrate (mg L^{-1})	0.005	10	10
pH			
Air equilibrated	--	0.05[b]	±0.1[b]
Initial ANC	--	0.05[b]	±0.1[b]
Initial BNC	--	0.05[b]	±0.1[b]
Phosphorus, total dissolved (mg L^{-1})	0.002	10 (>0.010 mg L^{-1}) 20 (≤0.010 mg L^{-1})	10 (>0.010 mg L^{-1}) 20 (≤0.010 mg L^{-1})
Potassium (mg L^{-1})	0.01	5	10
Silica (mg L^{-1})	0.05	5	10
Sodium (mg L^{-1})	0.01	5	10
Sulfate (mg L^{-1})	0.05	5	10

[a] %RSD = percent relative standard deviation. Unless otherwise noted, this is the precision goal at concentrations greater than or equal to 10 times the required detection limit.
[b] Precision of accuracy goal in terms of applicable units.
[c] The mean of six nonconsecutive blank measurements must not exceed 0.9 μS cm^{-1}.
[d] The absolute value of each laboratory calibration blank measurement was required to be less than or equal to 10 μeq L^{-1}.

Table A-2. Estimates of Limits of Detection Based on Analyses of Laboratory Blank Samples, NSS-I

			Analytical laboratories[a]							
			Laboratory 1				Laboratory 2			
Variable	Units	Detection Limit Objective	n	Mean	SD[b]	Estimated Limit of Detection[c]	n	Mean	SD[b]	Estimated Limit of Detection[c]
Al-ext	mg L^{-1}	0.005	26	<0.001	-	<0.001	42	0.001	0.0007	0.002
Al-total	mg L^{-1}	0.005	26	0.002	0.0017	0.005	42	0.010	0.0057	0.017
Ca^{2+}	mg L^{-1}	0.01	26	<0.01	-	0.01	42	<0.01	-	0.02
Cl^-	mg L^{-1}	0.01	26	0.00[d]	0.00	0.00[d]	42	<0.01	-	0.01
Cond-AL	μS cm^{-1}X	<0.9[e]	26	0.00[d]	0.00	-[e]	42	0.6	0.20	-[e]
DIC[f]	mg L^{-1}	0.05	26	0.00[d]	0.000	0.00[d]	42	<0.01	-	0.07
DOC	mg L^{-1}	0.1	26	<0.1	-	<0.1	42	<0.1	-	0.1
F^-	mg L^{-1}	0.005	26	0.002	0.0007	0.002	42	0.000[g]	0.0000	0.010[g]
Fe	mg L^{-1}	0.01	26	<0.01	-	0.003	42	<0.01	-	<0.01
K^+	mg L^{-1}	0.01	26	<0.01	-	<0.01	42	<0.01	-	0.02
Mg^{2+}	mg L^{-1}	0.01	26	<0.01	-	<0.01	42	<0.01	-	0.01
Mn	mg L^{-1}	0.01	26	<0.01	-	<0.01	42	<0.01	-	<0.01
Na^+	mg L^{-1}	0.01	26	0.00[d]	0.000	0.00[d]	42	<0.01	-	0.01
NH_4^+	mg L^{-1}	0.01	26	<0.01	-	<0.01	42	0.00	0.001	0.003
NO_3^-	mg L^{-1}	0.005	26	0.000[d]	0.000	0.000[d]	42	<0.001	-	0.009
P	mg L^{-1}	0.002	26	<0.001	-	0.001	42	<0.01	-	0.001
SiO_2	mg L^{-1}	0.05	26	<0.01	-	<0.01	38	0.04	0.022	0.07
SO_4^{2-}	mg L^{-1}	0.05	26	<0.01	-	<0.01	42	<0.01	-	0.04

			Processing laboratory[a]			
			n	Mean	s	Estimated limit of detection[c]
Al-mono	mg L^{-1}	0.010	65	0.009	0.0047	0.012
Al-Nonexch.	mg L^{-1}	0.010	65	0.014	0.0064	0.019
Cond-PL[h]	μS cm^{-1} X	<0.9	7	5.6	1.48	--[e]
Cond-PL[i]	μS cm^{-1} X	<0.9	39	0.6	0.27	--[e]
DIC-closed	mg L^{-1}	0.05	58	0.02	0.011	0.03

a n = number of samples; SD = standard deviation.
b Dashes indicate that the standard deviation is nearly zero.
c Estimated limit of detection = 3SD.
d All measurements reported as zero by laboratory.
e Detection limit objective expressed as the mean of the blank sample measurements
f DIC detection limits apply to both equilibrated and initial measurements.
g Laboratory reported all concentrations less than 0.010 mg L^{-1} as zero. Limit of detection set at 0.010.
h Values for blanks measured in the first 28 batches.
i Values for blanks measured in the remaining 40 batches.

Table A-3. Estimates of System Decision Limits Based on Analyses of Field Blank Samples Pooled Across Laboratories, NSS-I

		Parametric				Nonparametric		
Variable	Units	n	Mean	SD[b]	System decision limit (SDL_p)[a]	n	Median	System decision limit (SDL_{np})[c]
Al-ext	mg L^{-1}	61	0.002	0.0028	0.007	61	0.001	0.007
Al-total	mg L^{-1}	61	0.011	0.0081	0.024	61	0.010	0.027
Al-mono	mg L^{-1}	61	0.010	0.0038	0.016	61	0.010	0.015
Al-Nonexch	mg L^{-1}	61	0.014	0.0061	0.024	61	0.015	0.023
ANC	μeq L^{-1}	58	1.8	4.10	8.6	58	1.5	8.7
BNC	μeq L^{-1}	63	20.8	7.99	34.0	63	19.3	34.9
Ca^{2+}	mg L^{-1}	62	0.01	0.006	0.020	62	<0.01	0.02
Cl^-	mg L^{-1}	63	0.01	0.010	0.026	63	<0.01	0.03
Cond-PL[d]	μS cm^{-1}	26	3.5	2.59	7.8	26	2.0	8.0
Cond-PL[e]	μS cm^{-1}	33	1.5	1.08	3.2	33	1.2	2.2
Cond-AL	μS cm^{-1}	63	0.6	0.49	1.4	63	0.9	1.2
DIC-air eq	mg L^{-1}	63	0.11	0.075	0.236	63	0.10	0.23
DIC-init	mg L^{-1}	63	0.13	0.085	0.276	63	0.13	0.23
DOC	mg L^{-1}	63	0.2	0.25	0.6	63	0.2	0.5
F^-	mg L^{-1}	63	NC	NC	0.010[f]	63	NC	0.010[f]
Fe	mg L^{-1}	63	<0.01	--	0.01	63	<0.01	0.02
K^+	mg L^{-1}	62	<0.01	--	0.01	62	<0.01	0.02
Mg^{2+}	mg L^{-1}	62	<0.01	--	<0.01	62	<0.01	<0.01
Mn	mg L^{-1}	63	<0.01	--	0.010	63	<0.01	0.012
Na^+	mg L^{-1}	62	<0.01	--	0.01	62	<0.01	0.012
NH_4^+	mg L^{-1}	63	<0.01	0.008	0.02	63	0.01	0.32
NO_3^-	mg L^{-1}	62	0.008	0.0112	0.026	62	0.005	0.02
P	mg L^{-1}	63	0.001	0.0029	0.006	63	<0.001	0.006
pH-ANC		58	5.73	0.155	NC	58	5.69	NC
pH-BNC		58	5.77	0.131	NC	58	5.74	NC
pH-air eq		63	5.96	0.233	NC	63	5.89	NC
SiO_2	mg L^{-1}	63	0.03	0.043	0.10	63	0.02	0.09
SO_4^{2-}	mg L^{-1}	63	0.01	0.014	0.033	63	0.01	0.05
True color	PCU	63	6	3.7	12.1	63	5	10
Turbidity	NTU	63	0.3	1.36	2.5	63	0.1	0.2

[a] SDL_p = mean + 1.65SD.
[b] Dashes indicate that the standard deviation (SD) is nearly zero.
[c] SDL_{np} = 95th percentile of distribution of field blank measurements.
[d] Measurements for first half of survey.
[e] Measurements for second half of survey.
[f] Laboratory 2 reported all measured concentrations less than 0.010 mg L^{-1} as zero. System decision limit estimated as 0.010 mg L^{-1}.
NC = Not calculated.

Table A-4. Percent Accuracy Estimates for Laboratory 1 Measurements of Synthetic Audit Samples, NSS-I

Variable	Units	Accuracy objective (%)	Theoretical value[b]	Lot 14[a] n	Lot 14[a] Mean	Lot 14[a] CI	Lot 14[a] Percent accuracy	Lot 15[a] n	Lot 15[a] Mean	Lot 15[a] CI	Lot 15[a] Percent accuracy
Al-ext	mg L^{-1}	10	0.020	4	0.027	0.0254	35[ns]	3	0.015	0.0086	-25[ns]
Al-total	mg L^{-1}	10	0.020	5	0.018	0.0063	-10[ns]	3	0.029	0.0226	-21[ns]
Ca^{2+}	mg L^{-1}	10	0.19	14	0.22	0.026	16*	4	0.20	0.047	5
Cl^-	mg L^{-1}	10	0.34	13	0.33	0.006	-3*	4	0.33	0.012	-3
Cond-AL	μS cm^{-1}	5	17.5	14	16.3	0.18	-7*	4	16.0	0.20	-9*
DOC	mg L^{-1}	10	1.0	13	1.0	0.06	0	4	1.0	0.42	0
F^-	mg L^{-1}	10	0.042	13	0.040	0.0013	-5*	4	0.039	0.0043	-7
Fe	mg L^{-1}	10	0.06	9	0.03	0.011	-50*	4	0.03	0.041	-50[ns]
K^+	mg L^{-1}	10	0.20	13	0.20	0.001	0	4	0.19	0.004	-5*
Mg^{2+}	mg L^{-1}	10	0.45	14	0.43	0.002	-4	4	0.43	0.008	-4
Mn	mg L^{-1}	10	0.10	14	0.09	0.004	-10*	4	0.09	0.007	-10*
Na^+	mg L^{-1}	10	2.75	14	2.82	0.023	2*	4	2.78	0.036	1
NH_4^+	mg L^{-1}	10	0.17	13	0.17	0.003	0	4	0.16	0.011	-6
NO_3^-	mg L^{-1}	10	0.467	13	0.477	0.0243	2	3	0.487	0.0027	4*
P	mg L^{-1}	10	0.027	13	0.021	0.0025	-22*	3	0.015	0.0087	-44*
SiO_2	mg L^{-1}	10	1.07	14	1.20	0.015	12[ns]	4	1.19	0.036	10[ns]
SO_4^{2-}	mg L^{-1}	10	2.28	14	2.21	0.029	-3	4	2.25	0.028	-1

	Accuracy objective (%)	Index[e] value(CI)	Lot 14[a] n	Lot 14[a] Mean	Lot 14[a] CI	Lot 14[a] Percent accuracy	Index[e] value(CI)	Lot 15[a] n	Lot 15[a] Mean	Lot 15[a] CI	Lot 15[a] Percent accuracy
ANC	10	101.7(3.04)	14	104.7	1.56	3	109.2(3.07)	3	104.2	1.54	-5*
BNC	10	32.0(4.58)	13	22.6	2.10	-29*	22.8(4.04)	4	18.8	2.42	-18[ns]
DIC-eq	10	1.14(0.050)	14	1.33	0.049	17*	1.26(0.050)	4	1.23	0.081	-2
DIC-init	10	1.14(0.050)	14	1.41	0.030	24*	1.26(0.050)	4	1.39	0.099	10
pH-ANC	0.1[c]	7.22(0.044)	13	7.04	0.035	-0.18*,[d]	7.29(0.044)	4	7.06	0.083	-0.23*,[d]
pH-BNC	0.1[c]	7.22(0.044)	13	7.07	0.035	-0.15*,[d]	7.29(0.044)	4	7.08	0.078	-0.21*,[d]
pH-eq	0.1[c]	7.22(0.044)	14	7.17	0.159	-0.05[d]	7.29(0.044)	4	7.31	0.166	0.02[d]

[a] n = number of measurements.
CI = one-sided 95% confidence intervals.
ns = not significantly different from the theoretical or index value at $p = 0.05$.
* = significantly different from the theoretical or index value at $p \leq 0.05$.

[b] The theoretical value is the expected value of the synthetic audit sample assuming no preparation error and no external effects.

[c] Objective expressed in pH units.

[d] Accuracy expressed as the difference between the index value and the mean analytical laboratory value.

[e] Measured mean values from the support laboratory for Lots 14 and 15.

Table A-5. Percent Accuracy Estimates for Laboratory 2 Measurements of Synthetic Audit Samples, NSS-I

				Lot 14[a]				Lot 15[a]			
Variable	Units	Accuracy objective (%)	Theoretical value[b]	n	Mean	CI	Percent accuracy	n	Mean	CI	Percent accuracy
Al-ext	mg L^{-1}	10	0.020	5	0.021	0.0024	5	23	0.015	0.0008	-25*
Al-total	mg L^{-1}	10	0.020	4	0.035	0.0103	75*	23	0.031	0.0032	55*
Ca^{2+}	mg L^{-1}	10	0.19	9	0.19	0.017	0*	29	0.18	0.004	-5*
Cl^-	mg L^{-1}	10	0.34	8	0.32	0.018	-6*	28	0.33	0.011	-3
Cond-AL	$\mu S\ cm^{-1}$	5	17.5	9	19.5	0.21	11*	28	19.6	0.07	12*
DOC	mg L^{-1}	10	1.0	9	1.3	0.20	30*	28	1.1	0.08	10*
F^-	mg L^{-1}	10	0.042	9	0.043	0.0012	2	28	0.043	0.0004	2*
Fe	mg L^{-1}	10	0.06	5	0.04	0.003	-33*	23	0.02	0.006	-67*
K^+	mg L^{-1}	10	0.20	9	0.20	0.006	0	29	0.20	0.004	0
Mg^{2+}	mg L^{-1}	10	0.45	9	0.44	0.016	-2	28	0.44	0.004	-2*
Mn	mg L^{-1}	10	0.10	9	0.11	0.002	10	29	0.10	0.001	0
Na^+	mg L^{-1}	10	2.75	8	2.76	0.062	0	29	2.70	0.038	-2*
NH_4^+	mg L^{-1}	10	0.17	9	0.19	0.010	12*	28	0.17	0.005	0
NO_3^-	mg L^{-1}	10	0.467	8	0.465	0.0140	0	28	0.473	0.0132	1
P	mg L^{-1}	10	0.027	9	0.022	0.0026	-18	28	0.023	0.0012	15*
SiO_2	mg L^{-1}	10	1.07	9	0.92	0.044	-10*	28	0.92	0.024	-14*
SO_4^{2-}	mg L^{-1}	10	2.28	9	2.15	0.157	-6	29	2.30	0.046	1

			Lot 14[a]				Lot 15[a]			
	Accuracy objective (%)	Index[c] value(CI)	n	Mean	CI	Percent accuracy	Index[c] value(CI)	n	Mean	CI	Percent accuracy
ANC	10	101.7(3.04)	9	114.4	5.73	7*	109.2(3.07)	29	119.0	2.71	10*
BNC	10	32.0(4.58)	8	49.1	2.59	53*	22.8(4.04)	29	58.9	4.74	158*
DIC-eq	10	1.14(0.050)	9	1.37	0.202	20ns	1.26(0.050)	29	1.32	0.082	5
DIC-init	10	1.14(0.050)	9	1.62	0.074	42*	1.26(0.050)	29	1.51	0.102	20*
pH-ANC	0.1[d]	7.22(0.044)	9	6.73	0.049	0.49*[e]	7.29(0.044)	29	6.69	0.048	-0.6*[e]
pH-BNC	0.1[d]	7.22(0.044)	8	6.71	0.033	0.51*[e]	7.29(0.044)	29	6.69	0.049	-0.6*[e]
pH-eq	0.1[d]	7.22(0.044)	9	7.25	0.069	0.03[e]	7.29(0.044)	29	7.23	0.056	0.06[e]

a n = number of measurements.
ns = not significantly different from the theoretical or index value at $p = 0.05$.
* = mean value significantly different from the index value at $p \leq 0.05$.

b The theoretical value is the expected value of the synthetic audit sample assuming no preparation error and no external effect.

c Measured mean values from the support laboratory for Lot 14 and Lot 15.

d Objective expressed in pH units.

e Accuracy expressed as the difference between the index value and mean analytical laboratory values.

Table A-6. Method-Level and System-Level Precision Estimates by Concentration Ranges of Variables (Laboratories Pooled), NSS-I

Variable (units) and measurement range	Method-level precision (processing and analytical laboratory duplicate pairs)				System-level precision (field routine-duplicate pairs)			
	Number of pairs	Grand mean	Pooled SD	%RSD$_p$[a]	Number of pairs	Grand mean	Pooled SD	%RSD$_p$[a]
Al-ext (MIBK) (mg L^{-1})								
<0.007	3	0.004	0.0002	5.3	29	0.003	0.0016	51.5
0.007 to 0.050	35	0.019	0.0009	4.6	25	0.016	0.0059	37.2
0.050 to 0.100	15	0.071	0.0026	3.6	4	0.072	0.0021	2.9
>0.100	15	0.269	0.0055	2.0	7	0.278	0.0166	6.0
All data	68	0.085	0.0029	3.4	65	0.042	0.0067	16.1
Al-total (mg L^{-1})								
<0.027	9	0.014	0.0018	13.1	4	0.019	0.0035	18.7
0.027 to 0.100	6	0.056	0.0034	6.1	16	0.056	0.0079	14.1
0.100 to 0.500	51	0.204	0.0042	2.0	38	0.214	0.0807	37.8
0.500 to 1.000	1	0.791	0.0304	3.8	7	0.767	0.1953	25.5
>1.000	1	1.235	0.0573	4.6	0	--	--	--
All data	68	0.189	0.0087	4.6	65	0.222	0.0905	40.7
Al-mono (PCV) (mg L^{-1})								
<0.015	33	0.010	0.0011	11.0	30	0.010	0.0022	21.4
0.015 to 0.100	24	0.026	0.0017	6.4	29	0.031	0.0038	12.4
0.100 to 0.500	7	0.273	0.0033	1.2	6	0.283	0.0049	1.7
0.500 to 1.000	2	0.534	0.0045	0.8	0	--	--	--
>1.000	1	1.908	0.0030	0.2	0	--	--	--
All data	67	0.087	0.0019	2.1	65	0.045	0.0033	7.4
Al-Nonexch. (PCV) (mg L^{-1})								
<0.023	52	0.014	0.0022	5.8	47	0.016	0.0031	19.2
0.023 to 0.100	12	0.043	0.0033	7.6	18	0.042	0.0068	16.2
0.100 to 0.500	3	0.225	0.0139	6.2	0	--	--	--
All data	67	0.029	0.0039	3.4	65	0.023	0.0045	19.2
ANC (μeq L^{-1})								
<0	2	-6.8	0.70	--	7	-42.4	2.94	--
0 to 50	4	21.9	1.05	--	9	27.9	7.83	--
>50	62	401.2	4.42	--	49	425.0	11.22	--
All data	68	366.9	4.23	--	65	319.7	10.22	--
BNC (μeq L^{-1})								
0 to 50	24	32.6	2.68	--	28	36.2	6.38	--
>50	44	93.4	6.72	--	37	111.1	12.25	--
All data	68	71.9	5.64	--	65	78.8	10.14	--

Table A-6 (Continued)

Variable (units) and measurement range	Method-level precision (processing and analytical laboratory duplicate pairs)				System-level precision (field routine-duplicate pairs)			
	Number of pairs	Grand mean	Pooled SD	$\%RSD_p$[a]	Number of pairs	Grand mean	Pooled SD	$\%RSD_p$[a]
Ca^{2+} (mg L^{-1})								
0.02 to 1.00	6	0.59	0.009	1.5	4	0.56	0.015	2.7
1.00 to 5.00	35	2.37	0.041	1.7	35	2.55	0.057	2.2
5.00 to 10.00	12	7.06	0.034	0.5	19	6.82	0.090	1.3
>10.00	15	25.59	0.529	2.1	7	28.90	1.604	5.6
All data	68	8.16	0.251	3.1	65	6.51	0.530	8.1
Cl^- (mg L^{-1})								
<0.03	2	0.00	0.000	--	0	--	--	--
0.03 to 1.00	13	0.57	0.006	1.1	8	0.69	0.018	2.6
1.00 to 2.00	13	1.49	0.022	1.5	18	1.53	0.033	2.2
2.00 to 5.00	23	3.18	0.045	1.4	24	3.05	0.043	1.4
5.00 to 10.00	11	6.73	0.077	1.1	6	7.46	0.073	1.0
>10.00	6	5.89	0.336	2.1	9	18.21	0.734	4.0
All data	68	3.96	0.108	2.7	65	4.85	0.276	5.7
Cond-PL (μS cm^{-1})								
<25.0	5	20.1	1.11	5.5	5	20.4	0.26	1.3
25.0 to 50	22	37.8	1.94	5.1	24	37.7	1.26	3.3
50.0 to 100.0	21	75.0	5.27	7.0	24	70.1	1.32	1.9
>100.0	19	244.3	16.99	7.0	12	192.0	3.12	1.6
All data	67	106.7	9.59	9.0	65	76.8	1.75	2.3
Cond-AL (μS cm^{-1})								
<25.0	14	19.9	0.12	0.6	6	20.6	0.87	4.2
25.0 to 50.0	20	35.6	0.23	0.6	24	36.9	0.27	0.7
50.0 to 100.0	17	69.2	0.29	0.4	24	69.9	0.42	0.6
>100.0	17	206.9	0.49	0.2	11	197.4	1.22	0.6
All data	68	83.6	0.31	0.4	65	74.7	0.64	0.9
DIC-closed-sys (mg L^{-1})								
<1.00	9	0.60	0.025	4.2	7	0.46	0.020	4.3
1.00 to 2.00	8	1.56	0.040	2.5	9	1.43	0.063	4.4
2.00 to 5.00	26	3.42	0.068	2.0	31	3.37	0.092	2.7
5.00 to 10.00	18	6.50	0.168	2.6	13	6.65	0.184	2.8
>10.00	7	31.79	0.236	0.7	5	24.47	0.365	1.5
All data	68	6.56	0.123	1.9	65	5.07	0.147	2.9

Table A-6 (Continued)

Variable (units) and measurement range	Method-level precision (processing and analytical laboratory duplicate pairs)				System-level precision (field routine-duplicate pairs)			
	Number of pairs	Grand mean	Pooled SD	$\%RSD_p$[a]	Number of pairs	Grand mean	Pooled SD	$\%RSD_p$[a]
DIC-air eq (mg L^{-1})								
<0.23	1	0.07	0.002	2.9	10	0.12	0.054	45.3
0.23 to 1.00	4	0.74	0.029	4.0	12	0.55	0.099	18.1
1.00 to 2.00	8	1.69	0.031	1.8	12	1.50	0.162	10.8
2.00 to 5.00	24	3.60	0.067	1.9	22	3.49	0.261	7.5
5.00 to 10.00	18	7.27	0.086	1.2	5	6.90	0.184	2.7
> 10.00	13	19.21	0.639	3.3	4	26.22	1.050	4.0
All data	68	7.11	0.286	4.0	65	3.72	0.317	8.5
DIC-initial AL (mg L^{-1})								
<0.23	0	--	--	--	3	0.17	0.014	8.2
0.23 to 1.00	1	0.24	0.007	2.9	10	0.56	0.091	16.3
1.00 to 2.00	17	1.60	0.036	2.3	15	1.50	0.211	14.0
2.00 to 5.00	18	3.42	0.111	3.2	26	3.39	0.250	7.4
5.00 to 10.00	18	7.22	0.139	1.9	6	6.17	0.050	0.8
>10.00	14	18.82	0.780	4.1	5	24.46	1.009	4.1
All data	68	7.09	0.366	5.2	65	4.24	0.339	8.0
DOC (mg L^{-1})								
<0.5	4	0.3	0.02	6.5	2	0.3	0.02	6.1
0.5 to 2.0	27	1.2	0.05	4.0	41	1.2	0.24	20.8
2.0 to 5.0	16	3.3	0.11	3.3	15	3.1	0.44	14.3
5.0 to 10.0	14	7.2	0.15	2.1	7	7.2	0.58	8.1
>10.0	7	17.2	0.15	0.9	0	--	--	--
All data	68	4.5	0.10	2.3	65	2.23	0.34	15.4
F^- (mg L^{-1})								
0.010 to 0.050	29	0.037	0.0000	0.0	51	0.033	0.0011	3.4
>0.050	39	0.121	0.0021	1.7	14	0.082	0.0029	3.5
All data	68	0.085	0.0016	1.9	65	0.044	0.0017	3.8
Fe (mg L^{-1})								
<0.02	2	0.01	0.001	7.4	14	0.01	0.003	66.0
0.02 to 0.05	3	0.02	0.001	2.7	18	0.03	0.009	34.0
0.05 to 0.10	11	0.08	0.002	3.0	10	0.08	0.029	34.3
0.10 to 0.50	36	0.19	0.004	2.2	18	0.22	0.117	53.3
0.50 to 1.00	3	0.72	0.008	1.2	3	0.64	0.163	25.6
>1.00	12	6.85	0.114	1.7	2	1.55	0.377	24.4
All data	67	1.38	0.048	3.5	65	0.16	0.098	61.4

Table A-6 (Continued)

Variable (units) and measurement range	Method-level precision (processing and analytical laboratory duplicate pairs)				System-level precision (field routine-duplicate pairs)			
	Number of pairs	Grand mean	Pooled SD	%RSD$_p$[a]	Number of pairs	Grand mean	Pooled SD	%RSD$_p$[a]
K^+ (mg L^{-1})								
<0.15	1	0.11	0.001	1.3	1	0.03	0.003	8.3
0.15 to 0.35	10	0.26	0.006	2.5	5	0.26	0.003	1.0
0.35 to 0.45	2	0.39	0.002	0.6	6	0.40	0.005	1.3
>0.45	55	1.47	0.015	1.0	53	1.45	0.063	4.3
All data	68	1.24	0.014	1.1	65	1.24	0.056	4.5
Mg^{2+} (mg L^{-1})								
<1.00	26	0.54	0.004	0.8	19	0.68	0.013	2.0
1.00 to 2.00	21	1.47	0.013	0.9	23	1.48	0.014	0.9
2.00 to 5.00	15	3.42	0.033	1.0	18	3.04	0.058	1.9
>5.00	6	18.15	0.158	0.9	5	9.39	0.242	2.6
All data	68	3.02	0.050	1.7	65	2.29	0.075	3.3
Mn (mg L^{-1})								
<0.01	2	<0.01	0.001	11.8	19	<0.01	--	56.6
0.01 to 0.05	9	0.03	0.001	2.1	19	0.02	0.015	65.0
0.05 to 0.10	12	0.08	0.003	3.5	7	0.07	0.002	2.7
>0.10	44	1.00	0.017	1.7	20	0.24	0.023	9.5
All data	67	0.68	0.014	2.0	65	0.09	0.015	16.8
Na^+ (mg L^{-1})								
<0.50	4	0.23	0.001	0.6	4	0.28	0.001	0.5
0.50 to 1.00	8	0.73	0.027	3.7	4	0.84	0.030	3.6
1.00 to 2.00	11	1.47	0.017	1.1	24	1.42	0.028	1.9
2.00 to 5.00	33	3.40	0.028	0.8	25	3.52	0.037	1.1
>5.00	12	10.27	0.174	1.7	8	9.66	0.097	1.0
All data	68	3.80	0.076	2.0	65	3.14	0.045	1.4
NH_4^+ (mg L^{-1})								
<0.02	12	0.02	0.000	0.0	33	0.01	0.006	42.0
0.02 to 0.05	20	0.03	0.001	3.2	21	0.03	0.007	23.4
0.05 to 0.10	14	0.07	0.002	3.1	7	0.07	0.014	19.7
>0.10	22	0.35	0.004	1.2	4	0.17	0.011	6.6
All data	68	0.14	0.003	1.9	65	0.03	0.008	22.8
NO_3^- (mg L^{-1})								
<3.000	55	0.722	0.0162	2.2	53	0.686	0.0422	6.2
>3.000	13	8.182	0.1212	1.5	12	14.885	0.3239	2.2
All data	68	2.148	0.0549	2.6	65	3.307	0.1443	4.4

Table A-6 (Continued)

Variable (units) and measurement range	Method-level precision (processing and analytical laboratory duplicate pairs)				System-level precision (field routine-duplicate pairs)			
	Number of pairs	Grand mean	Pooled SD	%RSD$_p$[a]	Number of pairs	Grand mean	Pooled SD	%RSD$_p$[a]
P-tot dissolved (mg L^{-1})								
<0.001	2	-0.001	0.0003	30.5	7	-0.001	0.0009	62.9
0.001 to 0.005	24	0.003	0.0003	8.6	31	0.003	0.0016	53.7
0.005 to 0.015	20	0.008	0.0004	4.6	20	0.008	0.0034	43.8
>0.015	22	0.105	0.0018	1.7	7	0.025	0.0040	16.1
All data	68	0.037	0.0010	2.8	65	0.006	0.0026	40.5
pH-closed sys								
<4.00	4	3.75	0.000	--	0	--	--	--
4.00 to 5.00	4	4.51	0.012	--	6	4.55	0.032	--
5.00 to 6.00	7	5.61	0.041	--	13	5.69	0.036	--
6.00 to 7.00	25	6.63	0.012	--	24	6.66	0.036	--
7.00 to 8.00	26	7.43	0.028	--	19	7.26	0.036	--
>8.00	2	8.26	0.010	--	3	8.45	0.026	--
All data	68	6.59	0.023	--	65	6.53	0.035	--
pH-initial ANC (pH units)								
4.00 to 5.00	1	4.98	0.014	--	6	4.49	0.022	--
5.00 to 6.00	5	5.73	0.021	--	8	5.70	0.104	--
6.00 to 7.00	34	6.69	0.053	--	27	6.63	0.073	--
7.00 to 8.00	28	7.25	0.039	--	22	7.31	0.091	--
>8.00	0	--	--	--	2	8.10	0.034	--
All data	68	6.82	0.046	--	65	6.59	0.080	--
pH-initial BNC								
4.00 to 5.00	0	--	--	--	6	4.50	0.035	--
5.00 to 6.00	6	5.61	0.034	--	8	5.69	0.092	--
6.00 to 7.00	34	6.70	0.042	--	26	6.63	0.065	--
7.00 to 8.00	28	7.25	0.040	--	23	7.31	0.086	--
>8.00	0	--	--	--	2	8.12	0.062	--
All data	68	6.83	0.041	--	65	6.60	0.075	--
pH-air eq								
<4.00	2	3.73	0.005	--	0	--	--	--
4.00 to 5.00	7	4.55	0.009	--	6	4.53	0.017	--
5.00 to 6.00	4	5.55	0.000	--	4	5.73	0.041	--
6.00 to 7.00	3	6.86	0.004	--	11	6.73	0.113	--
7.00 to 8.00	34	7.55	0.019	--	40	7.48	0.171	--
>8.00	18	8.45	0.028	--	4	8.37	0.083	--
All data	68	7.22	0.020	--	65	7.03	0.144	--

Table A-6 (Continued)

Variable (units) and measurement range	Method-level precision (processing and analytical laboratory duplicate pairs)				System-level precision (field routine-duplicate pairs)			
	Number of pairs	Grand mean	Pooled SD	$\%RSD_p$[a]	Number of pairs	Grand mean	Pooled SD	$\%RSD_p$[a]
SiO_2 (mg L^{-1})								
<0.50	1	0.44	0.007	1.6	0	--	--	--
0.50 to 1.50	1	1.03	0.035	3.4	1	0.57	0.064	11.3
1.50 to 5.50	29	3.71	0.052	1.4	25	3.31	0.071	2.2
5.50 to 10.50	19	7.73	0.141	1.8	21	7.70	0.122	1.6
>10.50	18	16.38	0.195	1.2	18	14.51	0.730	5.0
All data	68	8.10	0.129	1.6	65	7.79	0.393	5.0
SO_4^{2-} (mg L^{-1})								
<0.05	2	<0.01	0.002	66.7	0	--	--	--
0.05 to 2.50	13	1.43	0.019	1.3	18	1.49	0.054	3.6
2.50 to 5.00	18	3.60	0.048	1.3	10	3.86	0.081	2.1
5.00 to 12.50	26	7.85	0.117	1.5	24	8.38	0.128	1.5
>12.50	9	22.56	0.239	1.1	13	21.28	0.243	1.1
All data	68	7.21	0.116	1.6	65	8.36	0.140	1.7
True color (PCU)								
<30	50	13	0.9	6.5	44	13	2.6	19.6
>30	17	12	98.7	6.8	21	50	1.9	3.9
All data	67	43	4.4	10.5	65	25	2.4	9.6
Turbidity (NTU)								
<2.0	28	1.1	0.07	6.5	27	1.0	0.08	8.6
2.0 to 20.0	38	8.1	0.26	3.2	36	7.7	0.39	5.0
20.0 to 100.0	1	33.5	0.71	2.1	2	24.0	1.41	5.9
All data	67	5.6	0.22	3.9	65	5.4	0.38	7.1

[a] $\%RSD_p$ = relative pooled standard deviation, calculated as (pooled SD :-grand mean) x 100.

Table A-7. Comparison of Method-Level, System-Level, and Among-Batch Precision Estimates, NSS-I

Variable (units) and measurement range	Within-batch: Method-level[a] Number of pairs	Method-level[a] Pooled SD	System-level[b] Number of pairs	System-level[b] Pooled SD	Among-batch[c] Number of samples	Among-batch[c] SD	Sample type[d]
Al-ext (MIBK) (mg L^{-1})							
<0.007	3	0.0002	29	0.0016	38	0.0034	BL
0.007 to 0.050	35	0.0009	25	0.0059	9	0.0106	S
0.050 to 0.100	15	0.0026	4	0.0021	--	--	
>0.100	15	0.0055	7	0.0166	37	0.0329	BM
Al-total (mg L^{-1})							
<0.027	9	0.0018	4	0.0035	38	0.0399	BL
0.027 to 0.100	6	0.0034	16	0.0079	19	0.0222	S
0.100 to 0.500	51	0.0042	38	0.0807	37	0.0255	BM
0.500 to 1.000	1	0.0304	7	0.1953	--	--	
>1.000	1	0.0573	0	--	--	--	
Al-mono (PCV) (mg L^{-1})							
<0.015	33	0.0011	30	0.0022	13	0.0074	S
0.015 to 0.10	24	0.0017	29	0.0038	--	--	
0.10 to 0.50	7	0.0033	6	0.0049	24	0.0117	BM
0.50 to 1.00	2	0.0045	0	--	--	--	
>1.00	1	0.0030	0	--	--	--	
Al-Nonexch (PCV) (mg L^{-1})							
<0.023	52	0.0022	47	0.0031	13	0.0080	S
0.023 to 0.10	12	0.0033	18	0.0068	24	0.0127	BM
0.10 to 0.50	3	0.0139	0	--	--	--	
ANC (μeq L^{-1})							
<0	2	0.70	7	2.94	39	4.88	BM
0 to 50	4	1.05	9	7.83	--	--	
>50	62	4.42	49	11.22	38	11.73	BL
BNC (μeq L^{-1})							
0 to 50	24	2.68	28	6.38	38	23.55	BL
>50	44	6.72	37	12.25	39	11.34	BM
Ca^{2+} (mg L^{-1})							
0.02 to 1.00	6	0.009	4	0.015	56	0.031	S
1.00 to 5.00	35	0.041	35	0.057	39	0.077	BM
5.00 to 10.00	12	0.034	19	0.090	--	--	
>10.00	15	0.529	7	1.604	--	--	

Table A-7 (continued)

Variable (units) and measurement range	Within-batch: Method-level[a] Number of pairs	Method-level[a] Pooled SD	System-level[b] Number of pairs	System-level[b] Pooled SD	Among-batch[c] Number of samples	Among-batch[c] SD	Among-batch[c] Sample type[d]
Cl^- (mg L^{-1})							
<0.03	2	0.000	0	--	--	--	
0.03 to 1.00	13	0.006	8	0.018	39	0.051	BM
1.00 to 2.00	13	0.022	18	0.033	--	--	
2.00 to 5.00	23	0.045	24	0.043	--	--	
5.00 to 10.00	11	0.077	6	0.073	--	--	
>10.00	6	0.336	9	0.734	--	--	
Cond-PL (μS cm^{-1})							
<25.0	5	1.11	5	0.26	12	8.35	S
25.0 to 50.0	22	1.94	24	1.26	26	1.76	BM
50.0 to 100.0	21	5.27	24	1.32	--	--	
>100.0	19	16.99	12	3.12	--	--	
Cond-AL (μS cm^{-1})							
<25.0	14	0.12	6	0.87	38	1.91	BL
25.0 to 50.0	20	0.23	24	0.27	39	0.89	BM
50.0 to 100.0	17	0.29	24	0.42	--	--	
>100.0	17	0.49	11	1.22	--	--	
DIC-closed sys (mg L^{-1})							
<1.00	9	0.025	7	0.020	27	0.062	BM
1.00 to 2.00	8	0.040	9	0.063	27	0.061	BL
2.00 to 5.00	26	0.068	31	0.092	--	--	
5.00 to 10.00	18	0.168	13	0.184	--	--	
>10.00	7	0.236	5	0.365	--	--	
DIC-air eq (mg L^{-1})							
<0.23	1	0.002	10	0.054	39	0.078	BM
0.23 to 1.00	4	0.029	12	0.099	--	--	
1.00 to 2.00	8	0.031	12	0.162	38	0.203	BL
2.00 to 5.00	24	0.067	22	0.261	--	--	
5.00 to 10.00	18	0.086	5	0.184	--	--	
>10.00	13	0.639	4	1.050	--	--	
DIC-initial AL (mg L^{-1})							
<0.23	0	--	3	0.014	--	--	
0.23 to 1.00	1	0.007	10	0.091	39	0.070	BM
1.00 to 2.00	17	0.036	15	0.211	38	0.214	BL
2.00 to 5.00	18	0.111	26	0.250	--	--	
5.00 to 10.00	18	0.139	6	0.050	--	--	
>10.00	14	0.780	5	1.009	--	--	

Table A-7 (continued)

Variable (units) and measurement range	Within-batch: Method-level[a] Number of pairs	Method-level[a] Pooled SD	System-level[b] Number of pairs	System-level[b] Pooled SD	Among-batch[c] Number of samples	Among-batch[c] SD	Among-batch[c] Sample type[d]
DOC (mg L^{-1})							
<0.5	4	0.02	2	0.02	39	0.42	BL
0.5 to 2.0	27	0.05	41	0.24	56	0.27	S
2.0 to 5.0	16	0.11	15	0.44	39	0.28	BM
5.0 to 10.0	14	0.15	7	0.58	--	--	
>10.0	7	0.15	0	--	--	--	
F^- (mg L^{-1})							
0.010 to 0.050	29	0.0000	51	0.0011	39	0.0033	BL
>0.050	39	0.0021	14	0.0029	39	0.0024	BM
Fe (mg L^{-1})							
<0.02	2	0.001	14	0.003	39	0.017	BL
0.02 to 0.05	3	0.001	18	0.009	42	0.018	S
0.05 to 0.10	11	0.002	10	0.029	39	0.017	BM
0.10 to 0.50	36	0.004	18	0.117	--	--	
0.50 to 1.00	3	0.008	3	0.163	--	--	
>1.00	12	0.114	2	0.377	--	--	
K^+ (mg L^{-1})							
<0.15	1	0.001	1	0.003	--	--	
0.15 to 0.35	10	0.006	5	0.003	39	0.016	BL
0.35 to 0.45	2	0.002	6	0.005	39	0.022	BM
>0.45	55	0.015	53	0.063	--	--	
Mg^{2+} (mg L^{-1})							
<1.00	26	0.004	19	0.013	56	0.032	S
1.00 to 2.00	21	0.013	23	0.014	--	--	
2.00 to 5.00	15	0.033	18	0.058	--	--	
>5.00	6	0.158	5	0.242	--	--	
Mn (mg L^{-1})							
<0.01	2	0.001	19	--	39	0.004	BL
0.01 to 0.05	9	0.001	19	0.015	--	--	
0.05 to 0.10	12	0.003	7	0.002	39	0.020	BM
>0.10	44	0.017	20	0.023	56	0.009	S
Na^+ (mg L^{-1})							
<0.50	4	0.001	4	0.001	--	--	
0.50 to 1.00	8	0.027	4	0.030	39	0.042	BL
1.00 to 2.00	11	0.017	24	0.028	--	--	
2.00 to 5.00	33	0.028	25	0.037	56	0.099	S
>5.00	12	0.174	8	0.097	--	--	

Table A-7 (continued)

Variable (units) and measurement range	Within-batch: Method-level[a] Number of pairs	Method-level[a] Pooled SD	System-level[b] Number of pairs	System-level[b] Pooled SD	Among-batch[c] Number of samples	Among-batch[c] SD	Among-batch[c] Sample type[d]
NH_4^+ (mg L^{-1})							
<0.02	12	0.000	33	0.006	39	0.010	BL
0.02 to 0.05	20	0.001	21	0.007	--	--	
0.05 to 0.10	14	0.002	7	0.014	39	0.009	BM
>0.10	22	0.004	4	0.011	56	0.015	S
NO_3^- (mg L^{-1})							
<3.000	55	0.0162	53	0.0422	39	0.0553	BM
>3.000	13	0.1212	12	0.3239	--	--	
P-tot dissolved (mg L^{-1})							
<0.001	2	0.0003	7	0.0009	39	0.0014	BL
0.001 to 0.005	24	0.0003	31	0.0016	39	0.0022	BM
0.005 to 0.015	20	0.0004	20	0.0034	--	--	
>0.015	22	0.0018	7	0.0040	53	0.0039	S
pH-closed sys							
<4.00	4	0.000	0	--	--	--	
4.00 to 5.00	4	0.012	6	0.032	--	--	
5.00 to 6.00	7	0.041	13	0.036	27	0.059	BM
6.00 to 7.00	25	0.012	24	0.036	14	0.085	S
7.00 to 8.00	26	0.028	19	0.036	27	0.049	BL
>8.00	2	0.010	3	0.026	--	--	
pH-initial ANC							
4.00 to 5.00	1	0.014	6	0.022	--	--	
5.00 to 6.00	5	0.021	8	0.104	39	0.159	BM
6.00 to 7.00	34	0.053	27	0.073	56	0.187	S
7.00 to 8.00	28	0.039	22	0.091	38	0.100	BL
>8.00	0	--	2	0.034	--	--	
pH-initial BNC							
4.00 to 5.00	0	--	6	0.035	--	--	
5.00 to 6.00	6	0.034	8	0.092	39	0.161	BM
6.00 to 7.00	34	0.042	26	0.065	56	0.200	S
7.00 to 8.00	28	0.040	23	0.086	38	0.122	BL
>8.00	0	--	2	0.062	--	--	

Table A-7 (continued)

Variable (units) and measurement range	Within-batch: Method-level[a] Number of pairs	Method-level[a] Pooled SD	System-level[b] Number of pairs	System-level[b] Pooled SD	Among-batch[c] Number of samples	Among-batch[c] SD	Among-batch[c] Sample type[d]
pH-air eq							
<4.00	2	0.005	0	--	--	--	
4.00 to 5.00	7	0.009	6	0.017	--	--	
5.00 to 6.00	4	0.000	4	0.041	39	0.071	BM
6.00 to 7.00	3	0.004	11	0.113	--	--	
7.00 to 8.00	34	0.019	40	0.171	56	0.179	S
>8.00	18	0.028	4	0.083	--	--	
SiO_2 (mg L^{-1})							
<0.50	1	0.007	0	--	--	--	
0.50 to 1.50	1	0.035	1	0.064	56	0.143	S
1.50 to 5.50	29	0.052	25	0.071	39	0.419	BM
5.50 to 10.50	19	0.141	21	0.122	39	0.537	BL
>10.50	18	0.195	18	0.730	--	--	
SO_4^{2-} (mg L^{-1})							
<0.05	2	0.002	0	--	--	--	
0.05 to 2.50	13	0.019	18	0.054	56	0.131	S
2.50 to 5.00	18	0.048	10	0.081	--	--	
5.00 to 12.50	26	0.117	24	0.128	39	0.167	BM
>12.50	9	0.239	13	0.243	--	--	
True color (PCU)							
<30	50	0.9	44	2.6	25	4.6	BM
>30	17	8.7	21	1.9	--	--	
Turbidity (NTU)							
<2.0	28	0.07	27	0.08	--	--	
2.0 to 20.0	38	0.26	36	0.39	--	--	
20.0 to 100.0	1	0.71	2	1.41	--	--	

[a] Method-level = within-batch precision calculated from laboratory routine-duplicate sample pairs.
[b] System-level = overall within-batch precision calculated from field routine-duplicate sample pairs.
[c] Among-batch = among-batch precision (across laboratories) calculated from audit sample measurements.
[d] Audit sample types from which precision estimate was derived: S = synthetic audit sample, BL = Bagley Lake sample, and BM = Big Moose Lake sample.
SD = standard deviation.

Table A-8. Summary of Data Quality Assessment for Chemical Variables with Respect to Detectability, Accuracy, and Precision, NSS-I[a].

Variable	Detectability	Accuracy	Precision
Al-ext (MIBK)	+	+	_b
Al-total	+	_b	_c
Al-mono (PCV)	+	+	_b
Al-Nonexch (PCV)	_b	+	_b,e
ANC	+	+	+
BNC	_b	_b	_b
Ca^{2+}	+	+	+
Cl^-	+	+	_b
Cond-PL	_d	_d,e	-
Cond-AL	+	_b	+
DIC-closed sys	+	+	+
DIC-air eq	+	+	+
DIC-initial AL	+	+	+
DOC	+	_b	_b,c
F^-	+	_b	_b,c
Fe	+	+	+
K^+	+	+	+
Mg^{2+}	+	+	+
Mn	+	+	_b
Na^+	+	+	+
NH_4^+	+	+	_b,c
NO_3^-	+	+	+
P-tot dissolved	+	_e	_b,c
pH-closed sys	+	+	+
pH-initial ANC	+	+	+
pH-initial BNC	+	+	+
pH-air eq	+	+	+
SiO_2	+	_b	+
SO_4^{2-}	+	+	+
True color	NE	+	+
Turbidity	NE	NE	+

[a] + = acceptable in terms of data quality objective or primary project objectives.
- = estimate not near data quality objective.
NE = not evaluated.
[b] Possible limitations at low concentrations.
[c] Overall within-batch precision estimate is larger than among-batch precision estimate.
[d] Estimates not of acceptable quality.
[e] Possible limitations at high concentrations.

APPENDIX B
PREDICTION OF SPRING UPPER REACH NODE CHEMISTRY IN THE SOUTHERN BLUE RIDGE SUBREGION (2As) DATA SET (PILOT SURVEY)

The Pilot Survey component of the NSS-I was implemented in the Southern Blue Ridge in 1985, a year before the full NSS-I survey, in order to test the logistics and sampling design of the NSS-I before initiating the full-scale survey effort (Messer et al., 1986). The Pilot Survey was originally designed to index stream chemistry using only lower reach node measurements. In the middle of the Pilot Survey spring sampling period, it became apparent that at least two points along a reach had to be sampled to characterize its chemistry. In addition, it was obvious that the upper reach nodes represented an important subpopulation for the determination of acid deposition impacts. For these reasons, upper reach node sampling was initiated. The end result, however, was an incomplete spring data set (20 of 54 sites) for the upper reach nodes. A full set of both upper and lower reach node chemical data was collected in the summer season. For this report, it was desirable to compare population estimates and medians among the nine different NSS-I subregions using data collected in the same season (e.g., not comparing Southern Blue Ridge summer values to Piedmont spring values). Thus, predictive relationships were used to calculate chemical data for the missing 34 spring upper nodes in the Southern Blue Ridge.

The missing spring upper reach node values for 22 chemical variables were calculated using multiple regression techniques. Using data from the 20 sites with measured spring upper reach node chemistry, a multiple regression model was constructed for each chemical variable, relating the observed spring upper reach node chemistry to the observed summer (upper and lower reach nodes) and spring lower reach node chemistry. The regression model was then used to predict the missing spring upper reach node chemical values, based on the measured summer upper, summer lower, and spring upper reach node values. For each chemical variable, all possible combinations of regression models (spring lower reach nodes and summer upper and lower reach nodes) were compared. The final model for each variable included those seasons and nodes that contributed significantly to the explained variation (r^2), without causing multi-colinearity among the predictors.

One of the 20 upper reach nodes with measured spring upper chemistry was excluded from the regression as an outlier (stream 2A07803) for ANC, Ca^{2+}, Mg^{2+}, specific conductivity, DIC, and HCO_3^- because it had concentrations of these species roughly an order of magnitude higher than those present in the other 19 samples (ANC = 2,200 μeq L^{-1}, Ca^{2+} = 1,840 μeq L^{-1}, specific conductivity = 224 μS cm^{-1}), and that one point tended to dominate the regression. The regression based on the remaining 19 data points (Table B-1) was used to calculate all of the missing 34 spring upper reach node data points except for those of two streams (2A08801 and 2A07702). These two streams had high ion concentrations, so their spring upper reach node data points were calculated based on the regression equations that included the high concentration outlier that had been removed to predict the other 32 upper nodes.

The regression equations used to calculate the spring upper node chemical variables (after removing the one high ionic concentration outlier) are presented in Table B-1. In general, the summer upper reach node chemistry was the best predictor of spring upper reach node chemical conditions. The best model was usually obtained by considering summer upper and spring lower reach node chemistry. In most cases the summer lower reach node data was not added to the model because it had a high degree of colinearity with the other predictors.

Table B-1. Regression Coefficients Used to Calculate the Missing Spring Upper Reach Node Chemical Data in the Southern Blue Ridge Subregion (Pilot Survey)

	REGRESSION COEFFICIENTS				Model	
Variable	Summer Upper	Spring Lower	Summer Lower	Intercept	R^2	RMSE[&]
Al-ext (MIBK)	0.3325	---	---	0.0657	0.702	0.05
Al-org (PCV)	-1.5767	3.9489	0.5959	-1.316	0.835	0.25
ANC	0.1347	0.6002	---	7.7087	0.952	26.96
Ca^{2+}	0.1917	0.5488	---	-1.3859	0.949	20.56
Cl^-	0.6171	---	---	7.3103	0.944	13.21
Specific Cond.	0.4902	0.1705	---	3.0204	0.939	4.60
DIC-initial lab	0.1660	0.6395	---	0.0320	0.950	0.35
DOC	0.0852	0.2826	0.1878	0.1273	0.692	0.21
Fe	0.4139	---	---	0.1227	0.722	0.18
F^-	0.5682	0.2087	---	0.1706	0.986	0.13
H^+	0.1806	0.2830	0.4050	0.0477	0.468	0.07
HCO_3^-	0.1199	0.6524	---	2.5846	0.960	23.41
K^+	0.1401	0.5395	---	3.6857	0.949	2.24
Mg^{2+}	0.3266	0.3572	---	4.5925	0.971	6.59
Mn	0.1068	0.1481	---	0.0166	0.671	0.05
Na^+	0.1909	0.0322	0.3011	27.6296	0.752	28.11
NH_4	0.1835	-.2563	-.1119	1.0634	0.339	0.58
NO_3^-	0.4753	0.5153	0.1322	-3.2143	0.948	3.09
pH	0.5000[#]	0.5000[#]	---	0[#]	#	#
P-total	0.1540	---	---	0.5421	0.459	<0.01
SiO_2	0.1977	0.7458	---	9.4919	0.807	27.67
SO_4^{2-}	0.5236	0.3817	---	-5.18	0.858	12.71
Regression Equations Including Outlier Stream 2A07803[$]						
ANC	0.4208	0.5206	---	-37.34		
Ca^{2+}	0.3742	0.5758	---	-27.91		
Specific conductivity	0.7621	---	---	0.0556		
DIC-initial lab	0.3588	0.7450	---	-0.6812		
HCO_3^-	0.3032	0.7966	---	-48.63		
Mg^{2+}	0.6482	0.0816	---	0.0085		

Regression Model: Spring upper value = b_1(summer upper value) + b_2(spring lower value) + b_3(summer lower value) + intercept.

--- Indicates the best regression model did not include this predictor.

[#] Due to colinearity problems, the spring upper reach node pH was predicted as the mean of the summer upper and spring lower pH value.

[&] RMSE is the model root mean square error (square root of the mean squared residual).

[$] These equations were used only to predict spring upper reach node stream chemistry in two streams, 2A08801 and 2A07702; see text for explanation.

APPENDIX C
POPULATION ESTIMATES AND STANDARD ERRORS FOR ANC AND pH REFERENCE RANGES

Tables C-1 and C-2 present the population estimates and standard errors of the number of upstream and downstream reach nodes within specified ranges of ANC (Table C-1) and pH (Table C-2). Tables C-3 and C-4 present the population estimates and standard errors of the combined length and percentage of NSS-I target stream reaches with spring baseflow ANC (Table C-3) and pH (Table C-4) less than reference values. Standard errors were calculated as the square root of the variance associated with each population estimate. The equations and theories involved in the calculations are discussed in Section 2.4 and are described in detail by Overton (1987).

Table C-1. Population Estimates of the Number (and standard Error) of Target Stream Lower (L) and Upper (U) Reach Nodes with Spring Index ANC (μeq L^{-1}) in Reference Ranges

	ANC Range (μeq L^{-1})									
	≤ 0		>0 - 50		>50 - 200		> 200		TOTALS	
SUBREGION	L	U	L	U	L	U	L	U	L	U
Poc./Cats.	*	209	157	528	802	831	2276	1676	3235	3244
(1D)	(-)	(102)	(85)	(215)	(239)	(217)	(331)	(311)	(347)	(347)
N. Appal.	326	499	1669	2421	3244	2764	3249	2979	8488	8663
(2Cn)	(206)	(250)	(612)	(712)	(685)	(614)	(631)	(616)	(814)	(807)
Val. & Ridge	*	636	47	808	4190	3554	9755	8040	13,992	13,038
(2Bn)	(-)	(445)	(47)	(462)	(1033)	(969)	(1283)	(1260)	(1213)	(1249)
MA Coast. Pl.	772	1334	1433	2069	2420	2890	6662	4991	11,287	11,284
(3B)	(362)	(524)	(565)	(652)	(711)	(767)	(1041)	(961)	(1078)	(1078)
S. Blue Ridge	*	*	95	127	1494	1576	441	328	2031	2031
(2As)	(-)	(-)	(44)	(47)	(328)	(328)	(130)	(120)	(326)	(326)
Piedmont	*	*	632	632	2369	3001	4514	3882	7515	7515
(3A)	(-)	(-)	(308)	(308)	(546)	(593)	(672)	(653)	(650)	(650)
S. Appal.	*	121	364	364	1027	971	3666	3480	5057	4936
(2X)	(-)	(121)	(206)	(206)	(346)	(323)	(531)	(538)	(526)	(529)
Oz./Ouach.	*	*	*	150	2700	2700	1416	1354	4116	4204
(2D)	(-)	(-)	(-)	(105)	(376)	(376)	(375)	(373)	(410)	(406)
Florida	225	678	670	531	368	131	292	387	1555	1727
(3C)	(107)	(344)	(240)	(233)	(185)	(63)	(92)	(189)	(306)	(437)

*No samples were observed within this range.

Table C-2. Population Estimates of the Number (and Standard Error) of Target Stream Lower (L) and Upper (U) Reach Nodes with Spring Index pH in Reference Ranges

	pH Range									
	≤ 5.0		5.0 - ≤5.5		5.5 - 6.0		> 6.0		TOTALS	
SUBREGION	L	U	L	U	L	U	L	U	L	U
Poc./Cats.	*	157	10	67	85	193	3140	2827	3235	3244
(1D)	(-)	(85)	(9)	(60)	(62)	(145)	(349)	(342)	(347)	(347)
N. Appal.	291	499	203	634	681	853	7313	6,677	8488	8663
(2Cn)	(203)	(250)	(150)	(385)	(402)	(425)	(814)	(792)	(814)	(807)
Val. & Ridge	*	318	*	443	47	683	13,945	11,594	13,992	13,038
(2Bn)	(-)	(317)	(-)	(339)	(47)	(448)	(1214)	(1289)	(1213)	(1249)
MA Coast. Pl.	772	1334	716	1320	955	2907	8844	5723	11,287	11,284
(3B)	(362)	(524)	(408)	(531)	(468)	(767)	(1090)	(1000)	(1078)	(1078)
S. Blue Ridge	*	*	*	*	*	*	2031	2031	2031	2031
(2As)	(-)	(-)	(-)	(-)	(-)	(-)	(326)	(326)	(326)	(326)
Piedmont	*	*	*	*	316	790	7199	6725	7515	7515
(3A)	(-)	(-)	(-)	(-)	(221)	(342)	(661)	(674)	(650)	(650)
S. Appal.	*	*	*	121	121	243	4936	4572	5057	4936
(2X)	(-)	(-)	(-)	(121)	(121)	(170)	(529)	(537)	(526)	(529)
Oz./Ouach.	*	*	*	225	75	225	4041	3754	4116	4204
(2D)	(-)	(-)	(-)	(127)	(75)	(127)	(414)	(429)	(410)	(406)
Florida	225	539	146	324	591	379	593	485	1555	1727
(3C)	(107)	(340)	(71)	(103)	(236)	(224)	(197)	(195)	(306)	(437)

*No samples were observed within this range.

Table C-3. Population Estimates of the Combined Length (km) and Percentage of NSS-I Target Stream Reaches with Spring Baseflow ANC Less than Reference Values (Standard Errors in Parentheses).#

Subregion	ANC ≤ 0 Length	ANC ≤ 0 %	ANC ≤ 50 Length	ANC ≤ 50 %	ANC ≤ 200 Length	ANC ≤ 200 %	Total Length (km)
Poconos/Catskills	543	3.6	1,606	10.6	5,489	36.2	15,144
	(270)	(1.8)	(500)	(3.3)	(1,100)	(7.3)	(1,912)
N. Appalachians	1,524	7.0	3,713	17.1	12,935	59.5	21,738
	(750)	(3.5)	(920)	(4.2)	(2,200)	(10)	(2,746)
Valley & Ridge	257	0.8	2,111	6.5	12,811	39.2	32,687
	(210)	(0.6)	(990)	(3.0)	(3,400)	(10)	(4,492)
MA Coastal Plain	2,527	6.3	9,636	23.9	21,091	52.3	40,296
	(1,200)	(2.9)	(2,700)	(6.6)	(4,400)	(11)	(5,799)
S. Blue Ridge	*	*	706	7.8	7,084	78.4	9,036
	-	-	(250)	(2.8)	(940)	(10)	(960)
Piedmont	*	*	2,390	7.1	13,554	40.4	33,531
	-	-	(1,300)	(3.9)	(2,900)	(8.5)	(4,402)
S. Appalachians	117	(0.5)	763	3.5	6,130	28.0	21,892
	(120)	(0.5)	(440)	(2.0)	(1,700)	(8.0)	(2,807)
Ozarks/Ouachitas	*	*	205	0.9	15,092	67.1	22,480
	-	-	(150)	(0.6)	(2,500)	(11)	(2,507)
Florida	461	12.0	2,356	61.2	2,939	76.4	3,848
	(160)	(4.1)	(530)	(14)	(590)	(15)	(678)
SUBTOTALS							
Interior MA	2,324	3.3	7,431	10.7	31,235	44.9	69,569
	(1,000)	(1.4)	(1,700)	(2.4)	(4,300)	(6.2)	(5,601)
Interior SE	117	0.1	4,064	4.7	41,860	48.1	86,939
	(120)	(0.1)	(1,300)	(1.5)	(4,300)	(4.9)	(5,871)
Mid-Atlantic (MA)	4,851	4.4	17,067	15.5	52,327	47.6	109,865
	(1,600)	(1.4)	(3,100)	(2.8)	(6,200)	(5.6)	(8,063)
Southeast (SE)	578	0.6	6,420	7.1	44,799	49.3	90,787
	(210)	(0.2)	(1,500)	(1.7)	(4,400)	(4.8)	(5,910)
Total NSS-I	5,429	2.7	23,487	11.7	97,125	48.4	200,652
	(1,500)	(0.8)	(3,400)	(1.7)	(7,700)	(3.8)	(9,996)

Calculated using linear interpolation between upper and lower reach nodes. Standard errors were approximated by an ad hoc procedure using the variances of separate length estimates based on the upstream and downstream nodes.

* No samples observed below this reference value; estimated percentage is less than 1%.

NOTE: To calculate upper and lower one-sided 95% confidence bounds, multiply the standard error by 1.645 and add or subtract that value from the length estimate. To calculate the two-sided 95% confidence bounds, multiply the standard error by 1.96.

Table C-4. Population Estimates of the Combined Length (km) and Percentage of NSS-I Target Stream Reaches with Spring Baseflow pH Less than Reference Values (Standard Errors in Parentheses).#

Subregion	pH ≤ 5.0 Length	pH ≤ 5.0 %	pH ≤ 5.5 Length	pH ≤ 5.5 %	pH ≤ 6.0 Length	pH ≤ 6.0 %	Total Length (km)
Poconos/Catskills	550	3.6	906	6.0	1,354	8.9	15,144
	(290)	(1.9)	(420)	(2.8)	(520)	(3.4)	(1,912)
N. Appalachians	1,424	6.6	1,870	8.6	3,044	14.0	21,738
	(700)	(3.2)	(710)	(3.2)	(900)	(4.2)	(2,746)
Valley & Ridge	257	0.79	1,937	5.9	4,116	12.6	32,687
	(260)	(0.8)	(1,300)	(4.0)	(1,900)	(5.9)	(4,492)
MA Coastal Plain	3,147	7.8	9,565	23.7	18,707	46.4	40,296
	(1,300)	(3.3)	(3,000)	(7.5)	(4,300)	(11)	(5,799)
S. Blue Ridge	*	*	*	*	*	*	9,036
	-	-	-	-	-	-	(960)
Piedmont	*	*	*	*	2,390	7.1	33,531
	-	-	-	-	(1,200)	(3.7)	(4,402)
S. Appalachians	*	*	313	1.4	920	4.2	21,892
	-	-	(310)	(1.4)	(540)	(2.5)	(2,807)
Ozarks/Ouachitas	*	*	410	1.8	2,437	10.8	22,480
	-	-	(290)	(1.3)	(990)	(4.4)	(2,507)
Florida	522	13.6	1,708	44.4	2,828	73.5	3,848
	(250)	(6.5)	(440)	(12)	(620)	(16)	(678)
SUBTOTALS							
Interior MA	2,231	3.2	4,712	6.8	8,514	12.2	69,569
	(780)	(1.1)	(1,700)	(2.4)	(2,300)	(3.4)	(5,601)
Interior SE	*	*	723	0.83	5,747	6.6	86,939
	-	-	(430)	(0.5)	(1,700)	(1.9)	(5,871)
Mid-Atlantic (MA)	5,378	4.9	14,277	13.0	27,221	24.8	109,865
	(1,500)	(1.4)	(3,400)	(3.1)	(4,800)	(4.4)	(8,063)
Southeast (SE)	522	0.57	2,431	2.7	8,576	9.5	90,787
	(250)	(0.3)	(800)	(0.9)	(1,900)	(2.1)	(5,910)
Total NSS-I	5,900	2.9	16,708	8.3	35,797	17.8	200,652
	(1,600)	(0.8)	(3,400)	(1.7)	(5,200)	(2.6)	(9,996)

Calculated using linear interpolation of $[H^+]$ between upper and lower reach nodes. Standard errors were approximated by an ad hoc procedure using the variances of separate length estimates based on the upstream and downstream nodes.

* No samples observed below this reference value; estimated percentage is less than 1%.

NOTE: To calculate upper and lower one-sided 95% confidence bounds, multiply the standard error by 1.645 and add or subtract that value from the length estimate. To calculate the two-sided 95% confidence bounds, multiply the standard error by 1.96.

APPENDIX D

STANDARD ERRORS OF THE GEOGRAPHIC AND CHEMICAL CLASSIFICATION POPULATION ESTIMATES

The following eight tables (D-1 through D-8) present the standard errors associated with the population estimates of the number of stream reaches present in the different NSS-I geographic site classes within chemical classes. Standard errors were calculated as the square root of the variance associated with each population estimate. The equation and theory involved in the variance calculation are discussed in subsection 2.4.4 and are described in detail by Overton (1987).

Table D-1. Population Estimates of the Number of Target Reach Lower Nodes ± Standard Error in Each Geographic Site Class Present in Inorganic Classified Streams

Geographic Site Class	$\hat{N}$	INORGANIC ANC ≤ 0	ANC > 0-50	ANC > 50-200
Allegheny Plateau				
High Plateau	218 ± 150	36 ± 35	25 ± 17	158 ±145
Forested Plateau	4178 ± 823	291 ± 203	1320 ± 541	760 ± 399
Forested Agric. Plateau	3547 ± 635	-----	-----	833 ± 368
NE Mid-Atlantic				
Pocono/Catskill Mts.	351 ± 164	----	2 ± 2	229 ± 144
Glaciated Agric. Plateau	866 ± 208	----	----	119 ± 83
Glaciated Forested Plateau	209 ± 102	----	80 ± 61	119 ± 83
Valley and Ridge Province				
Ridges	4359 ± 1035	----	427 ± 314	1012 ± 544
Valleys	11809 ± 1397	----	----	2370 ± 778
Arkansas/Oklahoma				
Boston Mts.	873 ± 267	----	----	723 ± 252
Ouachita Mts.	1126 ± 257	----	----	375 ± 162
Arkansas R. Valley	1365 ± 395	----	----	773 ± 258
Piedmont Province				
Piedmont	9258 ± 1173	----	----	1108 ± 467
Piedmont Lowlands	2297 ± 793	----	----	----
S. Appalachian Highlands				
Blue Ridge Mts.	2962 ± 496	----	67 ± 34	2053 ± 430
Cumberland Plateau	1307 ± 394	----	243 ± 170	821 ± 331
French Broad R. Valley	64 ± 37	----	----	----
Coastal Plain				
Eastern Mid-Atlantic	2036 ± 651	----	239 ± 238	239 ± 238
Western Mid-Atlantic	6133 ± 1030	----	478 ± 335	478 ± 335
New Jersey Pine Barrens	432 ± 249	239 ± 238	----	32 ± 32
Eastern Gulf	1580 ± 465	----	158 ± 157	474 ± 269
Western Gulf	753 ± 245	----	----	453 ± 207
Florida				
Panhandle Upland	689 ± 145	----	32 ± 32	32 ± 32
Peninsula Upland	442 ± 269	----	----	----
Panhandle Swamp	264 ± 113	----	----	32 ± 32
Peninsula Swamp	163 ± 70	----	----	----
NSS-I TOTALS	57,277 ± 2118	565 ± 315	3070 ± 778	13194 ± 1412

$\hat{N}$ represents the estimated number of reaches ± standard error within each geographic site class.

Table D-2. Population Estimates of the Number of Target Reach Lower Nodes ± Standard Error in Each Geographic Site Class Present in Organic-Influenced Classified Streams

Geographic Site Class	$\hat{N}$	ORGANIC INFLUENCED ANC ≤ 0	ANC > 0-50	ANC > 50-200
Allegheny Plateau				
High Plateau	218 ± 150	----	----	----
Forested Plateau	4178 ± 823	----	----	----
Forested Agric. Plateau	3547 ± 635	----	----	----
NE Mid-Atlantic				
Pocono/Catskill Mts.	351 ± 164	----	----	----
Glaciated Agric. Plateau	866 ± 208	----	----	----
Glaciated Forested Plateau	209 ± 102	----	----	----
Valley and Ridge Province				
Ridges	4359 ± 1035	----	----	----
Valleys	11809 ± 1397	----	----	16 ± 15
Arkansas/Oklahoma				
Boston Mts.	873 ± 267	----	----	----
Ouachita Mts.	1126 ± 257	----	----	150 ± 105
Arkansas R. Valley	1365 ± 395	----	----	----
Piedmont Province				
Piedmont	9258 ± 1173	----	----	397 ± 286
Piedmont Lowlands	2297 ± 793	7 ± 7	----	----
S. Appalachian Highlands				
Blue Ridge Mts.	2962 ± 496	----	28 ± 28	----
Cumberland Plateau	1307 ± 394	----	121 ± 121	----
French Broad R. Valley	64 ± 37	----	----	----
Coastal Plain				
Eastern Mid-Atlantic	2036 ± 651	----	----	239 ± 238
Western Mid-Atlantic	6133 ± 1030	----	239 ± 238	239 ± 238
New Jersey Pine Barrens	432 ± 249	161 ± 69	----	----
Eastern Gulf	1580 ± 465	----	474 ± 269	158 ± 157
Western Gulf	753 ± 245	----	----	75 ± 75
Florida				
Panhandle Upland	689 ± 145	----	227 ± 90	32 ± 32
Peninsula Upland	442 ± 269	----	----	----
Panhandle Swamp	264 ± 113	----	----	----
Peninsula Swamp	163 ± 70	----	----	----
NSS-I TOTALS	57,277 ± 2118	168 ± 69	1089 ± 391	1305 ± 482

$\hat{N}$ represents the estimated number of reaches ± standard error within each geographic site class.

Table D-3. Population Estimates of the Number of Target Stream Reach Lower Nodes ± Standard Error in Each Geographic Site Class Present in Organic-Dominated Classified Streams

Geographic Site Class	$\hat{N}$	ORGANIC DOMINATED ANC ≤ 0	ANC > 0-50	ANC > 50-200
Allegheny Plateau				
High Plateau	218 ± 150	----	----	----
Forested Plateau	4178 ± 823	----	----	----
Forested Agric. Plateau	3547 ± 635	----	----	----
NE Mid-Atlantic				
Pocono/Catskill Mts.	351 ± 164	----	----	----
Glaciated Agric. Plateau	866 ± 208	----	----	----
Glaciated Forested Plateau	209 ± 102	----	----	----
Valley and Ridge Province				
Ridges	4359 ± 1035	----	----	----
Valleys	11809 ± 1397	----	----	----
Arkansas/Oklahoma				
Boston Mts.	873 ± 267	----	----	----
Ouachita Mts.	1126 ± 257	----	----	----
Arkansas R. Valley	1365 ± 395	----	----	----
Piedmont Province				
Piedmont	9258 ± 1173	----	----	----
Piedmont Lowlands	2297 ± 793	----	----	----
S. Appalachian Highlands				
Blue Ridge Mts.	2962 ± 496	----	----	----
Cumberland Plateau	1307 ± 394	----	----	----
French Broad R. Valley	64 ± 37	----	----	----
Coastal Plain				
Eastern Mid-Atlantic	2036 ± 651	----	----	----
Western Mid-Atlantic	6133 ± 1030	239 ± 238	478 ± 335	478 ± 335
New Jersey Pine Barrens	432 ± 249	----	----	----
Eastern Gulf	1580 ± 465	----	----	158 ± 157
Western Gulf	753 ± 245	----	----	75 ± 75
Florida				
Panhandle Upland	689 ± 145	----	203 ± 93	32 ± 32
Peninsula Upland	442 ± 269	----	208 ± 207	170 ± 170
Panhandle Swamp	264 ± 113	129 ± 94	----	35 ± 35
Peninsula Swamp	163 ± 70	96 ± 54	----	35 ± 34
NSS-I TOTALS	57,277 ± 2118	464 ± 261	889 ± 404	983 ± 417

$\hat{N}$ represents the estimated number of reaches ± standard error within each geographic site class.

Table D-4. Population Estimates of the Number of Target Stream Reach Lower Nodes ± Standard Error in Each Geographic Site Class Present in Watershed Source of Sulfate and ANC > 200 Classified Streams

Geographic Site Class	$\hat{N}$	Substantial watershed sources of sulfate	ANC > 200
Allegheny Plateau			
High Plateau	218 ± 150	----	----
Forested Plateau	4178 ± 823	767 ± 403	1040 ± 445
Forested Agric. Plateau	3547 ± 635	600 ± 284	2114 ± 511
NE Mid-Atlantic			
Pocono/Catskill Mts.	351 ± 164	----	119 ± 83
Glaciated Agric. Plateau	866 ± 208	----	746 ± 197
Glaciated Forested Plateau	209 ± 102	----	10 ± 9
Valley and Ridge Province			
Ridges	4359 ± 1035	636 ± 445	2284 ± 774
Valleys	11809 ± 1397	318 ± 317	9106 ± 1268
Arkansas/Oklahoma			
Boston Mts.	873 ± 267	----	150 ± 105
Ouachita Mts.	1126 ± 257	75 ± 75	525 ± 188
Arkansas R. Valley	1365 ± 395	----	591 ± 321
Piedmont Province			
Piedmont	9258 ± 1173	----	7754 ± 1106
Piedmont Lowlands	2297 ± 793	----	2290 ± 793
S. Appalachian Highlands			
Blue Ridge Mts.	2962 ± 496	----	814 ± 274
Cumberland Plateau	1307 ± 394	121 ± 121	----
French Broad R. Valley	64 ± 37	----	64 ± 37
Coastal Plain			
Eastern Mid-Atlantic	2036 ± 651	365 ± 268	955 ± 468
Western Mid-Atlantic	6133 ± 1030	239 ± 238	3267 ± 841
New Jersey Pine Barrens	432 ± 249	----	----
Eastern Gulf	1580 ± 465	158 ± 157	----
Western Gulf	753 ± 245	----	150 ± 105
Florida			
Panhandle Upland	689 ± 145	----	129 ± 62
Peninsula Upland	442 ± 269	----	64 ± 44
Panhandle Swamp	264 ± 113	----	67 ± 47
Peninsula Swamp	163 ± 70	----	32 ± 32
NSS-I TOTALS	57,277 ± 2118	3277 ± 834	32,272 ± 2034

$\hat{N}$ represents the estimated number of reaches ± standard error within each geographic site class.

Table D-5. Population Estimates of the Number of Target Reach Upper Nodes ± Standard Error in Each Geographic Site Class Present in Inorganic Classified Streams

Geographic Site Class	$\hat{N}$	INORGANIC ANC ≤ 0	ANC > 0-50	ANC > 50-200
Allegheny Plateau				
High Plateau	221 ± 150	63 ± 38	----	158 ± 145
Forested Plateau	4327 ± 826	436 ± 247	1464 ± 606	589 ± 284
Forested Agric. Plateau	3448 ± 624	----	291 ± 203	955 ± 383
NE Mid-Atlantic				
Pocono/Catskill Mts.	351 ± 164	----	140 ± 130	209 ± 103
Glaciated Agric. Plateau	818 ± 203	----	----	60 ± 59
Glaciated Forested Plateau	266 ± 117	77 ± 60	60 ± 59	60 ± 59
Valley and Ridge Province				
Ridges	7190 ± 1217	695 ± 449	1044 ± 484	2119 ± 731
Valleys	8342 ± 1249	----	60 ± 59	1970 ± 707
Arkansas/Oklahoma				
Boston Mts.	873 ± 267	----	----	648 ± 244
Ouachita Mts.	1126 ± 257	----	75 ± 75	525 ± 188
Arkansas R. Valley	1452 ± 400	----	----	773 ± 258
Piedmont Province				
Piedmont	8940 ± 1134	----	----	1739 ± 546
Piedmont Lowlands	2290 ± 793	239 ± 238	----	----
S. Appalachian Highlands				
Blue Ridge Mts.	2962 ± 496	----	231 ± 129	2134 ± 430
Cumberland Plateau	1307 ± 394	----	121 ± 121	364 ± 206
French Broad R. Valley	64 ± 37	----	----	----
Coastal Plain				
Eastern Mid-Atlantic	2036 ± 651	----	239 ± 238	716 ± 408
Western Mid-Atlantic	6133 ± 1030	----	478 ± 335	239 ± 238
New Jersey Pine Barrens	436 ± 249	239 ± 238	32 ± 32	----
Eastern Gulf	1580 ± 465	----	474 ± 269	790 ± 342
Western Gulf	753 ± 245	----	75 ± 75	302 ± 183
Florida				
Panhandle Upland	623 ± 141	64 ± 44	32 ± 32	----
Peninsula Upland	492 ± 273	----	----	----
Panhandle Swamp	117 ± 67	----	----	----
Peninsula Swamp	495 ± 337	----	----	----
NSS-I TOTALS	56,642 ± 2158	1812 ± 618	4815 ± 959	14, 353 ± 1448

$\hat{N}$ represents the estimated number of reaches ± standard error within each geographic site class.

Table D-6. Population Estimates of the Number of Target Reach Upper Nodes ± Standard Error in Each Geographic Site Class Present in Organic-Influenced Classified Streams

Geographic Site Class	$\hat{N}$	ORGANIC INFLUENCED ANC ≤ 0	ANC > 0-50	ANC > 50-200
Allegheny Plateau				
High Plateau	221 ± 150	----	----	----
Forested Plateau	4327 ± 826	----	29 ± 29	----
Forested Agric. Plateau	3448 ± 624	----	168 ± 168	----
NE Mid-Atlantic				
Pocono/Catskill Mts.	351 ± 164	2 ± 2	----	----
Glaciated Agric. Plateau	818 ± 203	----	----	----
Glaciated Forested Plateau	266 ± 117	69 ± 60	----	----
Valley and Ridge Province				
Ridges	7190 ± 1217	----	----	60 ± 59
Valleys	8342 ± 1249	----	----	----
Arkansas/Oklahoma				
Boston Mts.	873 ± 267	----	----	75 ± 75
Ouachita Mts.	1126 ± 257	----	----	150 ± 105
Arkansas R. Valley	1452 ± 400	----	----	----
Piedmont Province				
Piedmont	8940 ± 1134	----	----	397 ± 286
Piedmont Lowlands	2290 ± 793	----	----	----
S. Appalachian Highlands				
Blue Ridge Mts.	2962 ± 496	----	17 ± 17	----
Cumberland Plateau	1307 ± 394	121 ± 121	----	279 ± 199
French Broad R. Valley	64 ± 37	----	----	----
Coastal Plain				
Eastern Mid-Atlantic	2036 ± 651	----	----	----
Western Mid-Atlantic	6133 ± 1030	----	716 ± 408	478 ± 335
New Jersey Pine Barrens	436 ± 249	107 ± 67	----	----
Eastern Gulf	1580 ± 465	----	158 ± 157	158 ± 157
Western Gulf	753 ± 245	----	----	75 ± 75
Florida				
Panhandle Upland	623 ± 141	75 ± 52	71 ± 49	32 ± 32
Peninsula Upland	492 ± 273	----	----	----
Panhandle Swamp	117 ± 67	----	----	----
Peninsula Swamp	495 ± 337	----	----	----
NSS-I TOTALS	56,642 ± 2158	375 ± 159	1160 ± 472	1704 ± 528

$\hat{N}$ represents the estimated number of reaches ± standard error within each geographic site class.

Table D-7. Population Estimates of the Number of Target Reach Upper Nodes ± Standard Error in Each Geographic Site Class Present in Organic-Dominated Classified Streams

Geographic Site Class	$\hat{N}$	ORGANIC DOMINATED ANC ≤ 0	ANC > 0-50	ANC > 50-200
Allegheny Plateau				
High Plateau	221 ± 150	----	----	----
Forested Plateau	4327 ± 826	----	----	----
Forested Agric. Plateau	3448 ± 624	----	----	----
NE Mid-Atlantic				
Pocono/Catskill Mts.	351 ± 164	----	----	----
Glaciated Agric. Plateau	818 ± 203	----	----	----
Glaciated Forested Plateau	266 ± 117	----	----	----
Valley and Ridge Province				
Ridges	7190 ± 1217	----	15 ± 15	----
Valleys	8342 ± 1249	----	----	----
Arkansas/Oklahoma				
Boston Mts.	873 ± 267	----	----	----
Ouachita Mts.	1126 ± 257	----	----	----
Arkansas R. Valley	1452 ± 400	----	----	----
Piedmont Province				
Piedmont	8940 ± 1134	----	----	----
Piedmont Lowlands	2290 ± 793	----	----	----
S. Appalachian Highlands				
Blue Ridge Mts.	2962 ± 496	----	----	----
Cumberland Plateau	1307 ± 394	----	----	----
French Broad R. Valley	64 ± 37	----	----	----
Coastal Plain				
Eastern Mid-Atlantic	2036 ± 651	----	----	239 ± 238
Western Mid-Atlantic	6133 ± 1030	716 ± 408	239 ± 238	478 ± 335
New Jersey Pine Barrens	436 ± 249	----	----	----
Eastern Gulf	1580 ± 465	----	----	----
Western Gulf	753 ± 245	----	----	----
Florida				
Panhandle Upland	623 ± 141	----	221 ± 100	64 ± 44
Peninsula Upland	492 ± 273	----	208 ± 207	----
Panhandle Swamp	117 ± 67	78 ± 55	----	----
Peninsula Swamp	495 ± 337	460 ± 336	----	35 ± 34
NSS-I TOTALS	56,642 ± 2158	1255 ± 531	683 ± 330	815 ± 411

$\hat{N}$ represents the estimated number of reaches ± standard error within each geographic site class.

Table D-8. Population Estimates of the Number of Target Stream Reach Upper Nodes ± Standard Error in Each Geographic Site Class Present in Watershed Source of Sulfate and ANC > 200 Classified Streams

Geographic Site Class	$\hat{N}$	Substantial watershed sources of sulfate	ANC > 200
Allegheny Plateau			
High Plateau	221 ± 150	----	----
Forested Plateau	4327 ± 826	769 ± 403	1040 ± 445
Forested Agric. Plateau	3448 ± 624	167 ± 146	1867 ± 483
NE Mid-Atlantic			
Pocono/Catskill Mts.	351 ± 164	----	----
Glaciated Agric. Plateau	818 ± 203	----	758 ± 197
Glaciated Forested Plateau	266 ± 117	----	----
Valley and Ridge Province			
Ridges	7190 ± 1217	443 ± 339	2813 ± 820
Valleys	8342 ± 1249	123 ± 123	6189 ± 1109
Arkansas/Oklahoma			
Boston Mts.	873 ± 267	----	150 ± 105
Ouachita Mts.	1126 ± 257	75 ± 75	300 ± 146
Arkansas R. Valley	1452 ± 400	75 ± 75	604 ± 324
Piedmont Province			
Piedmont	8940 ± 1134	----	6804 ± 1051
Piedmont Lowlands	2290 ± 793	---	2051 ± 759
S. Appalachian Highlands			
Blue Ridge Mts.	2962 ± 496	----	579 ± 243
Cumberland Plateau	1307 ± 394	----	421 ± 243
French Broad R. Valley	64 ± 37	----	64 ± 37
Coastal Plain			
Eastern Mid-Atlantic	2036 ± 651	365 ± 268	478 ± 335
Western Mid-Atlantic	6133 ± 1030	478 ± 335	2312 ± 737
New Jersey Pine Barrens	436 ± 249	58 ± 30	----
Eastern Gulf	1580 ± 465	----	----
Western Gulf	753 ± 245	----	300 ± 146
Florida			
Panhandle Upland	623 ± 141	----	64 ± 44
Peninsula Upland	492 ± 273	----	284 ± 181
Panhandle Swamp	117 ± 67	----	39 ± 39
Peninsula Swamp	495 ± 337	----	----
NSS-I TOTALS	56,642 ± 2158	2551 ± 709	27,118 ± 1972

$\hat{N}$ represents the estimated number of reaches ± standard error within each geographic site class.

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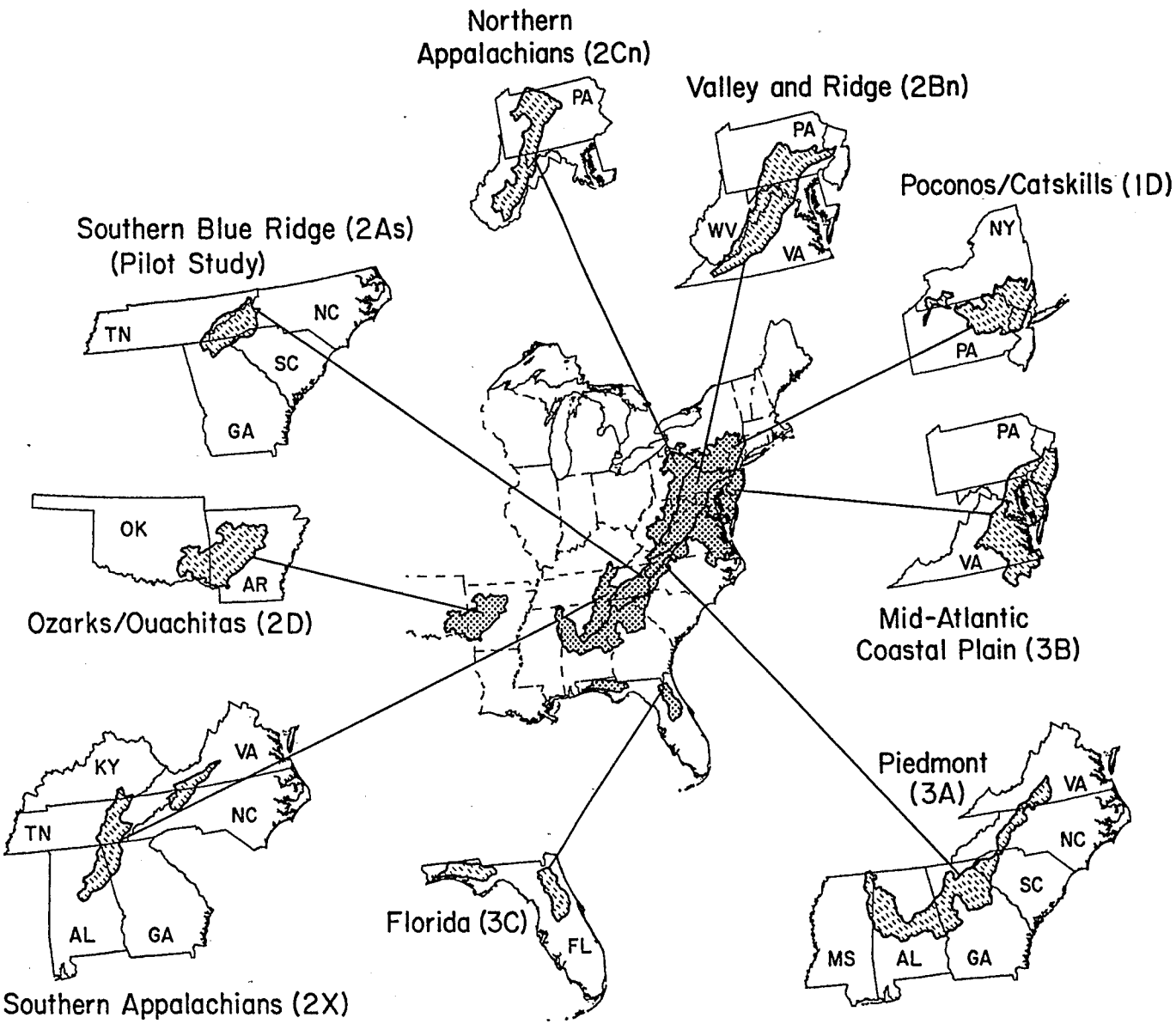

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