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# National Surface Water Survey: National Stream Survey Phase I--Pilot Survey

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# National Surface Water Survey:

## National Stream Survey Phase I—Pilot Survey

Aquatic Effects Research Program

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December 1986

# National Surface Water Survey:

## National Stream Survey
## Phase I–Pilot Survey

A contribution to the
National Acid Precipitation Assessment Program

By:

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# Notice

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# Abstract

A pilot survey of streams in the Southern Blue Ridge Province was conducted by the U.S. Environmental Protection Agency during the spring and summer of 1985 as a means of testing a proposed methodology for (1) determining the present extent and location of acidic and low acid neutralizing capacity (ANC) streams in the United States and (2) classifying sampled streams that are representative of important classes of streams and, therefore, should be selected for intensive study or long-term monitoring. Data from the National Stream Survey Phase I-Pilot Survey are presented in the context of evaluating a statistical sampling design, logistics plan, quality assurance plan, and data management program. Results indicate that the design is capable of producing robust population estimates for important chemical variables using a single synoptic sampling of streams, and that it has the potential of producing a relatively simple geochemical classification of streams. The study showed that, with 95% confidence, less than 3.2% of the combined length of streams in the target population exhibited average spring non-episodic pH values below 6.4 (the lowest value for which a confidence level could be used). The best estimate of the percentage of stream length with ANC less than or equal to 200 $\mu$eq $L^{-1}$ was 74.4%.

# Executive Summary

## Introduction and Objectives

The National Stream Survey (NSS) Phase I-Pilot Survey was conducted in the spring and summer of 1985 as part of the U.S. Environmental Protection Agency's National Surface Water Survey (NSWS). The NSWS is an important contribution to the National Acid Precipitation Assessment Program, which is charged by the U.S. Congress with providing sound technical information regarding the effects of acid deposition on the environment. The three primary objectives of Phase I of the NSWS are:

- To determine the percentage, extent, and location of low pH lakes and streams in potentially susceptible regions of the United States.
- To determine the percentage, extent, and location of lakes and streams in such regions that have low acid neutralizing capacity (ANC).
- To determine which lakes and streams are representative of important classes of water bodies in each region, and thus should be selected for additional study or long-term monitoring.

The NSS Phase I-Pilot Survey was designed to provide an otherwise unavailable data base with which to answer certain questions relating to the proper design and implementation of a full Phase I effort in 1986. The Phase I–Pilot Survey objectives were:

- To test the ability of a proposed sampling design to meet the Phase I objectives.
- To evaluate the proposed Phase I logistics plan, together with alternative sample collection, preparation, and analytical techniques.
- To develop and test a data analysis plan for Phase I results.

The results of the study, conducted in the mountains of the Southern Blue Ridge Province, were deemed to be adequate for meeting both sets of objectives for the region.

## Sampling and Logistical Design

To accomplish the survey objectives, a probability sample of 54 stream reaches was drawn from a target population represented by the blue line streams on 1:250,000-scale topographic maps, draining catchments of less than 60 square miles and satisfying certain site inclusion criteria. The resulting statistical sample can be used to make quantitative population estimates with known confidence limits for any characteristic associated with the reaches. The characteristics measured during the survey include a suite of geographic, physical, and chemical variables appropriate to the NSWS objectives. All variables were measured using extensively reviewed techniques and protocols, and were subjected to a high degree of quality control and assurance, from sample collection to the final disposition in the data base.

In addition to the 54-stream probability sample, seven "special interest" reaches also were included in the field sampling. The data from these streams were not used to generate population estimates, but they allow the estimates to be compared to historical stream data collected in the region.

Prior to field sampling, site reconnaissance activities were carried out for each stream in conjunction with local district soil conservationists to identify and resolve any physical or legal access problems. Water samples were collected on three occasions at approximately biweekly intervals during the spring (17 March-30 April) and on one occasion in the summer (30 May-17 July), at the downstream node of each reach. Samples also were collected at the upstream node at 17 sites during the last spring sampling interval, and at all 54 probability sample reaches on the summer sampling data. Site access was by foot, four-wheel drive vehicle, boat, or horseback, with samples returned to a mobile laboratory for processing within 12 hours of collection. In all, 724 field and audit samples were analyzed during the survey.

## Survey Results

### *Techniques and Protocols*

A number of field evaluations of instruments and protocols were carried out to test the logistics plan and field sampling protocols for the 1986 field activities. This experience proved extremely helpful in selecting and/or modifying the field measurement techniques, all of which were found to be acceptable for use in the 1986 field work. Among the most important findings in this regard was that the important chemical constituents in a wide variety of field samples were found to be stable when held at 4°C for at least 24 hours following collection, and that the plastic syringes used to hold dissolved inorganic carbon and pH samples during transport to the field laboratories were impervious to carbon dioxide when maintained at 4°C. These findings were deemed sufficient to recommend locating the "mobile" processing laboratories at a central location for Phase I field work, thus allowing many more sites across a wider geographic range to be sampled. A simple field pH measurement technique also was found to produce results equivalent to those of more complex techniques involving closed-headspace measurements and research-grade apparatus.

### *Population Estimates*

Univariate population distributions are described in terms of an index value, which is the mean value of the chemical variable for the three spring measurements (excluding samples collected during rainfall episodes) made at the downstream node of each reach. Distribution estimates for pH and ANC were found to be similar, whether expressed on the basis of numbers, length, or surface area of the stream target population. Two additional measurement variables involving discharge and mass export coefficients appear possible, but are presently incomplete. The inclusion of samples collected during episodes tended to depress ANC and pH values below their relatively stable index values by 24% and 0.19 units, respectively.

When episodes were excluded, population estimates based on any of the three spring sampling intervals were essentially identical. The summer sample clearly produced higher population estimates for ANC, however. Samples collected at the upstream nodes exhibited markedly lower concentrations for pH, ANC, sulfate, and nitrate than did the corresponding samples at the downstream nodes on both spring and summer sampling dates.

A "worst case" estimate based on spring index chemistry and expressed in terms of length of reaches indicates that, at the 95% confidence level, fewer than 3.2% of the target population exhibited pH values below 6.4. Indeed, no pH measurement made during the survey using the most consistent and reliable technique exhibited a value below 6.0, including measurements made during episodes and at upstream nodes. This does not mean that low pH conditions do not occur in the study area in very small headwater reaches, during rain-driven episodes, or during other seasons or other years. However, it suggests that chronic acidification of medium-sized streams in the study region during a season commonly associated with the shortest hydrologic residence times in the watersheds is not common. Despite the fact that the pH values observed during the survey are well above the levels usually associated with fish mortality, some estimate of transient chemical changes that may occur during hydrologic episodes is needed before a critical evaluation of chemical habitat quality can be complete.

Despite the generally circumneutral pH values, the population estimates for ANC indicate that a majority of target streams were characterized as possessing relatively low acid neutralizing capacity. Again, based on index chemistry and expressed on a length basis, 6.3% of the combined reach length was estimated to exhibit ANC values of 50 $\mu$eq $L^{-1}$ or less, while 74.4% was estimated to be less than 200 $\mu$eq $L^{-1}$. Although these values have been cited in the literature as "extremely" and "moderately" sensitive waters, respectively, the susceptibility of streams in the region cannot be fully evaluated without additional consideration of soil chemistry, which may act to delay the surface water response to acid deposition, according to some theories.

### *Classification*

With respect to the potential for classification, analysis of the survey data provided several lines of subjective and objective evidence indicating that a reasonable geochemical classification is possible. Geographic analysis indicates that reaches within broad ANC classes tend to cluster spatially. The highest ANC sites were located along the western border of the study region, while intermediate ANC sites were located in the Broad and French Broad River valleys that contain the main population centers of the region. The lowest ANC sites occurred in the north and central highlands, including Great Smoky Mountains National Park. ANC appears to be highly correlated with weathering of one of the dominant minerals in the area (K-feldspar), which suggests an underlying geochemical control of ANC in the region. Finally, agglomerative cluster analysis, an objective multivariate statistical technique, when applied to a full chemical data set, produced classes very similar to those based on ANC alone. This analysis also indicated that the special interest sites included in the survey were typical of the low end of the ANC spectrum in the area, but none was found to be an outlier.

## Conclusions and Recommendations

The Phase I-Pilot Survey demonstrated that a regional scale synoptic survey of streams will produce population estimates, with known confidence bounds, for important chemical variables such as pH and ANC. The population estimates appear to be robust, and are not particularly sensitive to small changes in chemistry that occur over weekly time scales during the spring. Intra-site temporal variability does not preclude chemical classification of target streams in the Southern Blue Ridge, if effects of episodes are removed.

The Phase I-Pilot Survey was also useful in increasing the probability of success and decreasing the cost of a full Phase I survey. It was determined that the proposed design could be modified slightly to meet the needs and increase the efficiency of the 1986 Phase I effort. Major recommendations included:

- Make minor alterations in the inclusion criteria and the statistical sampling method to better address the assessment objectives of the survey and to increase the sampling efficiency.

- Reduce sampling to two visits in the spring prior to leafout, to satisfy the classification objective, or to one visit to satisfy the objective of population estimation.

- Sample the reaches at both their upstream and downstream nodes on each visit to characterize intra-reach spatial variability.

- Increase sample holding time protocols to 24 hours to allow central placement of the mobile analytical laboratories, and thereby greatly increase the logistical efficiency of the survey.

- Adopt certain field measurement techniques that provide accurate and reliable data.

- Alter certain quality control/quality assurance and data management techniques to increase efficiency and decrease lags in data availability, to the extent that data quality can be maintained.

- Further develop new data analysis techniques that aid in data interpretation in an assessment context.

These recommended changes were incorporated into the draft planning documents for the NSS Mid-Atlantic Phase I and Southeast Screening Surveys, which were peer reviewed in January, 1986. We believe that the NSS Phase I design can provide important incremental information in the assessment process, and will serve as an important stepping stone to the regionalization of site-specific results gathered during both past and future studies.

# Project Contributors

The NSS Phase I-Pilot Survey and this report are the result of the cooperative efforts of many individuals and organizations. The project was administered by Rick Linthurst (U.S. EPA) with Jay J. Messer (Utah State University) as Technical Director. W. Scott Overton (Oregon State University) designed the statistical sampling plan and provided guidance on the data analysis. James Omernik, research geographer at U.S. EPA-CERL, co-authored the alkalinity maps which served as a basis for delineating the study area. Jack Tuschall (Northrop Services, Inc.) helped to draft the project plan and served as liaison with the local cooperators before the field sampling. Charles W. Ariss (Utah State University) served as technical liaison during the field effort and later provided data analysis support, as did Barry Gall (Western Washington University). Finally, the participants at the peer review workshop held in Washington, DC, in December 1984 gave valuable suggestions for improving the study design.

Under the direction of James Omernik, Andrew Kinney (Northrop Services, Inc.) oversaw the detailed map work, assisted by geographers Anastasia B. Allen, Douglas B. Brown, and Suzanne Pierson (all of Northrop).

Field operations commenced under the direction of Project Officer Robert E. Crowe (U.S. EPA-EMSL-LV) and Project Manager, Steve L. Pierett (Lockheed EMSCO, Inc.). John R. Baker (Lockheed) supervised all field operations and logistics; as base coordinator/science supervisor, he was responsible for the field implementation of the survey. Ken Asbury (Lockheed) served as technical supervisor.

On-site field coordinators Frank A. Morris, Randy G. Cameron, Al W. Groeger, C. Mel Knapp, Ky B. Ostergaard, Cindy L. Mayer, Cindy A. Hagley, and Barry Baldigo, all of Lockheed EMSCO, Inc., supervised the dedicated efforts of the large crews who accomplished the field sampling.

David V. Peck served as training coordinator and Gerald J. Filbin as laboratory supervisor for the Las Vegas laboratories (both of Lockheed). Lab analysts were Linda A. Drewes, C. Hunter Holen, and J. M. Henshaw (all of Lockheed). Kevin J. Cabble (Lockheed) provided technical support to the laboratory operations.

Robert A. Schonbrod, U.S. EPA-EMSL-LV, served as project officer for quality assurance/quality control and analytical methods development. Sevda Drousé (Lockheed) managed QA operations and reporting. Bryant C. Hess and Carol MacLeod, QA scientists, and Martin Stapanian, statistician, along with programmers David T. Hoff, In Seung Lau, Rick K. Maul, and Joseph Scanlan, all of Lockheed, supported the QA operations.

Dan C. J. Hillman (Lockheed) served as technical supervisor for analytical methods. Technical writer for the QA/QC and Methods Group was Jan Engles (Lockheed).

Michael J. Sale (Martin Marietta Energy Systems, Oak Ridge National Laboratory) coordinated the NSS Phase I-Pilot Survey data base management and oversaw the many exacting data transfers among the reporting

laboratories. Jan M. Coe (Martin Marietta, ORNL) managed the data base; Henriette I. Jager (Science Applications International Corp.) and Mary Alice Faulkner (Martin Marietta, ORNL) developed statistical program applications.

The synthesis of all of the above efforts at U.S. EPA-CERL to produce this report was directed by Jay J. Messer, with the assistance of Keith N. Eshleman (Northrop Services, Inc.). Chapters 1 (Introduction) and 6 (Conclusions) were co-written by Messer and Eshleman. Philip R. Kaufmann (Utah State University) contributed to Chapter 2 (Study Design) and Chapter 5 (Population Estimates and Classification). Sharmon M. Stambaugh (Northrop) contributed to Chapter 3 (Field Operations) and provided technical editing/production assistance.

Chapter 2 (Study Design) contributors included W. Scott Overton, Jay J. Messer, James Omernik, and Andrew Kinney. The contributors to Chapter 3 (Field Operations) were John Baker and David M. Peck.

The quality assurance and data base management report (Chapter 4) was written by Sveda Drousé, Michael J. Sale, and Charles W. Ariss.

Chapter 5 addresses the two major objectives of the NSS Phase I-Pilot Survey. Messer, Eshleman, and Kaufmann co-wrote this chapter with statistical graphics provided by ORNL. Barry Gall (Western Washington University) performed the cluster analyses on the ANC data for the classification section.

Additional project administration at U.S. EPA headquarters was provided by William Fallon (Battelle NW Laboratories). Barbara Emmel (Radian Corporation) served as technical writer throughout the project. Nancy Lanpheare (Northrop) ably typed the draft of this report.

The NSS Phase I-Pilot Survey also acknowledges the illustrative experiences and advice from the Aquatic Effects Research Team, in particular, the National Lake Survey project team.

The NSS thanks the principal reviewers of this report, distinguished by their expertise in appropriate disciplines and knowledge of streams in the study region. They were: Donald Porcella (EPRI), Gary Larson (Oregon State University), Jerry Elwood (Oak Ridge National Laboratories-Environmental Sciences Division), and Ken Reckhow (Duke University). In addition, this report was reviewed by state air and water quality staffs in North Carolina, Tennessee, South Carolina, and Georgia and by U.S. EPA Region IV staff.

The authors gratefully acknowledge all who contributed to the NSS Phase I-Pilot Survey but who may not have been named in this section. The success of the project reflects these participants' contributions of ideas, efficiency, enthusiasm, and hard work.

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## Ancillary Reports

In addition to this data report, supplemental information on the National Stream Survey Phase I-Pilot Survey can be found in the series of ancillary manuals and reports. Many of the technical manuals used in working draft form at the time the Phase I-Pilot Survey was conducted. These publications include:

Field Operations Report, National Surface Water Survey, National Stream Survey, Pilot Survey. 1986. Knapp, C. H., C. L. Mayer, D. V. Peck, J. R. Baker, and G. J. Filbin. Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada 89109 (draft).

Quality Assurance Plan for the National Surface Water Survey. Stream Survey (Middle Atlantic Phase I, Southeast Screening and Middle Atlantic Episodes Pilot). 1986. Drousé, S. K., D. C. Hillman, L. W. Creelman, and S. J. Simon. Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada 89114 (draft).

Evaluation of Quality Assurance and Quality Control Sample Data for the National Stream Survey (Phase I-Pilot Survey). 1986. Drousé, S. K. Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada 89109 (draft).

Analytical Methods Manual for the National Surface Water Survey. Stream Survey (Middle Atlantic Phase I, Southeast Screening, and Middle Atlantic Episodes Pilot). 1986. Hillman, D. C., S. H. Pia, and S. J. Simon. Lockheed Engineering Management Services Company, Inc., Las Vegas, Nevada 89114 (draft).

Data Management and Analysis Procedures for the National Stream Survey. 1987. Sale, M. J. (editor). ORNL/TM. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831 (draft).

Draft Research Plan, National Surface Water Survey: National Stream Survey, Mid-Atlantic Phase I and Southeast Screening. 1985. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC 20460.

Draft Sampling Plan for Streams in the National Surface Water Survey. 1985. Technical Report 114 (July 1986). Overton, W. S. Department of Statistics, Oregon State University, Corvallis, Oregon 97331.

A Sampling and Analysis Plan for Streams in the National Surface Water Survey. 1987. Technical Report 117. Overton, W. S. Department of Statistics, Oregon State University, Corvallis, Oregon 97331.

# 1. Introduction

## 1.1 Overview

The relationship between acid deposition and the acidification of surface waters has become one of the most critical environmental issues of the 1980s. Studies on a variety of individual water bodies and regional populations of lakes and streams have produced data that suggest that surface waters in some areas of Europe and North America have experienced declines in pH and/or acid neutralizing capacity over the past half century (Beamish and Harvey, 1972; Beamish et al., 1975; Oden, 1976; Wright and Gjessing, 1976; Watt et al., 1979; Pfeiffer and Festa, 1980; Haines and Akielaszek, 1983; Smith and Alexander, 1983). Acidic atmospheric deposition arising from the combustion of fossil fuels has been the most commonly attributed cause for such declines (Drablos and Tollan, 1980; National Research Council, 1981, 1983, 1984; Office of Science and Technology Policy, 1984; Office of Technology Assessment, 1984; U.S. EPA, 1984a; Jeffries et al., 1985). Alternative hypotheses and discrepancies in the atmospheric acidification scenario also have been discussed and debated in the recent literature (e.g., Havas et al., 1984; Howells, 1984; Cogbill et al., 1984; Lefohn and Brocksen, 1984; Krug et al., 1985; Pierson and Chang, 1986).

The latter arguments notwithstanding, previous studies have left two critical gaps in our ability to assess the quantitative risk associated with the effects of acid deposition on surface water resources in the United States:

1. It is impossible to combine the results of previously conducted independent regional surveys and historical data from monitoring networks or site-specific research projects in order to produce a quantitative estimate with known confidence bounds of the present extent of low pH waters, or of waters whose chemistry is indicative of potential susceptibility to acid deposition inputs. The problems stem primarily from an inadequate statistical sampling plan, inconsistencies in field or laboratory methods, insufficient chemical measurements to adequately characterize water quality, or inadequate quality assurance data by which to evaluate potential bias between or among data collected during the different studies.
2. It is virtually impossible to quantitatively extrapolate the results from intensive, process-oriented (cause and effect) research in a few watersheds to the larger lake or stream population comprising the resource at risk in a given geographic region. This inability stems from the lack of statistically defensible population estimates noted above, together with the absence of a companion lake or stream classification strategy based on the regional distribution of water body characteristics. It is seldom quantitatively known whether research sites are broadly typical of the majority of other systems in the region, representative of a relatively small (but perhaps potentially important) subpopulation, or relatively unique. Given the common research requirements that a study site be relatively pristine, the possibility that the site is pristine because it is otherwise relatively unique is not unlikely.

The National Surface Water Survey was designed to overcome these obstacles to assessment by sampling water quality in lakes and streams on a regional basis using a statistically rigorous survey design, appropriate field and analytical techniques, a sufficient set of measurement variables, and an adequate quality assurance and control program to maximize the confidence of the resulting data. The initial survey component (Phase I) would provide a snapshot of the present condition of surface water in the regions most likely to exhibit effects from acid deposition. The Phase I data would also serve as a basis for classification of the lakes and streams, so that results from past and subsequent intensive studies on subpopulations of interest or at individual study sites would be extrapolated with known confidence to the regional populations.

The purpose of this report is to describe the results of the Phase I-Pilot Survey, a component of the National Stream Survey conducted in the Southern Blue Ridge Province of the southeastern U.S. conducted in 1985. The objectives of the Phase I-Pilot Survey were to test the logistics plan and statistical sampling design proposed for a full Phase I effort in 1986. We will demonstrate the adequacy of a modification to the original design by examining the types of project outputs that could be expected, based on the Phase I-Pilot Survey results. At this level of analysis, no attempt has been made to interpret the data with respect to the likelihood of past or future changes from acid deposition in the region. Such analyses are presently the target of considerable research effort, however, and will be the subject of future project outputs.

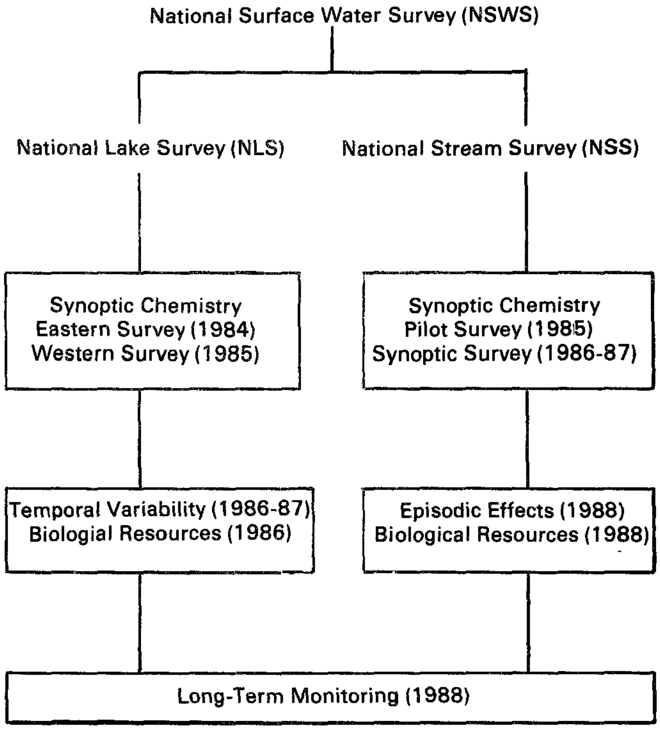
## 1.2 The National Surface Water Survey

In response to the need for knowledge regarding the present extent of the acidic or potentially susceptible aquatic resource and its associated biota, the U.S. Environmental Protection Agency and cooperating scientists were asked in 1983 to design a program to 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/or biological resources.

The resulting 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 ("acid rain") on human, terrestrial, aquatic, and material resources.

**Figure 1-1. Organization of the National Surface Water Survey, showing two major components (lake and stream surveys), each consisting of three phases.**



In order to satisfy its five major research goals, the NSWS was designed in two parallel components, the National Lake Survey (NLS) and the National Stream Survey (NSS) (Figure 1-1). Both components consist of phases, each of which depends on the preceding phases to satisfy its objectives (Table 1-1). This 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 U.S., 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 phase designed to characterize and quantify the chemistry of lakes and streams throughout the U.S., focusing on the areas expected to contain the majority of low-alkalinity waters.

Phase I data cannot be used to prove that a causal link exists between observed aquatic effects and acid deposition. Although the major concern over the aquatic effects of acid deposition is its impact on biological resources, it is more efficient to first characterize surface waters in terms of the physicochemical factors that are expected to impact biota, rather than to begin the process with a biotic survey of all surface waters in a region, regardless of water quality. The present study design, based on the Phase I chemical classification, can be used not only to quantify the present status of the aquatic resource, but also to allow correlative relationships to be examined among 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.

The second phase of the NSWS will quantify the biota and short-term (seasonal, weekly, or episodic) variability in water chemistry within and among

**Table 1-1. Objectives of the National Surface Water Survey**

| Phase I Synoptic Chemical Survey | Biological Resources/Temporal Variability | Long-Term Monitoring |
|---|---|---|
| 1. Quantitatively estimate the percentages (number/length/ area) and location of acidic streams in regions of the U.S. potentially susceptible to acid deposition. | 1. Determine how many representative lakes and streams are fishless. | 1. Determine what chemical and biological changes are occurring over time in representative lakes and streams. |
| 2. Quantitatively estimate the percentages (number/length/ area) and locations of lakes/ streams with low acid neutralizing capacity in regions of the U.S. potentially sensitive to acid deposition. | 2. Assess the temporal variability in chemistry in representative lakes and streams. | 2. Measure the rate at which changes are occurring. |
| 3. Determine which lakes/streams are representative of important aquatic resources in the region and should be selected for further study in later phases. | 3. Determine the lake and stream chemical characteristics associated with fish presence/ absence. | |
| | 4. Determine which chemically and biologically representative systems should be selected for long-term monitoring. | |

representative lakes and streams in each geographic region. The definition of representativeness will be based on Phase I water chemistry, hydrology, biotic composition, regional acid deposition inputs, land use, physiographic features, and other characteristics. Some regionally representative sites will later become the foundation for a long-term monitoring program to detect and quantify any future changes in the chemistry and biology of potentially susceptible aquatic ecosystems in the region. Many lakes and streams that have been the focus of intensive and/or long-term studies in the past are included in the Survey as "special interest" sites. Such sites that are found to be representative of large numbers of other aquatic systems in their respective regions could serve as the nucleus of a long-term monitoring effort.

Phase I of the Eastern Lake Survey has been completed. A total of 1798 lakes in the eastern U.S. were sampled in the fall of 1984, and 752 lakes were sampled in selected areas of the western U.S. in the fall of 1985. Phase II field work was begun to determine seasonal chemical variability in northeastern lakes in the spring of 1986. The status of the National Stream Survey is discussed below.

## 1.3 National Stream Survey

### *1.3.1 Phase I Planning*

Planning for Phase I of the National Stream Survey (NSS) began in mid-1984 and resulted in a Draft Research Plan (U.S. EPA, 1984b). Phase I of the NSS 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 *description* and *classification* of the streams in the target population. More specifically, the primary objectives of Phase I of the NSS are to determine:

1. The percentage, extent (e.g., number, length, and drainage area), and location of streams in the United States that are *presently acidic.*
2. The percentage, extent, and location of streams that have low acid-neutralizing capacity, and thus might *become acidic* in the future.
3. Which streams are *representative* of important classes of streams in each region and should be selected for more intensive studies or long-term monitoring.

The NSS was specifically designed to achieve these objectives within known confidence limits. It was also designed to allow the objectives to be met for any chemical variable measured. For example, the percentage of the population of stream reaches within a given region that have sulfate, nitrate, aluminum, and/or calcium concentrations above or below any criterion value of interest could also be determined. Should sensitivity to acidification be acceptably defined in the future, based on one or several of the variables being measured, the Survey design will also permit post-stratification to determine the number and areal extent of streams that fall into such sensitivity categories.

The sampling design also lends itself to many comparative evaluations. For example, other questions that could be answered by the design include:

1. Are acidic streams found primarily at high elevation?
2. Are acidic streams found in small watersheds?
3. Are acidic streams found within areas with the highest acid deposition rates?
4. Are sulfate and base cation concentrations in different regions of the U.S. correlated with regional deposition chemistry or with the nature of watershed soils or geology?
5. Can existing alkalinity maps be refined?
6. What associations exist among water chemistry, land use, vegetation type, and geographic data?

The principal restriction on these secondary objectives was that they must not result in a design that compromises the Phase I primary objectives. In many cases, such secondary objectives might best be met in later phases of the project.

### *1.3.2 Phase I—Pilot Survey*

The initial research plan for Phase I underwent peer review at a workshop in Washington, D.C., in December, 1984. The workshop participants recommended that a full Phase I survey should be preceded by a pilot study whose findings might increase the efficiency and quality of future field efforts. Planning was begun immediately for such a pilot study with the following objectives:

1. test the ability of the proposed sampling design to meet the Phase I objectives, based on analysis of data collected during the Pilot Survey;
2. evaluate the Phase I logistics plan (including safety issues and questions of legal and physical site access) and alternative sample collection, preparation, and analytical techniques; and
3. develop and test a data analysis plan for Phase I using actual data collected in the Pilot Survey.

Field work for the Phase I-Pilot Survey began in the Southern Blue Ridge Province (Figure 2-1) in March, 1985, and was completed in June of the same year.

## 1.4 Phase I—Pilot Survey Report

This report summarizes the design and results of the Phase I-Pilot Survey. A description of the Phase I-Pilot Survey design is presented in Chapter 2. The Survey employed the random placement of a systematic sampling grid over 1:250,000-scale topographic maps of the Southern Blue Ridge Province to obtain a sample of stream reaches within a pre-selected approximate size range and which met certain other site inclusion criteria. By this method, a sample of 115 reaches was selected for the estimation of stream length, drainage area, and other geographical characteristics. A random systematic subsample of 54 reaches was selected from the initial 115, to be visited by field crews to make on-site physical and chemical measurements and to collect water samples for laboratory chemical analysis. The Pilot Survey utilized an "index" sample to describe the chemical characteristics of each of the 54 reaches. The average, non-event, spring stream chemistry is analogous to the index samples taken from the deepest part of lakes during fall overturn in the Eastern Lake Survey (Linthurst et al., 1986).

Chapter 3 describes the field and laboratory methods used to collect data, as well as results of field and laboratory experiments and evaluations. Such information served as the basis for changes in protocols of sample handling and analysis used in subsequent Phase I Survey activities.

Chapter 4 presents, in detail, the quality assurance and data base management programs employed in the Survey. A variety of quality assurance and quality control samples were employed to evaluate the performance of the field sampling and analytical activities, and to ensure that field and laboratory activities were being conducted according to established guidelines. Chapter 4 also summarizes the QA results of the Pilot Survey. The data base management tasks described in the section include protocols for data flows and the statistical techniques used to ensure data quality.

Chapter 5 evaluates the ability of the Phase I-Pilot Survey design to meet the NSS Phase I objectives and includes:

1. population distribution estimates for water quality index variables, along with their associated upper confidence bounds, including an evaluation of the number and timing of field data collections which led to the construction of such estimates;
2. examples of potential classification approaches for Phase I streams that could be used in future phases of the study, and an evaluation of the impact of sample timing and frequency on such classifications; and
3. promising directions for further analysis of synoptic data.

Chapter 6 summarizes the conclusions from the study and presents recommendations for the design and implementation of the Phase I Survey.

It is important to recognize that the results from the Phase I-Pilot Survey are strictly applicable only to a defined target population of small to medium-sized streams in the Southern Blue Ridge Province during the spring and summer of 1985. The chemical characteristics of this target population were described using chemical index samples, excluding those collected during major rainfall events. No data were collected on very small intermittent or headwater streams, and no attempt was made to determine the lowest pH during storm-related episodes which may be a critical factor affecting survival of sensitive life stages or particular species of fish. Further interpretation from an assessment standpoint is being addressed in both present and planned projects within the NAPAP Aquatic Effects Research Program, and will be the subject of future reports. Many of these projects will require additional data collection (e.g., to determine low pH conditions during storm-related episodes).

With respect to future design decisions, it was recognized that differences in weather patterns, hydrology, and watershed biogeochemistry may alter many of the relationships observed in streams in the Southern Blue Ridge. Therefore, the Southern Blue Ridge results cannot be extrapolated quantitatively to streams in other parts of the country. Consequently, conclusions regarding design recommendations are generally not based on rigorous statistical tests, but on finding consistent, reasonable patterns in the data that allow important differences of potential assessment significance to be discerned. Ultimately, completion of the Phase I field work will allow full appraisal of the success of the final design.

## 1.5 Project Organization

The National Stream Survey is administered by the U.S. Environmental Protection Agency, Office of Acid Deposition, Environmental Monitoring, and Quality Assurance in Washington, D.C. The Environmental Research Laboratory—Corvallis (ERL-C) is responsible for coordinating the activities of the Survey and for project design, data validation, and data interpretation. The Environmental Monitoring Systems Laboratory—Las Vegas (EMSL-LV) is responsible for quality assurance/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 provided statistical programming to implement the target population characterization, as well as mapping and other geographic analyses for the survey

# 2. Study Design

## 2.1 Overview

The design of the National Stream Survey is guided by the general goals and approach of the National Surface Water Survey, as described in Chapter 1, and by a set of data quality objectives (DQOs) that are intended to assure that resources expended in sampling and analysis yield sufficiently precise and accurate data to enable a useful interpretation of that information with quantifiable confidence. This chapter reiterates the overall goals of Phase I of the NSS in the context of the NAPAP Aquatic Effects Research Team "index" concept and the Regionalized Integrative Studies (RIS) approach and presents a concise statement of the DQOs. Subsequent sections describe the process of defining the target population, drawing statistical samples from that target population, and characterizing some of the physical and chemical attributes of the streams therein.

## 2.2 RIS and the "Index" Concept

### *2.2.1 Regionalized Integrated Studies*

The NSWS seeks to achieve the regional characterization of surface waters by linking chemical, biological, soils, and watershed studies through the selection of common study sites. Such linkages are critical to the Regionalized Integrative Studies (RIS) approach. This approach begins with a large scale classification study, such as the NSWS, to identify regionally characteristic systems. Subsequently, a smaller number of such characteristic systems will be the focus of detailed research designed to elucidate the mechanisms responsible for acidification, to determine relationships between chemistry and biological resources, or to detect long-term changes, should they occur. Processes, relationships, or changes observed in lakes and streams that are typical of the various types of systems comprising the regional population then can be extrapolated with quantifiable confidence to a regional scale. Much of the NAPAP aquatic effects research will hinge on this "regional classification" approach, the cornerstone of the RIS concept.

### *2.2.2 The "Index" Concept*

Extrapolating from intensive studies to regional population estimates relies on prior estimates of the total population resource in a region, and of the fraction of that population represented by the intensively studied systems. The classification, or determination of "representativeness," of the test system must be based on the major factors thought to control acidification in the population. Such underlying factors could include regional hydrology, geochemistry, and major vegetation types. Because such factors are quite complex, however, it will probably be necessary to rely on "indices" to represent many of them. Data upon which to base such indices must be available (or derivable from maps and remote imagery) for a sufficiently large and representative sample to estimate their frequency of occurrence in the population. Examples of simple physical and biological indices include stream drainage density, mean watershed slope, elevation, and percent coniferous vegetation. Phase I of the NSWS relies on grab samples taken from a number of water bodies during an appropriate season to provide an "index" of the chemical characteristics of the population of water bodies in the region. Index samples for the lakes in the NSWS were collected following fall overturn, when intralake spatial variability is minimized. Ideally, if the integrative capacity of a lake basin is sufficient, a single sample collected at this time may provide an "index" of chemical conditions at other times of the year. The predictive success of a fall overturn water chemistry index is influenced by many processes, but is generally proportional to the hydraulic residence time of the lake. Long residence times tend to integrate the inputs of water and dissolved materials from the lake watershed, reducing that portion of temporal variability due to changes in input rates. In streams, which have little or no temporal integrative capacity in their channels, it is necessary to draw the index sample during a period of the year that is expected to exhibit characteristics most closely linked to acid deposition or to its most deleterious effects. Spring appears to be the most appropriate period because stream water acid neutralizing capacity (ANC) is typically low and life stages of aquatic biota that are sensitive to low pH are likely to be present at this time.

Although pH and ANC depressions also can occur during other seasons, short hydraulic residence times in soil zones in the spring minimize acid neutralization. Also, acid-sensitive swim-up fry life stages of key fish species are typically present in the streams during the spring in many parts of the country. However, the short hydraulic residence times that contribute to low pH and low ANC conditions in the spring also may result in order-of-magnitude changes in some chemical variables over the course of hours or days during hydrologic events. In order to reduce error in the population estimates caused by such "atypical" samples, replicate measurements on each reach were planned for the Phase I-Pilot Survey, so that atypical values could either be averaged, or identified and excluded. The philosophy of indexing, if not the exact methodology, is identical in the stream and lake components of the NSWS. The multiple samples of reach water chemistry in the NSS should be thought of as replicates, with averages replacing the single NLS index sample in making regional population estimates. Examples of how this index sample might be used in stream classification are provided in Chapter 5.

### *2.2.3 Data Quality Objectives*

The data quality objectives (DQOs) of the National Stream Survey were designed to overcome some of the historical problems in past data sets noted in Chapter 1. Few of the DQOs in a descriptive and classificatory project such as the NSS can be specified in terms of narrowly defined precision limits, outside of which the data would be rendered useless. Instead, the DQOs represent ideal targets. However, even the qualitative specification of DQOs in the planning process has resulted in significant improvements to project designs and protocols.

Specifically, the DQOs are as follows:

1. The target population should accurately represent the population of streams that constitute the most important resource at risk from acid deposition.
2. The NSS data should describe a probability sample of streams from the target population.
3. The set of variables measured should be sufficiently complete to provide information on the suitability of the stream for key fish species and on the geochemical parameters that can be used to classify the streams and hypothesize mechanisms relating to past and future acidification (Phase I data may be supplemented during later phases to meet certain 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.
5. Sample variances must be sufficiently small to provide useful population estimates and robust stream classifications, to the extent that natural classes exist in the target populations.

In most cases the data quality objectives can only be met subjectively. In the case of DQO #4, however, the results of the Phase I-Pilot Survey can be used to provide a benchmark against which future analytical data quality can be compared.

## 2.3 Identifying the Target Population

A sampling design depends upon the identification of a "target population," i.e., a collection of entities about which we want to make estimates (and ultimately management decisions). Only when such a target population is explicitly defined can samples be drawn from it in order to make statistical inferences regarding the properties of that population. In the case of the National Stream Survey, DQO #1 indicates that the target population should best represent the resource at risk. In order to design the NSS sampling plan, we have construed this to mean that the target population should be located in an area of historically low ANC surface water that receives acid deposition, and in which streams (as opposed to lakes) are the predominant surface water resource. We further presume that the primary resource of interest is sport fisheries, and that 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.

These general criteria define a conceptual population of interest which is not easily defined in explicit terms. Such a definition must be quantified before it lends itself to statistical sampling. Ideally, there may be a single size range of streams that satisfies these abstract criteria. In practice, however, even with well-defined habitat characteristics, it has been very 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; 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 satisfactorily defined, we must then contend with bias and imprecision associated with our abstract representation of the assemblage of streams on maps, lists and remote imagery.

Given the difficulty in defining the conceptual population of interest, the most expedient approach for the National Stream Survey 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, and to proceed with an evaluation of whether that target population is a reasonable representation of the population of interest. The target population is, therefore, our best attempt to make explicit this conceptual population of interest. Its precise definition was influenced by the expertise of local fisheries 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 which could be sampled.

### *2.3.1 Selection of the Study Area*

The Southern Blue Ridge was chosen for the location of the Phase I-Pilot Survey for two reasons. The first was the need for a geographically compact, physiographically homogeneous area expected to contain predominantly low ANC streams, and to provide a range of logistical difficulties that would serve as a reasonable test of the field sampling design. The second was that the Southern Blue Ridge would provide "delayed response" types of watersheds that could be compared with "direct response" watersheds associated with northeastern U.S. lakes studied in the NLS (Galloway et al., 1983; U.S. EPA, 1985c; U.S. EPA, 1985d). Delayed response watersheds usually contain thick soil mantles and have geochemical properties that tend to neutralize hydrogen ions added by acid deposition. Because of this buffering effect, streams draining such watersheds may not exhibit significant pH changes for 10-100 years under present acid deposition rates. Direct response watersheds generally have shallow soils that exhibit little or no acid neutralizing capacity. They are in virtual equilibrium with acid deposition inputs. Streams draining such watersheds are expected to exhibit pH and ANC depressions relatively quickly following changes in acid deposition loading.

Figure 2-1 shows the location and boundaries of the Southern Blue Ridge study area as determined from physiographic maps of Fenneman (1946) and the EPA alkalinity map for the region (Omernik and Powers, 1983). A northern spur of the Southern Blue Ridge Province (not shown in Figure 2-1) was excluded from the survey in order to avoid sites with driving times greater than two hours from the base operations site. It should be noted that the NSS Phase I-Pilot Survey area falls within the larger subregion 3A of the ELS-Phase I, but does not share the same boundaries. The geography of the area (Figure 2-2) is composed of uniformly dissected mountains with elevations ranging from 500-2000 m above mean sea level. The 27,000 $km^2$ area is drained by clearwater streams with dendritic drainage patterns. Three major river valleys, the Hiwassee, Little Tennessee, and French Broad provide the major relief in the area as they drain northward into the Tennessee River. All of the major rivers in the area have been dammed, and reservoirs of all sizes are common. Based on historical data, streams draining watersheds $< 70$ $km^2$, especially at elevations $> 750$ m above mean sea level, exhibit low acid neutralizing capacity, particularly in the spring of the year (Silsbee and Larson, 1982; Talbot and Elzerman, 1985).

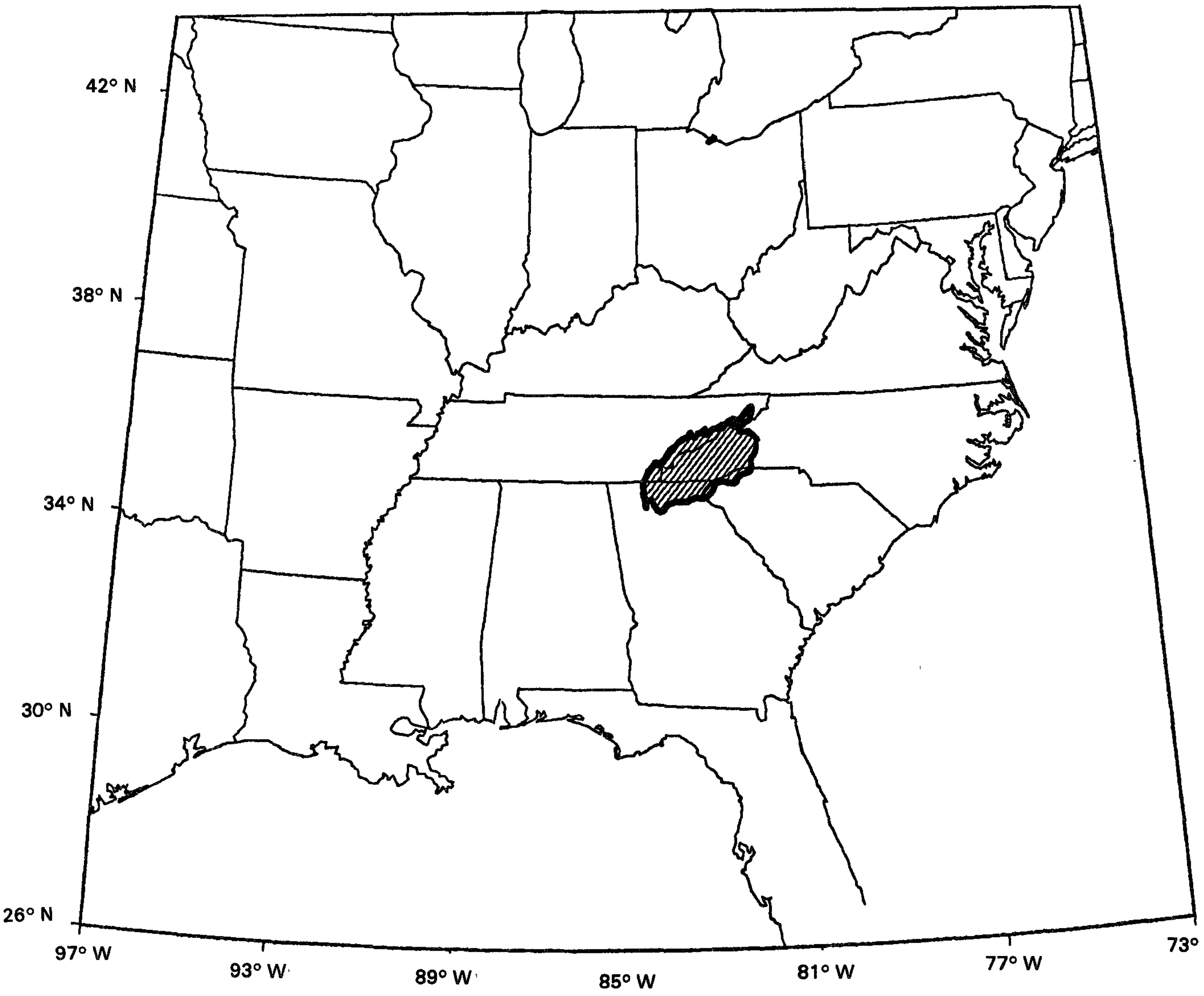
Vegetation in the area is mostly Appalachian oak forest with pockets of northern hardwoods. Land use is mostly forest and ungrazed woodlands, with mixed cropland and pasture in the valley bottoms. The French Broad River Valley contains the cities of Asheville and Hendersonville, and is moderately urbanized or farmed in most places. The highlands are sparsely settled, and Great Smoky Mountains National Park occupies much of the northwestern portion of the study area.

### *2.3.2 Stream Population of Interest*

Identification of the target population of streams (DQO #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 U.S., 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,

Figure 2-1. Location of the Southern Blue Ridge Phase I- Pilot Survey study area.

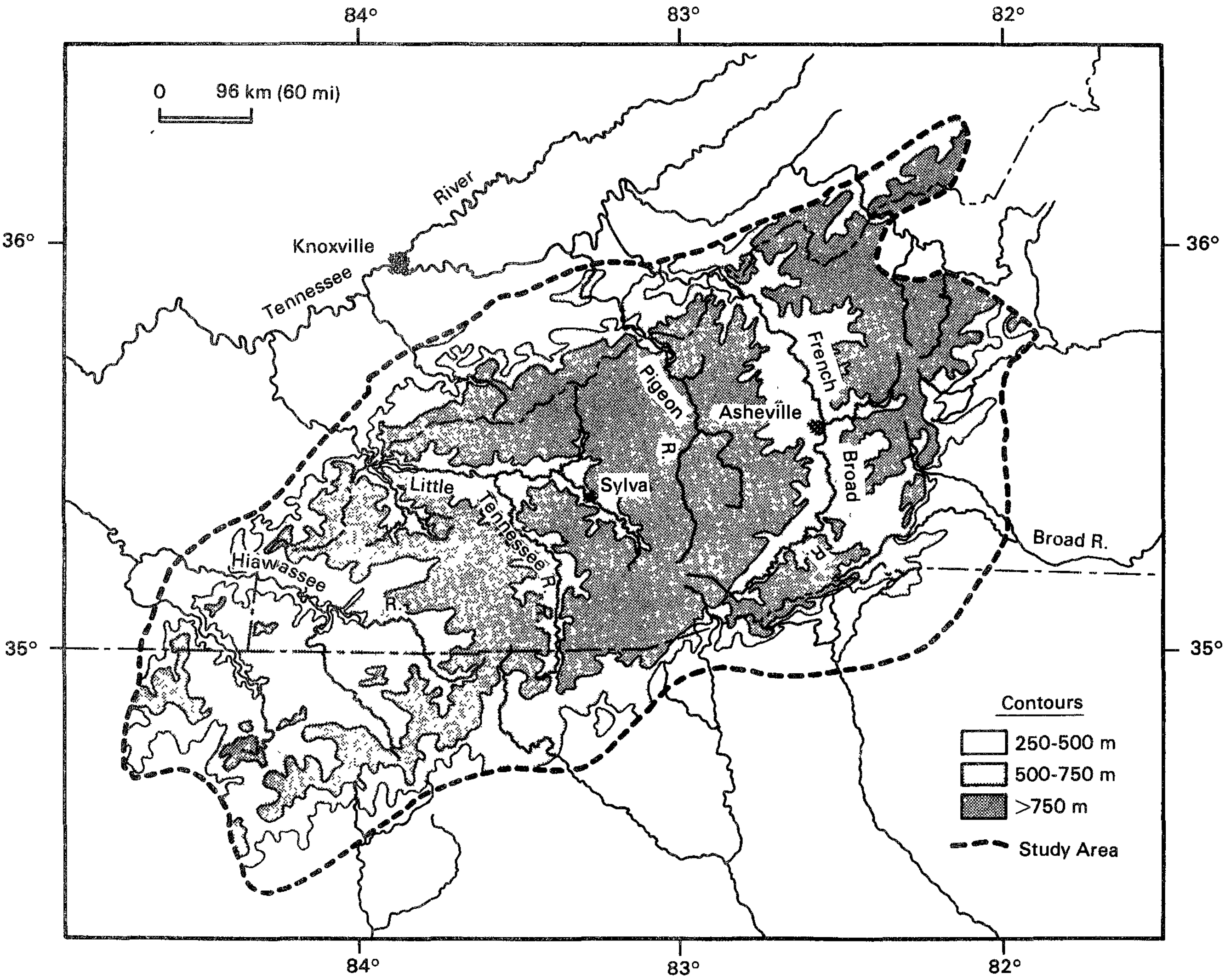


offer quantitatively less fish habitat, and for that reason may not best represent the biological resource at risk. While the impacts of acidification on spawning and detritus processing in very small headwater and intermittent streams should not be discounted, it would be very difficult, given the present 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 are 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 watersheds of drastically different sizes (Overton, 1987). On the other hand, populations of very small streams are poorly represented on maps, are often very difficult to access physically, and their flow may dry up entirely in some years.

A decision ultimately was made to target the NSS on the population of medium-sized streams draining

Figure 2-2. Geography of the NSS Phase I-Pilot Survey study area.



watersheds of approximately 1 to 200 km$^2$. Such streams in the Southern Blue Ridge typically are less than 1 m in depth and less than 10 m in width during spring "baseflow" conditions. They typically represent streams of Strahler order 2 to 4, as determined from 1:24,000-scale USGS topographic maps.

There was also some question of how to deal with anthropogenic impacts that may mitigate or exacerbate the effects of acid deposition on streamwater chemistry. Inclusion of streams affected by non-atmospheric, non-point source pollutants would decrease our ability to apply geochemical models that depend on relatively "pristine" geochemistry to infer acid deposition impacts. Conversely, restricting the target population to pristine streams would preclude making robust and meaningful population estimates for all streams of interest in a region. This dilemma reflects the inability to optimize on both primary and secondary objectives, as noted in Chapter 1. Based on the primary Phase I objectives of identifying the regional extent of all low pH and low ANC streams, it was reasoned that only grossly polluted streams (e.g., urban drainage ditches) should be excluded. The effects of nonpoint source pollution on streams otherwise affected by acid deposition are "part and parcel" of the existing environmental conditions and these streams were, therefore, included in population estimates. Such streams may make poor candidates for further study, however, and will likely be excluded from field study in subsequent phases of the survey.

Another problem arose in delineating the geographic boundaries expected to contain the majority of low ANC streams. A decision originally was made to strictly adhere to the 400 $\mu$eq L$^{-1}$ ANC boundaries shown on the most recent (working) versions of the U.S. EPA regional alkalinity maps. This decision resulted in exclusion of two small "islands" of higher ($> 400$ $\mu$eq $L^{-1}$) ANC surface waters in the center of the study area (Omernik and Powers, 1983). However, local water quality experts indicated on the basis of recent data that the maps were in error in this regard, and these areas were subsequently included in the Survey. Owing to similar uncertainties in the accuracy of historical data bases, subregional boundaries have been drawn with a "broad brush" in the areas covered by the NSS in the 1986 Phase I design (U.S. EPA 1985a; U.S. EPA 1985b).

## 2.4 Target Population Estimates

### *2.4.1 Methods for Identifying the Target Population*

In Section 2.3.2, we identified the conceptual population of interest 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 waters with acid neutralizing capacity (ANC) predominantly less than 400 $\mu$eq $L^{-1}$. A probability sampling technique was used to choose a set of such streams upon which to make field measurements. The sampling plan began by identifying a sampling "frame." Sampling frames are often "list frames" which literally list the units of the target universe that are available for sampling. The NLS employed a list frame: the names (or site descriptors) of each lake of surface area greater than 4 hectares (ha) in each region of interest, as shown on 1:250,000-scale topographic maps. The first step in creating a sampling frame for the NSS was determining how to specify sampling units: whether to specify individual stream reaches for the frame or to identify collections of reaches specified within networks or watersheds. Individual reaches were chosen over networks or watersheds, for reasons discussed in Section 2.6.

Next, the reach units were identified. Alternatives included blue-line representations on different scales of topographic maps, remote imagery collected by satellite or aircraft, and various computerized data files originally constructed for other purposes. 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) is comprised of only those reaches large enough to appear on 1:500,000-scale topographic maps. At this scale, a large number of smaller streams that could be potentially sensitive to acid deposition but are still large enough to offer abundant fish habitat are not included (Sports Fishing Institute Bulletin, 1984). Such streams, which appear on larger scale (e.g., 1:250,000 and 1:24,000) maps, are generally too small to be of interest to water supply managers and therefore have not historically been represented in computerized water resources data bases.

For the foregoing reasons, reaches represented on larger-scale maps or by remote imagery were deemed the best alternatives. Remote imagery was rejected as being too costly and time-consuming for constructing a frame of thousands of reaches. Of the two applicable map scales (1:250,000 and 1:24,000), the former was chosen because it best represented the conceptual population of interest. An earlier survey (TIE, 1981) indicated that historical fishery and aquatic resource values are more closely associated with blue-line streams on the smaller scale (1:250,000) maps. Although the relationship varies from map to map, 1:250,000-scale maps generally exclude the first and second order streams that appear on the corresponding 1:24,000-scale maps in the eastern U.S. While it would be possible to identify streams to be included in the sampling frame on 1:24,000-scale maps by excluding headwater reaches according to some specified protocol, the somewhat arbitrary way in which headwater reaches are interpreted on such maps (Chorley and Dale, 1972) makes any such representation equally arbitrary. While there is no ideal way to identify the true universe of streams of management interest, identification of streams on 1:250,000-scale maps appeared to be the most reasonable delineation of the target population for the NSS sampling frame.

There is theoretically no reason why a list frame could not have been created to identify the target population of streams in the Phase I-Pilot Survey area. However, we now estimate that the combined mid-Atlantic and Southeast study areas planned for 1986 field work may contain well over 90,000 individual reaches. It thus would have required approximately 4-5 workyears to create a quality-assured, computerized list of such reaches for the full Phase I Survey. The alternative was to design a sampling procedure that estimates the number, length, and other geographical characteristics of the target population from a sample of reaches drawn from that population. A subsample of streams also must be selected for making physical and chemical measurements.

### *2.4.2 First Stage of Sampling*

The previous sections described in some detail the decisions involved in developing an explicit definition of the target population. The target population was explicitly defined using blue-line representation of streams on USGS topographic maps of 1:250,000-

scale in combination with site inclusion criteria described in Section 2.4.3. Throughout the remainder of this report, this target population was assumed to adequately represent the subset of the total population of streams which is in a size range of interest from the standpoint of the resource at risk (sport fisheries). The lack of exact correspondence is acknowledged and will be clarified in future work. Additional data collection and analysis is presently underway to identify the relationships among these populations and to aid in interpreting the target population estimates in the context of the various regional conceptual populations of interest.

In the sampling design chosen here, the procedure for sampling stream reaches from which to estimate the structure of the target population was termed the "first stage" of sampling. This activity utilized geographic data only, and was not concerned with describing the chemical conditions in the population. The method of selecting stream reaches for making physical and chemical measurements was called the "second stage" of sampling, and is described in Section 2.4.6.

In order to avoid the delay associated with constructing a list frame for all stream reaches in an area, it was decided instead to construct a "point frame." A point frame employs the random placement of a systematic sampling grid over a region to choose study reaches. The probabilistic sample obtained is more efficient at representing the spatial variability of reaches in the region than a totally random sample because this systematic sample is more evenly distributed over the land area. The point frame used in the Phase I-Pilot Survey was a grid of dots on an acetate transparency placed at random on 1:250,000-scale topographic maps. To select reaches corresponding to grid dots, a line was drawn perpendicular to the elevation contours, proceeding downslope from each grid point toward a stream reach (Figure 2-3). A stream "reach" was included in the first stage sample if it was the first reach intersected by the line, and was defined as the stream segment bounded by an upstream and a downstream node. The downstream node was determined by the first confluence with another 1:250,000 blue-line stream. The upstream node was determined by either a similar upstream confluence, or by the origin, as indicated on the 1:250,000-scale topographic map. The example in Figure 2-3 shows sampling frame points corresponding to a uniform rectangular geographic grid with 8 mi between each point. Point 98 in the figure results in the selection of a blue-line non-headwater reach, while point 99 results in selection of a blue line headwater reach. The direct drainage area of downstream reach sampling nodes are identified as "$a_1$." The area draining into the upstream node of the non-headwater reach is represented by "$a_2$." Total drainage to the upstream node of the headwater reach is represented by "$a_3$."

It is convenient, although not critical, that the grid points in the point sampling frame be spaced with a sufficiently low density that no two grid points could correspond to the same reach. Such sampling overlaps can be accommodated by the statistical models used in data analysis and have no effect on the validity of the population estimates (Overton, 1985, 1987). An 8-mile (approximately 13 km) distance between points has thus far yielded an appropriate grid density.

### *2.4.3 Site Inclusion Criteria ("Site Rules")*

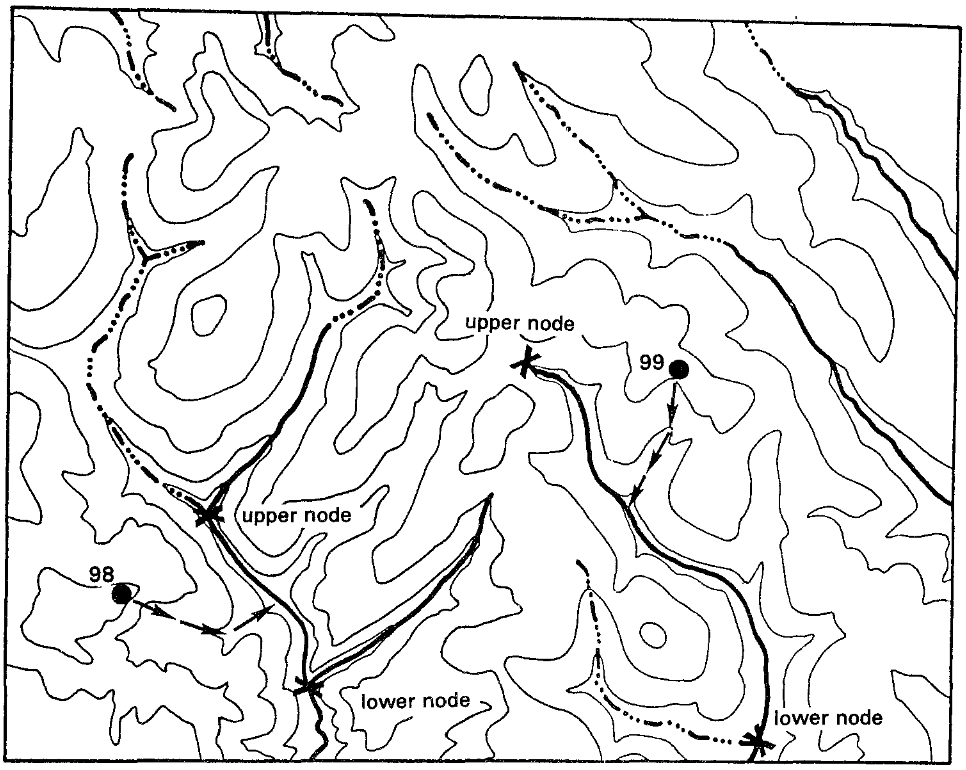
The reaches identified by the grid points are categorized into various "target" or "non-target" categories according to criteria discussed below. The target population thus defined is identical to that which might have been defined by a list frame. Unlike the exhaustive population defined by a list frame, 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 Phase I-Pilot Survey sites are shown in Table 2-1. 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 DQO #1 (Section 2.2.3).

Each grid dot may lead to a non-target reach, a target reach, or no reach at all. 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). Non-target reaches are excluded because some characteristic puts them into a non-interest category. Boundary reaches may penetrate sufficiently into suspected high ANC regions external to the study area that such reaches are unlikely to have low alkalinity over much of their length. A reach was excluded if any part of the blue line was outside the study area or if $>$ 25% of the drainage area defined by the downstream reach node was outside the boundary.

Large rivers were excluded by the site rules for reasons cited above (2.3.2). Sixty square miles was subjectively chosen as an upper limit for total drainage area. The use of watershed area to express stream size was chosen because of the objective, relatively precise way in which watershed areas are determined from topographic maps, as compared to stream order (Hughes and Omernik, 1981; 1983).

Reaches draining into or out of reservoirs also were excluded from the Phase I-Pilot Survey. It was reasoned that reservoir tailwaters could be domi-

Figure 2-3. Representation of the point frame sampling procedure for NSS study reaches. The sampling frame points correspond to a uniform rectangular geographic grid with 8 miles between each point. The lower left point results in inclusion of the reach shown.



Non-Headwater Reach

Headwater Reach

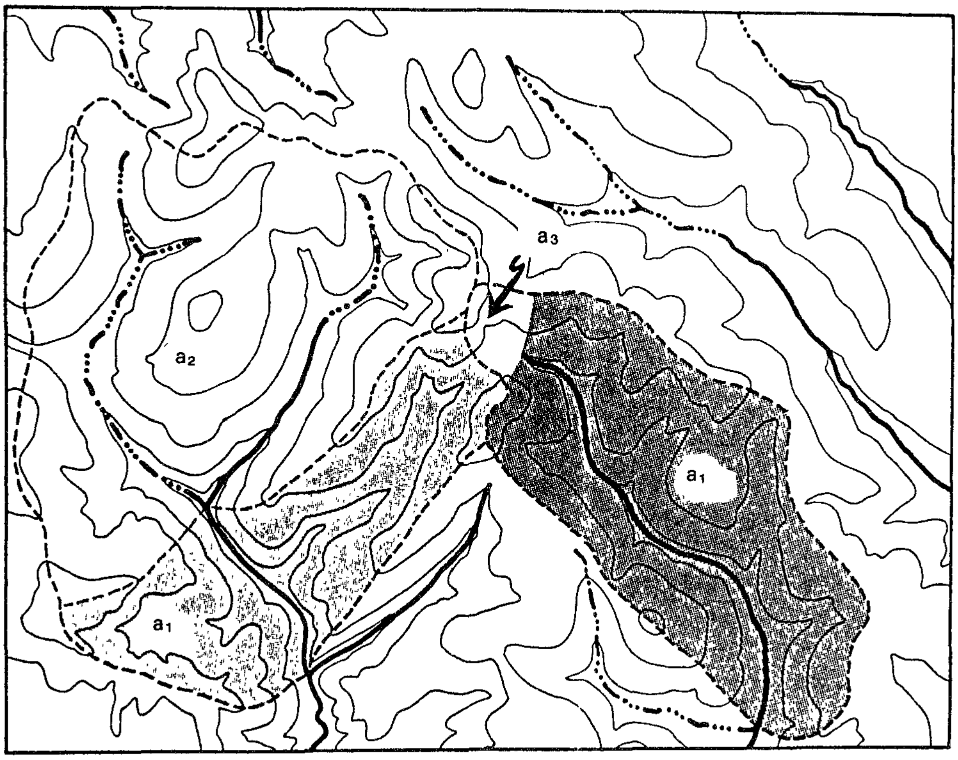


Table 2-1. NSS Phase I-Pilot Survey Site Inclusion Criteria

| | |
|---|---|
| *Non-Reach Grid Dots* | |
| Reach Out: | Topographic fall line yields a reach lying entirely outside the study area. |
| No Reach: | Dot identifies a lake, reservoir, or wetland. |
| *Non-Target Reaches* | |
| Boundary Reach: | Any part of the blue line crosses the study area boundary. |
| Watershed Out: | > 25% of drainage area outside study area. |
| Large River: | Total drainage area above downstream node is > 60 $mi^2$ (ca. 155 $km^2$). |
| Reservoir Reach: | Reach drains into or out of a reservoir. |
| *Target Reaches* | |
| Target Reach: | Reach lying entirely inside study area boundary, not draining into or out of a reservoir, with a watershed of $\leq$ 60 $mi^2$, at least 75% of which lies within the study area. |

nated by unusual water quality characteristics because of hypolimnetic processes in the reservoir. Downstream nodes of streams draining into reservoirs were difficult to identify due to inaccurate map representations and fluctuating reservoir operating schedules.

### 2.4.4 *First Stage Data*

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

1. Site identification code: a seven-digit code (e.g., 2A08901) containing three fields indicating the NSS Phase I subregion code (2A), the 1:250,000-scale map ID (089), and the grid dot sequence (01). The last field has been increased to 3 digits in Phase I.
2. Stream name: recorded from 1:250,000-scale, or 1:24,000-scale map, where indicated.
3. Site inclusion criteria applicable to the grid point (Section 2.4.3). For target reaches, certain additional information was collected that locates the reach geographically for sampling and identification purposes, including:
4. County(ies) and state(s) in which the reach is located.
5. State(s) 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.

The latter information was critical in the reconnaissance procedures described in Chapter 3.

In addition, data were collected for certain quantitative geographic variables including:

8. The area of *direct* drainage, $a_1$ (Figure 2-3): This is the portion of the watershed that drains directly into the chosen reach, and also the area within which a grid point will select this 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 origins (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 is made on 1:24,000-scale maps as noted above.
12. Headwater drainage area, $a_3$, being the area draining into the upper node of each stream (identical to $a_2$ for reaches with $R > 1$).

13. In the field, it was not always possible or desirable to collect stream samples exactly at the coordinates indicated on the field maps. In each case, *actual* sampling coordinates were marked by field personnel on the field maps, and new variables ($a_4$, $a_5$, and $L_2$) analogous to $a_1$, $a_2$, and L, were created, based on actual field sampling locations.

In all cases, measurements were made based on triplicate measurements with a Model 1250 Numonics planimeter with a resolution of ± 0.010 seconds and an accuracy of ± 0.020 seconds.

### 2.4.5 *Population Estimates*

The sampling design outlined above produced a probability sample of 115 reaches with expected probability of inclusion proportional to the direct drainage area, $a_1$, of each reach. This design has two advantages over a list frame, from which reaches are chosen randomly:

1. The reaches are approximately uniformly distributed in space, so that any intraregional geographic chemical patterns should become apparent.
2. It is less time-consuming than constructing a list frame because reach attributes need only be measured on the selected sample reaches.

Many attributes of the target universe of stream reaches can be estimated from the first stage sample (or second stage sample). The basic estimator is of the form:

$$\hat{T}y = d \sum_s zy/a_1 = \sum_s zyd/a_1 = \sum_s zyw \qquad [2.1]$$

where:

y is any reach attribute of interest (e.g., length);

$\hat{T}y$ is an estimate of the sum of that attribute over the target universe (e.g., combined stream length);

z is an indicator variable (0, 1) for a particular class of interest (e.g., all reaches with $a_1 + a_2 < 10$ mi$^2$);

$a_1$ is the area of direct drainage of the sample reach, as defined above;

d is the areal density of points in the geographic grid used to construct the point frame (the NSS Pilot uses an 8 mile grid resulting, respectively, in 64 mi$^2$ and 128 mi$^2$ per point for Stage I and Stage II sampling);

$\sum_s$ indicates summation over the number of sample reaches, s, in the stratum of interest; and

w is a weighting factor ($d/a_1$) which is inversely proportional to the inclusion probability for each particular stream reach.

The estimation of some attribute of interest in the target universe is accomplished by employing Equation 2.1. When an estimation of that attribute is desired for a subset (stratum or population) of the target universe, summation is restricted to the pertinent subset. This is accomplished by setting of the value of the indicator variable z to 1 if the sample reach is in the population or to 0 if it is not. For example, to estimate total stream miles by category of watershed size, one can sum over only those reaches belonging to that watershed size category. Similarly, to estimate the total stream length which lies in some criterion region (e.g., those stream miles with values of ANC within some specified range), we only sum over sample reaches having ANC values in that range.

The number of populations or classes of reaches that can be identified by physical or chemical characteristics is essentially unlimited. The following examples are chosen only to illustrate the possibilities of the estimation procedure. The total number of reaches (N), within any subset, z, of the target universe (such as those reaches with ANC < 100 $\mu$eq L$^{-1}$) can be determined as the sum of interest reaches, each multiplied by its individual probability weighting factor:

$$\hat{N}_z = d \sum_s zy/a_1 = \sum_s zd/a_1 = \sum_s zw \qquad [2.2]$$

Similarly, $\hat{A}_z$, the total area of watershed directly drained by the reaches in subset z of the target universe can be estimated by:

$$\hat{A}_z = d \sum_s zy/a_1 = \sum_s za_1d/a_1 = \sum_s zd \qquad [2.3]$$

An estimate of the total length ($L_z$) of reaches in subset z can be calculated as:

$$\hat{L}_z = d \sum_s zy/a_1 = \sum_s zLd/a_1 = \sum_s zLw \qquad [2.4]$$

Examples of other types of classifications (stratifications) that were found to be useful in the Phase I-Pilot Survey analysis included:

1. Categories of watershed size:

   a. Class A: reaches with $0 < (a_1+a_2) \leq 5$ mi$^2$ (13 km$^2$).
   b. Class B: reaches with $5 < (a_1+a_2) \leq 15$ mi$^2$ (39 km$^2$).
   c. Class C: reaches with $15 < (a_1+a_2) \leq 60$ mi$^2$ (155 km$^2$).

2. Shreve reach order (1:250,000 blue lines):
   a. $R = 1$ (headwaters)
   b. $R = 2$
   c. $R > 2$

The basic estimator can be generalized to yield the following formula for a reach attribute:

$$\hat{T}_y = \Sigma\ yw, \qquad [2.5]$$

where summation is over the sample data that are in the subpopulation of interest. Variances are calculated for each parameter of interest according to the equation:

$$\hat{V}(\hat{T}_y) = \sum_{s} y^2[w(w-1)] + \sum_{i}\sum_{j\neq 1} w_i y_i y_j (w_j - w_{j.i}) \qquad [2.6]$$

where:

$$w_{j.i} = [nw_j - (w_j + w_i)/2w_i]/(n-1) \qquad [2.7]$$

if i and j are from the same stratum, and

$$w_{j.i} = w_j \qquad [2.8]$$

if i and j are from different strata (Overton, 1985).

The effective sample size, n, is the number of grid points that fall in the study area, and includes non-target reaches and points that do not lead to a reach. For any subpopulation, the formulae are identical and summation is made over the sample data from that exact subpopulation. A detailed discussion of the variance estimation procedure is presented by Overton (1987).

### *2.4.6 Second Stage of Sampling*

The second stage of sampling was designed to subsample the 115 target reaches in the first stage sample to obtain a reduced number of reaches for making chemical measurements within the time and resource constraints of the project. Previous experience in Phase I of the Eastern Lake Survey had shown a second stage sample size of approximately 50 per stratum to be satisfactory. It was also desired that the second stage sites be well dispersed geographically within the region so that any correlations of aquatic chemistry with geologic type or acid deposition loading could be detected.

A systematic random sample was chosen as the best means to draw such a sample. Every other grid dot was drawn in the second stage sample, beginning with a random start, and without regard to the site rules associated with each dot (i.e., non-reach and non-target dots were included). The site rules then were applied, and the resulting second stage sample was found to contain 54 target reaches. The locations of these sites are shown in Figure 2-4, along with the last four digits of the site identification code. Geographic site data for these reaches are provided in Appendix B (Table B.1).

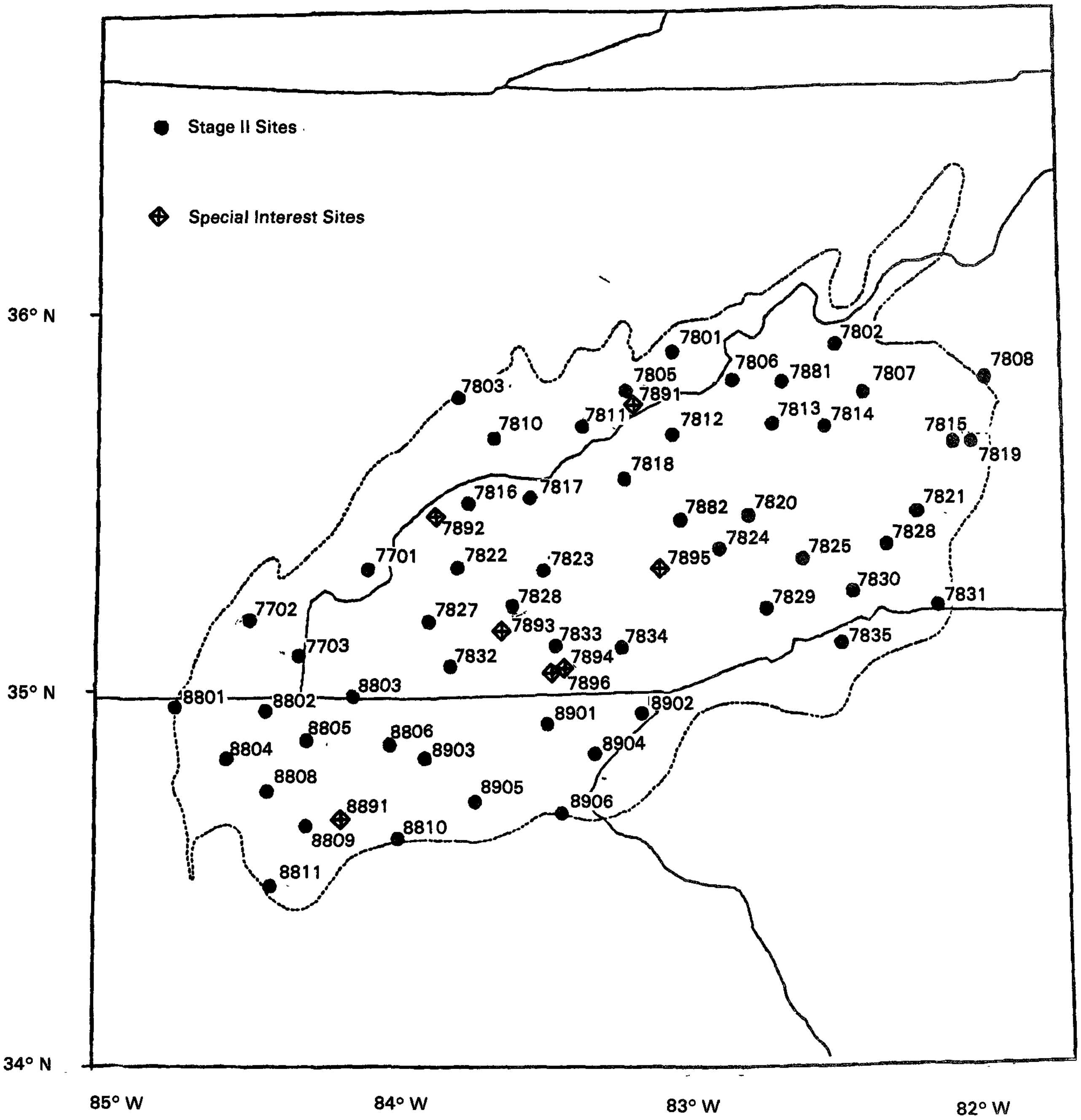
Population estimates and their associated variances were calculated as in the first stage sample, although n was smaller in the second stage sample. A systematic random subsample from the first stage sample retains the characteristic of non-uniform inclusion probabilities of the reaches in the first stage sample. Although the non-uniform inclusion probabilities can be accommodated by the sampling statistics, it is critical that future users not treat the sample as if the inclusion probabilities are equal. That is, population statistics associated with the sample should *not* be calculated as unweighted medians, means, and standard deviations.

### *2.4.7 Target Population Geographic Estimates*

Examples of the types of estimates that can be made for some geographical attributes of the target population are presented in Table 2-2. Estimates of the numbers, length (L), direct drainage areas ($a_1$), and discharge indices of target reaches in the Southern Blue Ridge are shown, along with the associated standard errors of the estimates. The percentages of stream reaches, length, and water surface areas represented by the subpopulations of drainage area and order categories, as described in Section 2.4.5, are also shown. Interpretation of the total discharge index and the significance of the various geographic estimates will be discussed in Chapter 5 in the context of reach chemistry.

Based on the first stage sample, the target population is estimated to contain 2,156 reaches with a combined length of 9,508 km (5,908 mi). The streams are estimated to directly drain 19,062 km$^2$ (7,360 mi$^2$) or 7,360/10,501 = 70% of the study area. The remainder of the area drains directly into reservoirs,

**Figure 2-4.** **NSS Phase I-Pilot Survey study area showing second stage (II) probability sites and special interest reaches. Numbers represent the last four digits of the corresponding site code.**



large rivers, or into boundary reaches. Sixty-six percent of the target reaches are portrayed as headwaters (R = 1) on 1:250,000-scale maps, and 50.6% are estimated to drain watersheds $< 5$ mi$^2$ (13 km$^2$). The percentages for headwater reaches are somewhat higher (ca. 74%) if the estimates are based on length or drainage area, thus indicating that the headwater reaches typically are longer and have larger direct drainages than the stream segments lower in the watersheds (R $> 1$).

The same types of estimates can be made from the smaller (n = 54) second stage sample. Differences in the estimates (e.g., 8,963 versus 9,508 kilometers) between the two samples are generally small for the entire population, and for headwater reaches (e.g., 6,714 versus 7,047 kilometers). Standard errors based on the second stage sample are higher, due to the smaller sample size. The estimates diverge the most for relatively small subsets of the sample (e.g., second order reaches). The differences in the

Table 2-2. **Geographic Attribute Estimates and Standard Errors for the NSS Phase I-Pilot Survey Target Populations Based on Stage I and Stage II Samples**

| | Stage I[a] | | | Stage II[b] | | |
|---|---|---|---|---|---|---|
| Attribute Description | Est. | S.E. | %[c] | Est. | S.E. | %[c] |
| Number of Target Reaches | 2,155.6 | 265.0 | | 2,020.9 | 326.7 | |
| Headwater Reaches | 1,422.4 | 180.5 | 66.0 | 1,432.7 | 296.1 | 70.9 |
| Second Order Reaches | 372.5 | 199.1 | 17.3 | 79.1 | 53.7 | 3.9 |
| Remaining Reaches | 360.7 | 106.0 | 16.7 | 509.0 | 191.9 | 25.2 |
| Class A Reaches | 1,090.9 | 185.9 | 50.6 | 1,120.9 | 302.8 | 55.5 |
| Class B Reaches | 698.5 | 204.9 | 32.4 | 449.9 | 119.7 | 22.3 |
| Class C Reaches | 366.1 | 97.4 | 17.0 | 450.1 | 170.2 | 22.3 |
| Direct Watershed Area (Sq. km) | 19,062.4 | 954.7 | | 17,902.1 | 1,417.7 | |
| Headwater Reaches | 14,089.6 | 1,019.5 | 73.9 | 13,260.8 | 1,477.6 | 74.1 |
| Second Order Reaches | 1,989.1 | 525.6 | 10.4 | 994.6 | 550.1 | 5.6 |
| Remaining Reaches | 2,983.7 | 628.1 | 15.7 | 3,646.7 | 997.8 | 20.4 |
| Reach Length, Total (km) | 9,508.0 | 645.0 | | 8.963.2 | 952.7 | |
| Headwater Reaches | 7,046.5 | 636.7 | 74.1 | 6,714.1 | 938.3 | 74.9 |
| Second Order Reaches | 1,054.3 | 315.4 | 11.1 | 482.5 | 296.4 | 5.4 |
| Remaining Reaches | 1,407.2 | 339.0 | 14.8 | 1,766.6 | 553.7 | 19.7 |
| Total Discharge Index (Sq. km) | 47,286.6 | 7,368.8 | | 51,123.7 | 12,487.4 | |
| Headwater Reaches | 14,089.6 | 1,019.5 | 29.8 | 13,260.8 | 1,477.6 | 25.9 |
| Second Order Reaches | 9,471.6 | 3,608.8 | 20.0 | 2,362.6 | 1,317.5 | 4.6 |
| Remaining Reaches | 23,725.4 | 6,913.3 | 50.2 | 35,500.3 | 12,864.3 | 69.4 |
| Class A Reaches | 6,464.6 | 890.7 | 13.7 | 5,967.4 | 1,240.5 | 11.7 |
| Class B Reaches | 14,981.2 | 3,715.0 | 31.7 | 10,038.7 | 3,116.8 | 19.6 |
| Class C Reaches | 25,840.8 | 6,845.0 | 54.6 | 35,117.7 | 12,613.9 | 68.7 |

[a] n = 115
[b] n = 54
[c] Percentages refer to the estimated number (length, areas) of streams in the correpsonding interest categories (see Section 2.4.5).

two estimates are discussed further in the context of the chemical distributions in Chapter 5.

### *2.4.8 Special Interest Reaches*

In addition to the reaches in the probability sample, seven "special interest" sites also were visited during the survey. Four of these sites were being monitored for episodic pH depressions in conjunction with another NAPAP Task Group E project (Olem, 1984), and two sites represented long-term monitoring sites on control watersheds at the Coweeta Hydrologic Laboratory (gauges 8 and 36). Although the data gathered at these sites were not analyzed as part of the probability sample, they ultimately will serve as part of the data needed to establish the representativeness of these sites with respect to the Southern Blue Ridge target population. Locations of the special interest sites, along with their corresponding site codes, also are shown in Figure 2-4.

## 2.5 Third Stage of Sampling

The sampling design establishes the physical and chemical measurements that are made on each second stage reach, and when and where to take them in order to best characterize the reach. These decisions were based on the expected temporal and spatial variability in the chemical concentrations within each reach and on the potential utility of the field information relative to the project objectives to:

1. Estimate the current population distribution of streams at risk (e.g., having low pH or high concentrations of toxic aluminum species at times when sensitive life stages of fish are present).

2. Estimate the population distribution of streams potentially at risk in the future (e.g., having low ANC during periods when sensitive biota are present).

3. Classify reaches into representative "types"for future intensive studies.

The first two objectives require that measurements be taken during geochemically and ecologically relevant periods of time, i.e., during seasons of low pH, highest relative proportion of "recent" hydrologic inputs to the system, and presence of sensitive biota. From a population estimation standpoint, it also would be desirable to minimize within-stream sampling variance in order to reduce the error bounds on the population estimates.

The last objective requires that a balance be struck between measuring chemistry at a time when within-stream variation is minimized and when between-stream variability is maximized, in order to provide classes that are both distinct and robust. Any such classification should separate streams into categories that ultimately represent the most important ecological and geochemical types with respect to the first two objectives. Ideally, a sampling design would simultaneously meet all three of these objectives; in reality, it probably cannot.

In addition to specifying the sampling season or seasons, it also is necessary to specify which variables are to be measured, where on a reach, and how frequently. The first issue relates to the ecological and geochemical objectives of interest, including ecological effects, mechanisms of acid deposition processing within watersheds, and geochemical classification. The spatial issue relates to the spatial variability known or expected to occur within the sampling unit (the reach). The final issue is a function of the expected temporal variance of the chemical variables at a site, and the desired precision or robustness of the population descriptions and classification. These issues are addressed in the following sections.

### 2.5.1 Variables Measured

Data quality objective #3 (Section 2.2.3) specifies that sufficient variables be measured so that one can determine: (1) the chemical and physical quality of the streams with respect to fish habitat; and (2) the geochemical nature of the waters with respect to past and future susceptibility to acid deposition. It was not cost effective to measure all possible variables on a large number of streams, but it was necessary to measure the critical ones. Table 2-3 lists the measurements made on second stage sample reaches, except for the geographic variables noted above.

**Table 2-3. Variables Measured During the NSS Phase I-Pilot Survey**

| Site Data | *In situ* Measurements | Laboratory Measurements |
|---|---|---|
| gage height (stage) | pH (open head space)[a] | pH (closed head space)[a,b] |
| stream width | pH (closed head space)[a] | pH (equilibrated, 300 ppm $CO_2$) |
| stream depth | temperature | DIC[b] |
| land use | specific conductance | DOC |
| bank vegetation | dissolved oxygen | true color[a] |
| stream substrate | | turbidity[a] |
| cloud cover | | conductivity |
| weather conditions | | ANC |
| | | BNC |
| | | Aluminum (total) |
| | | Aluminum (MIBK extractable)[b] |
| | | Aluminum (non-exchangeable)[b] |
| | | suspended solids |
| | | calcium |
| | | magnesium |
| | | potassium |
| | | sodium |
| | | nitrate |
| | | sulfate |
| | | chloride |
| | | fluoride |
| | | silica |
| | | ammonium ion |
| | | iron |
| | | manganese |
| | | total phosphorus |

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[a] In open headspace pH determinations, samples were exposed to the atmosphere during collection and measurement; in closed headspace determinations they were not. See Section 3.3.2 for more detailed information.

[b] Samples prepared at field lab, then measured at analytical lab.

The site information recorded at each sampling location was primarily meant to assist in the initial interpretation of physical/chemical data from each site, and to aid in locating the site in future studies. This site information ("Site Data" in Table 2-3) was not quality-assured and, although it is recorded in an NSS data file, it should not be used to draw quantitative inferences about the other chemical or physical data. For example, it would be inappropriate to regress turbidity or temperature against substrate type or stream bank vegetation, even though reasonable relationships may exist. It would be useful, however, if a site with high turbidity could be determined to be bordered by unvegetated stream banks, to have a silty bottom, or to have experienced a rainy period prior to sampling.

The physical and chemical variables may have many interpretations, depending on the way in which they are used. Some variables are of primary interest with respect to the immediate NSS objectives (e.g., pH and ANC). Other variables are important in interpreting the primary variable data (e.g., DOC, color, and fluoride are useful in understanding the speciation of aluminum). Other variables such as nitrate, sulfate, and DOC are needed to describe the ionic composition of waters, and some may be useful indicators of non-atmospheric pollution (e.g., chloride, total phosphorus, and ammonium-nitrogen). Finally, some variables may provide clues to the geochemical processes controlling water chemistry in a region, and also may be useful in classification of stream reaches for further study (e.g., silica, sodium, potassium, or calcium). Complete chemical analysis for all major ions is needed for conducting verification checks on the accuracy of chemical analyses on the basis of cation/anion balances and conductivity checks (see Chapter 4).

Brief descriptions of the chemical variables measured during the Phase I-Pilot Survey are presented below:

1. pH: The pH of a stream is a direct indication of free hydrogen ion activity. The pH is an important geochemical constituent and affects toxicity through its effects on fish physiology and the speciation of toxic metals such as aluminum.

2. Base Neutralizing Capacity (BNC): The BNC is a measure of acids in water including both terrestrial and atmospheric mineral acids, carbon dioxide, and organic acids associated with decomposition of plants and detritus. This term is used interchangeably with acidity throughout this report.

3. Acid Neutralizing Capacity (ANC): ANC is a measure of all bases and is an indication of buffering capacity. Alkalinity is a more appropriate term if the ANC is primarily controlled by the inorganic carbonate system. Alkalinity is used synonymously with ANC throughout this report.

4. Specific Conductance: The specific conductance of stream water is a measure of the resistance of the water to electrical current. Because resistance to electron flow is inversely proportional to the concentration of ions in solution, specific conductance can be used to check the overall accuracy of ion analyses.

5. True Color: True color is a potential indicator of naturally occurring organic protolytes and DOC. Substances that impart color may also be important natural chelators of aluminum and other metals.

6. Dissolved Inorganic Carbon (DIC): In carbonate systems, a measure of DIC (and either pH or ANC) can be used to describe the equilibrium distribution of carbonate solutes, and determine whether the solution is saturated with respect to atmospheric $CO_2$.

7. Dissolved Organic Carbon (DOC): DOC is an important source of energy for stream metabolism, but also provides an indication of the presence of natural organic acids which can influence pH. DOC is also a natural chelator of aluminum and other trace metals.

8. Dissolved ions ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $NH_4^+$, $F^-$, $Cl^-$, $SO_4^{2-}$, and $NO_3^-$): These constituents are measured in order to chemically characterize streams and calculate ion balances.

9. Total Extractable Aluminum: Total extractable aluminum is an estimate of dissolved aluminum and includes most mononuclear aluminum species. Aluminum is considered to be highly toxic, especially to fish. It was further fractionated into operationally-defined inorganic and less-toxic organic monomeric forms based on affinity for a cation exchange resin.

10. Total Aluminum: Total aluminum is associated with the weathering rate of soils in a watershed, and is often associated with high flow in streams.

11. Dissolved Silica ($SiO_2$): Dissolved silica is a potentially important factor in identifying mineral weathering reactions and source materials in poorly buffered streams.

12. Total Phosphorus: This is an indicator of potentially available nutrients for periphyton productivity and may provide a check on unobserved pollutant sources.

13. Turbidity: Turbidity is a measure of suspended material present in water at low concentrations and is often a useful indicator of increased discharge.

14. Total Non-Filterable Residue (Suspended Solids): This parameter is a useful estimate of the amount of particulate material entering the stream and potentially capable of interacting with chemical species in the water. It also is often a useful indicator of episodes resulting from storms or snowmelt.

Those variables in Table 2-3 that are least stable in a sample following collection due to temperature changes or gas exchange, and for which portable instrumentation was available, were measured *in situ* or at streamside. A second set of variables that are less labile and/or for which portable field instrumentation was inadequate (e.g., aluminum fractionation) or for which apparatus was unavailable (e.g., dissolved inorganic carbon) are indicated in Table 2-3. These variables were measured within 12 hours of sample collection at a specially equipped mobile analytical laboratory that was centrally-located in the study area (Sylva, North Carolina). Suspended solids were measured at a local contract laboratory. The remaining variables were stabilized (if necessary) and samples were sent to a central contract analytical laboratory (New York State Department of Health, Albany) for analysis. The specific analytical procedures for these variables are summarized in Table 2-4. Sample collection and handling protocols are described in Chapter 3.

### 2.5.2 Sampling Season

In order to determine the optimum seasonal sampling window, a literature search was followed by meetings with hydrologists, biogeochemists, and fishery experts in the study area. Although many of the data discussed at these meetings were still being prepared for publication, the following

**Table 2-4. Chemical Variables and Corresponding Measurement Methods for the National Stream Survey**

| Parameter | Method[a] |
|---|---|
| 1. Acidity (BNC) | Titration with Gran plot |
| 2. Alkalinity (ANC) | Titration with Gran plot |
| 3. Aluminum, total | EPA Method 202.2—AAS (furnace) |
| 4. Aluminum, extractable | Extraction with 8-hydroxyquinoline into MIBK followed by AAS (furnace) |
| 5. Aluminum, non-exchangeable | Cation exchange, followed by extraction with 8-hydroxyquinoline into MIBK followed by AAS (furnace) |
| 6. Ammonium, dissolved | EPA Method 350.1 |
| 7. Calcium, dissolved | EPA Method 215.1—AAS (flame) |
| 8. Chloride, dissolved | Ion chromatography |
| 9. Fluoride, dissolved-total | Ion selective electrode |
| 10. Inorganic carbon, dissolved (DIC) | Instrumental (Similar to DOC) |
| 11. Iron, dissolved | EPA Method 236.1—AAS (furnace) |
| 12. Magnesium, dissolved | EPA Method 242.1—AAS (flame) |
| 13. Manganese, dissolved | EPA Method 243.1—AAS (flame) |
| 14. Nitrate, dissolved | Ion chromatography |
| 15. Organic carbon, dissolved (DOC) | EPA Method 415.2 |
| 16. pH | pH electrode and meter |
| 17. Potassium, dissolved | EPA Method 258.1—AAS (flame) |
| 18. Silica, dissolved | USGS Method I-2700-78 |
| 19. Sodium, dissolved | EPA Method 273-1—AAS (flame) |
| 20. Sulfate, dissolved | Ion chromatography |
| 21. Specific conductance | EPA Method 120.1 |
| 22. Phosphorus, total | USGS Method I-4600-78 or Modified USGS Method |

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[a] AAS methods are taken from U.S. EPA (1983). Laboratories that have ICP instrumentation may use EPA Method 200.7, reproduced in Appendix A of Hillman *et al.* (1986a) for determining Ca, Fe, Mg, and Mn, providing they can demonstrate the specified detection limits. If the ICP instrumentation is not able to meet the required detection limits, it may still be used to analyze samples which contain the analytes at concentrations greater than 10 times the ICP detection limit. Other samples must be analyzed by furnace or flame AAS.

generalizations were based on quantitative data when available, and on expert opinion where data were lacking:

1. Alkalinity and pH are typically low during March 15-May 15 of normal years in the region.
2. Low pH episodes may also occur in the fall or winter in streams which also experience such episodes in the spring. However, the fall episodes do not appear to be "worse" than those occurring in the spring, and some streams with low spring pH may not exhibit such conditions in the fall.
3. Chemistry may be highly variable (e.g., from hours to days) during the spring in streams in the area. Temporal variability during other times of the year is usually (although not always) lower.
4. Studies have indicated that all life stages of fish are not equally susceptible to acidity and other chemical parameters that accompany low pH episodes 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 Leivestad, 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 increased sensitivity of fry to low pH conditions (Schofield, 1976; Haines, 1981). Fry of the most important sport fisheries are present in the study area during the March 15-May 15 period. Fry of some trout (*Salmo*) populations may *also* be present at other times of the year.
5. Physical access to most sites during spring was not expected to present significant problems. Winter access is difficult in places because of seasonal closure of unimproved roads and icy conditions on intermediate roads and highways.

Based on the above considerations, two sampling periods were chosen for the Phase I-Pilot Survey: March 17-May 30 (during which 3 samples were collected from each reach at three-week intervals) and July 1-July 17 (during which each reach was sampled once). No attempt was made to either target or avoid sampling during rainstorm events. The first sampling period coincided with periods of highest biogeochemical interest (i.e., low seasonal pH and the presence of sensitive fry), but in which temporal variability was potentially high enough to make robust population descriptions and reach classification impossible. The second sampling period was investigated to determine whether the presumably more stable summer "baseflow" chemistry could be used to provide an "index" of the spring conditions.

### *2.5.3 Sampling Locations on Each Reach*

Alternative locations for sampling on any particular reach included the upstream node, centroid, and downstream nodes. The downstream node was selected in order to provide not only an index of the chemistry over the entire reach, but also an integrated index of water draining the watersheds above the reach ($a_1 + a_2$). While the latter concept is fundamental to most watershed studies, it was anticipated that representing the chemistry of the entire reach by the chemistry at the downstream node would overestimate pH and ANC. It was subsequently decided that the upstream node of each reach could be added to the sampling itinerary without jeopardizing the primary design, and 21 upstream sites were added to the itinerary during the final spring sample. The chemistry of all probability sample reaches was measured at both upstream and downstream nodes during the summer sampling period. Special interest sites were sampled at the locations specified by the permanent investigators.

## 2.6 The Watershed Alternative to the Reach Frame

Almost everyone associated with the NSS was at one time attracted to the idea of employing watersheds, rather than reaches, as the statistical sampling unit. This proclivity no doubt arose in response to the proven utility of watersheds as units with convenient external boundaries for constructing mass balances useful in biogeochemical process research. The ordering of stream networks within watersheds also is useful in studying "continuum processes" with a strong hierarchical gradient. As sampling units of a large target population, however, watersheds offer some critical drawbacks, given the NSS primary objectives.

The principal problems with the watershed approach have to do with maintaining a large number of sampling units for making population estimates, and the amount of data needed to describe the extent of chemical conditions within a sampling unit. The chemistry of a reach can be approximated by measurements taken at two nodes. The chemistry of the simplest topological network (three reaches) requires measurements at four nodes, resulting in a three-row matrix of chemical variable scalars to specify the water chemistry. Under an equal effort sampling constraint, this reduces the sample size from 50 to 25 units, while greatly increasing the complexity of each unit for classification purposes. Increasing the network to Shreve order 3 (5 reaches) requires 6 measurements thus reducing n to 16.

This problem is further exacerbated by the fact that areas do not partition uniquely into small watersheds. If all watersheds smaller than 60 $mi^2$ are included, a region is partitioned into many different orders of watersheds, some large mainstem sideslopes, and sideslopes of adjacent areas. Small watersheds draining into large mainstems will have different chemical patterns than their equal ordered counterparts draining into intermediate-ordered streams at higher elevations. There is no "typical" order 3 (or any other) watershed in an area. These characteristics have rendered artificial, if not completely unworkable or inappropriate, any watershed-based sampling designs thus far considered.

In fact, the reach-based sampling plan can be used to construct "artificial" watersheds, based on the reach orders sampled in each subregion. Population estimates can be made for "headwater" reaches, second order reaches, (e.g., Table 2-3) and so on, provided enough reaches have been sampled in that category to provide meaningful estimates. Of course, these estimates are valid for *all* reaches of order R, regardless of where they occur, but they cannot be used to estimate the chemical pattern in any *particular* watershed. Nonetheless, the reach-based sampling design appeared to be the best way of meeting all of the NSS primary Phase I objectives.

# 3. Field Operations

## 3.1 Introduction

Several activities were performed before and during NSS Phase I-Pilot Survey field work to assure that samples were collected, processed, and analyzed in a consistent, safe, and timely manner. Protocols for collecting samples and making *in situ* or streamside measurements were developed prior to field sampling and were documented in a field operations manual (unpublished).Equipment and supplies for field sampling teams and the field laboratory were procured and evaluated, and the necessary personnel were hired and trained. Potential field station sites were visited and evaluated, and a reconnaissance program was established for acquiring pertinent access information on each stream reach selected for sampling. Safety protocols for sampling sites in rugged, unfamiliar terrain were developed. Protocols were occasionally modified during the course of field operations, and alternative methodologies and equipment were evaluated. In all cases, appropriate QA/QC protocols were developed for each procedure.

Field sampling and laboratory operations were conducted between March 1 and July 16, 1985. Over the course of the study, 339 routine samples were collected from 61 stream reaches (Table 3-1) and a total of 724 samples were analyzed during the project. A detailed description of the field operations,including planning and preparation, reconnaissance, field sampling, and field laboratory activities can be found in Knapp et al. (1987). These activities are briefly summarized in the following sections.

## 3.2 Preparation for Field Operations

### *3.2.1 Protocol Development*

While most analytical protocols for the field and contract analytical laboratories were adopted from the Eastern Lake Survey (ELS) component of the NSWS, much of the collection and measurement apparatus used in the ELS was unsuitable for use in streams, primarily because of large size and limited portability. Consequently, new field equipment was procured and tested, and protocols were written for the new procedures. In addition, a protocol was developed for fractionation of the total extractable aluminum (monomeric) aliquot in the field laboratory. This protocol was based on the methodology of Driscoll (1984), and involved passing filtered samples through a cation exchange column prior to complexing the nonexchangeable fraction with 8-hydroxyquinoline and extracting into methyl isobutyl ketone (MIBK). A protocol for measuring conductivity in the field laboratory also was developed late in the Survey.

### *3.2.2 Training Programs*

Training programs for field sampling and field laboratory personnel were conducted in Las Vegas over a five-day period before field work was begun. The field training program was designed to familiarize personnel with the objectives and research design of the NSS, sampling and analytical protocols, site reconnaissance, equipment troubleshooting, and field safety. Additional training, conducted in the field, included basic stream hydrology and site

**Table 3-1. Summary of Routine Samples Collected During the NSS Phase I-Pilot Survey**

| Sampling Interval | Dates | Upstream | Downstream | Special Interest Reaches |
|---|---|---|---|---|
| SPO[a] | 3/17 – 3/19 | 0 | 18 | 0 |
| SP1 | 3/20 – 4/02 | 0 | 54 | 7 |
| SP2 | 4/03 – 4/16 | 0 | 54 | 7 |
| SP3 | 4/17 – 4/30 | 23 | 54 | 7 |
| SU | 6/30 – 7/16 | 54 | 54 | 7 |

[a] These samples represent a three-day training run; they are included in the data base but were not used for population estimates.

coordination responsibilities. Field laboratory personnel underwent a five-day training course that covered all aspects of field laboratory operations, safety, and quality assurance.

### *3.2.3 Field Station Site Selection and Site Reconnaissance*

Potential sites from which to conduct Phase I-Pilot Survey field operations were visited in early 1985 and evaluated on their ability to support field sampling and field laboratory operations. The field laboratory was eventually located at Southwest Technical College in Sylva, North Carolina (Figure 2-2). This location also served as a base for field sampling activities. Field station personnel and a local communications center were housed in Cullowhee, North Carolina, approximately five miles from the field laboratory.

After stream reaches had been identified on USGS 1:24,000-scale topographic maps, it was necessary to assemble access information for each sampling-site. This was accomplished through telephone contact with "local cooperators" who were familiar with areas where reaches were located, and included personnel from federal, state and local agencies. Information on ease of access, driving or hiking times, and names of landowners to be contacted for access permission were obtained from the cooperators, and dossiers were compiled for each sampling site. Each dossier contained maps, telephone numbers of local cooperators, landowners, emergency contacts, and information on travel routes and site access. The dossiers were updated as new information was gathered in the field.

Each site was visited by field sampling personnel before sampling commenced. This field reconnaissance visit served to verify access information and to obtain access permission if necessary. Descriptive information on site characteristics in the immediate area was recorded on a standardized field form (Form 7, Figure 3-1), and the area was photographed to aid in describing the site and locating it on subsequent visits. A hydrologic staff gauge was installed and an initial reading was taken at each site; the cross-sectional area at the gauge was also measured.

## 3.3 Field Operations

### *3.3.1 Field Station Operations*

The Phase I-Pilot Survey was conducted in 1985 during two separate periods: a spring sampling period (March 17-April 30), and a summer sampling period (June 30-July 16). The field station in Sylva, North Carolina, was staffed by 11 people: a site coordinator, six field samplers, a laboratory supervisor, and three analysts. The site coordinator was responsible for the overall operation of the field station (Figure 3-2). Duties included devising sampling itineraries, organizing each day's samples into a batch for processing, shipping preserved samples to the contract analytical laboratory, and shipping data forms to the data management center at Oak Ridge National Laboratory (ORNL) and the QA support group at the EPA Environmental Monitoring Systems Laboratory at Las Vegas (EMSL-LV). The site coordinator also filed a daily operations report with the NSS communications center in Las Vegas.

### *3.3.2 Field Sampling Operations*

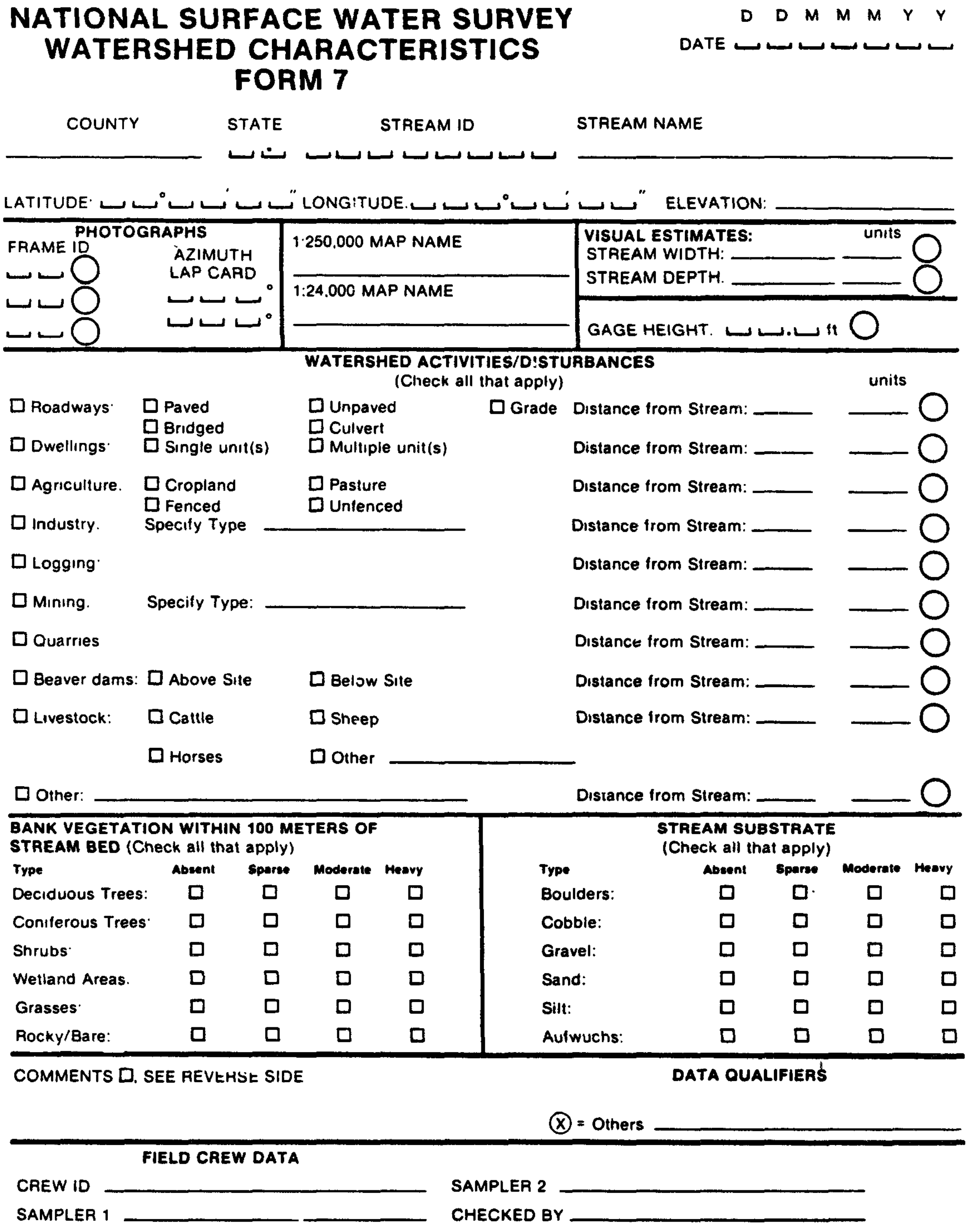
Samples were collected and field measurements were made by two-person teams who accessed stream sites by four-wheel drive vehicle, hiking, boating, or horseback. Each team was responsible for sampling 20-21 stream reaches during each two-week sampling interval, and visited one to three sites on each working day. The activities conducted at each site are summarized in Figure 3-3.

Water samples (termed "routine" samples) were collected from each stream by pumping water through 1/4-inch surgical grade Tygon tubing held in the center of the stream cross-section using a 6-foot sampling boom. Samples were pumped using portable peristaltic pumps driven by gel/cell batteries, each sample representing an integrated 10-minute sample of the streamflow. Samples were pumped into containers that had been acid-washed, rinsed, and quality-assured by the supplier. A bulk sample was collected into a four-liter Cubitainer. Three 60 ml polypropylene syringes equipped with gastight valves were filled in such a way that the samples were not exposed to the atmosphere. An aliquot for total suspended solids analysis was collected into a 500-ml amber high-density polyethylene wide-mouth bottle. Each container was rinsed three times with sample water prior to filling with the routine sample, and new Tygon tubing was used at each site.

Water samples were transported from streamside in portable soft coolers containing chemical refrigerant packs. Cooler temperatures were checked periodically and found to be approximately 4°C. When field crews arrived at a vehicle, samples were transferred to rigid insulated containers containing chemical refrigerant packs. Samples were held in these containers at approximately 4°C until they arrived at the field laboratory, usually within 10 hours of collection.

Two types of quality assurance samples were collected each day. Each team collected a "field

**Figure 3-1. NSS Data Form 7: Watershed Characteristics.**



# NATIONAL SURFACE WATER SURVEY
# WATERSHED CHARACTERISTICS
# FORM 7

D D M M M Y Y
DATE ⎵ ⎵ ⎵ ⎵ ⎵ ⎵ ⎵

COUNTY ________ STATE ⎵ ⎵ STREAM ID ⎵ ⎵ ⎵ ⎵ ⎵ ⎵ ⎵ ⎵ ⎵ STREAM NAME ________

LATITUDE: ⎵ ⎵° ⎵ ⎵' ⎵ ⎵" LONGITUDE: ⎵ ⎵ ⎵° ⎵ ⎵' ⎵ ⎵" ELEVATION: ________

**PHOTOGRAPHS**

| FRAME ID | AZIMUTH LAP CARD |
|---|---|
| ⎵ ⎵ ○ | ⎵ ⎵ ⎵° |
| ⎵ ⎵ ○ | ⎵ ⎵ ⎵° |
| ⎵ ⎵ ○ | |

1:250,000 MAP NAME ________

1:24,000 MAP NAME ________

**VISUAL ESTIMATES:** units
STREAM WIDTH: ________ ____ ○
STREAM DEPTH: ________ ____ ○

GAGE HEIGHT: ⎵ ⎵.⎵ ft ○

**WATERSHED ACTIVITIES/DISTURBANCES**
(Check all that apply)

| | | | | | units | |
|---|---|---|---|---|---|---|
| ☐ Roadways: | ☐ Paved<br>☐ Bridged | ☐ Unpaved<br>☐ Culvert | ☐ Grade | Distance from Stream: ____ | ____ | ○ |
| ☐ Dwellings: | ☐ Single unit(s) | ☐ Multiple unit(s) | | Distance from Stream: ____ | ____ | ○ |
| ☐ Agriculture: | ☐ Cropland<br>☐ Fenced | ☐ Pasture<br>☐ Unfenced | | Distance from Stream: ____ | ____ | ○ |
| ☐ Industry: | Specify Type ________ | | | Distance from Stream: ____ | ____ | ○ |
| ☐ Logging: | | | | Distance from Stream: ____ | ____ | ○ |
| ☐ Mining: | Specify Type: ________ | | | Distance from Stream: ____ | ____ | ○ |
| ☐ Quarries | | | | Distance from Stream: ____ | ____ | ○ |
| ☐ Beaver dams: | ☐ Above Site | ☐ Below Site | | Distance from Stream: ____ | ____ | ○ |
| ☐ Livestock: | ☐ Cattle | ☐ Sheep | | Distance from Stream: ____ | ____ | ○ |
| | ☐ Horses | ☐ Other ________ | | | | |
| ☐ Other: ________ | | | | Distance from Stream: ____ | ____ | ○ |

**BANK VEGETATION WITHIN 100 METERS OF STREAM BED** (Check all that apply)

| Type | Absent | Sparse | Moderate | Heavy |
|---|---|---|---|---|
| Deciduous Trees: | ☐ | ☐ | ☐ | ☐ |
| Coniferous Trees: | ☐ | ☐ | ☐ | ☐ |
| Shrubs: | ☐ | ☐ | ☐ | ☐ |
| Wetland Areas: | ☐ | ☐ | ☐ | ☐ |
| Grasses: | ☐ | ☐ | ☐ | ☐ |
| Rocky/Bare: | ☐ | ☐ | ☐ | ☐ |

**STREAM SUBSTRATE**
(Check all that apply)

| Type | Absent | Sparse | Moderate | Heavy |
|---|---|---|---|---|
| Boulders: | ☐ | ☐ | ☐ | ☐ |
| Cobble: | ☐ | ☐ | ☐ | ☐ |
| Gravel: | ☐ | ☐ | ☐ | ☐ |
| Sand: | ☐ | ☐ | ☐ | ☐ |
| Silt: | ☐ | ☐ | ☐ | ☐ |
| Aufwuchs: | ☐ | ☐ | ☐ | ☐ |

COMMENTS ☐, SEE REVERSE SIDE

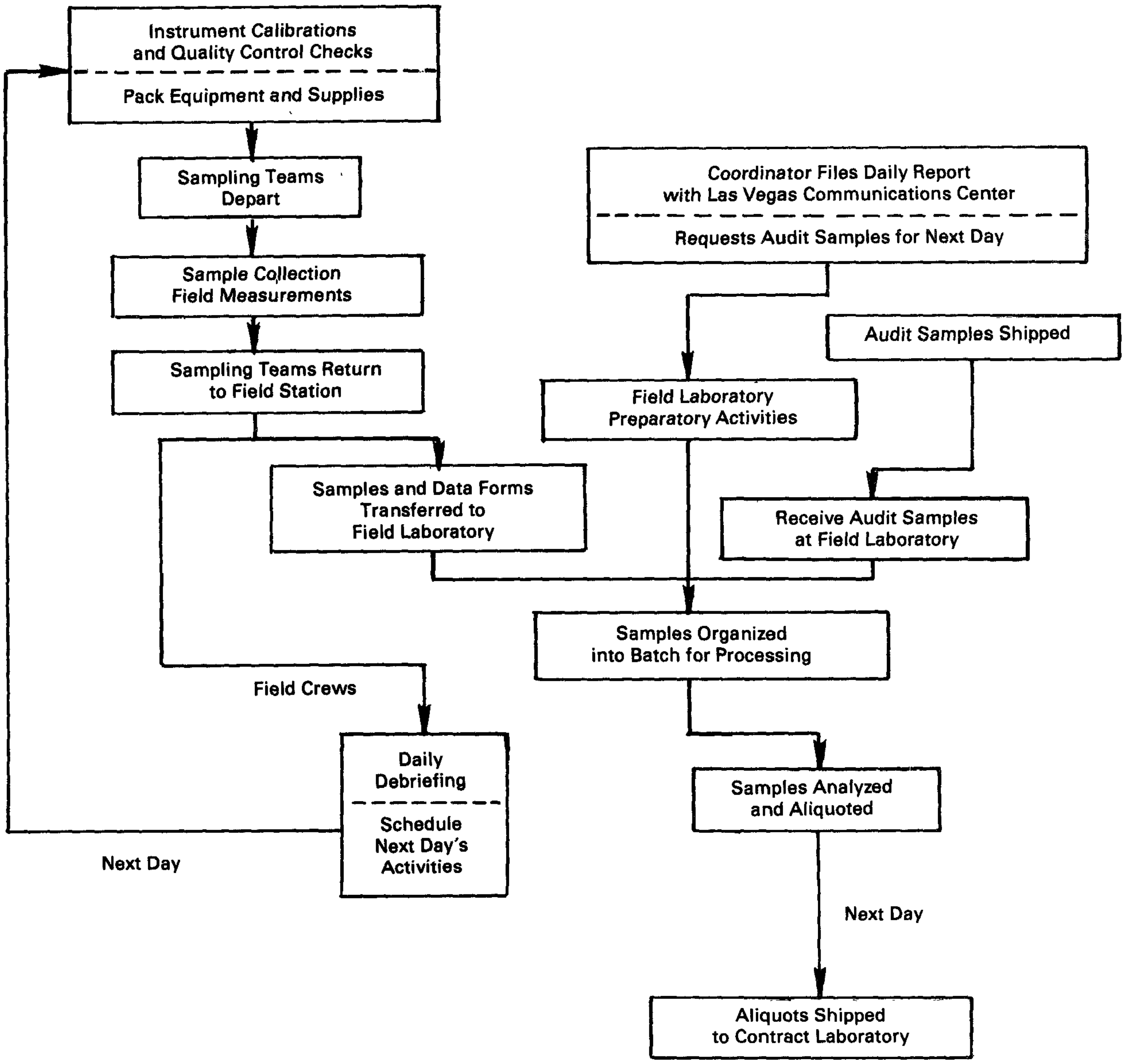
**DATA QUALIFIERS**

ⓧ = Others ________

**FIELD CREW DATA**

CREW ID ________
SAMPLER 1 ________
SAMPLER 2 ________
CHECKED BY ________

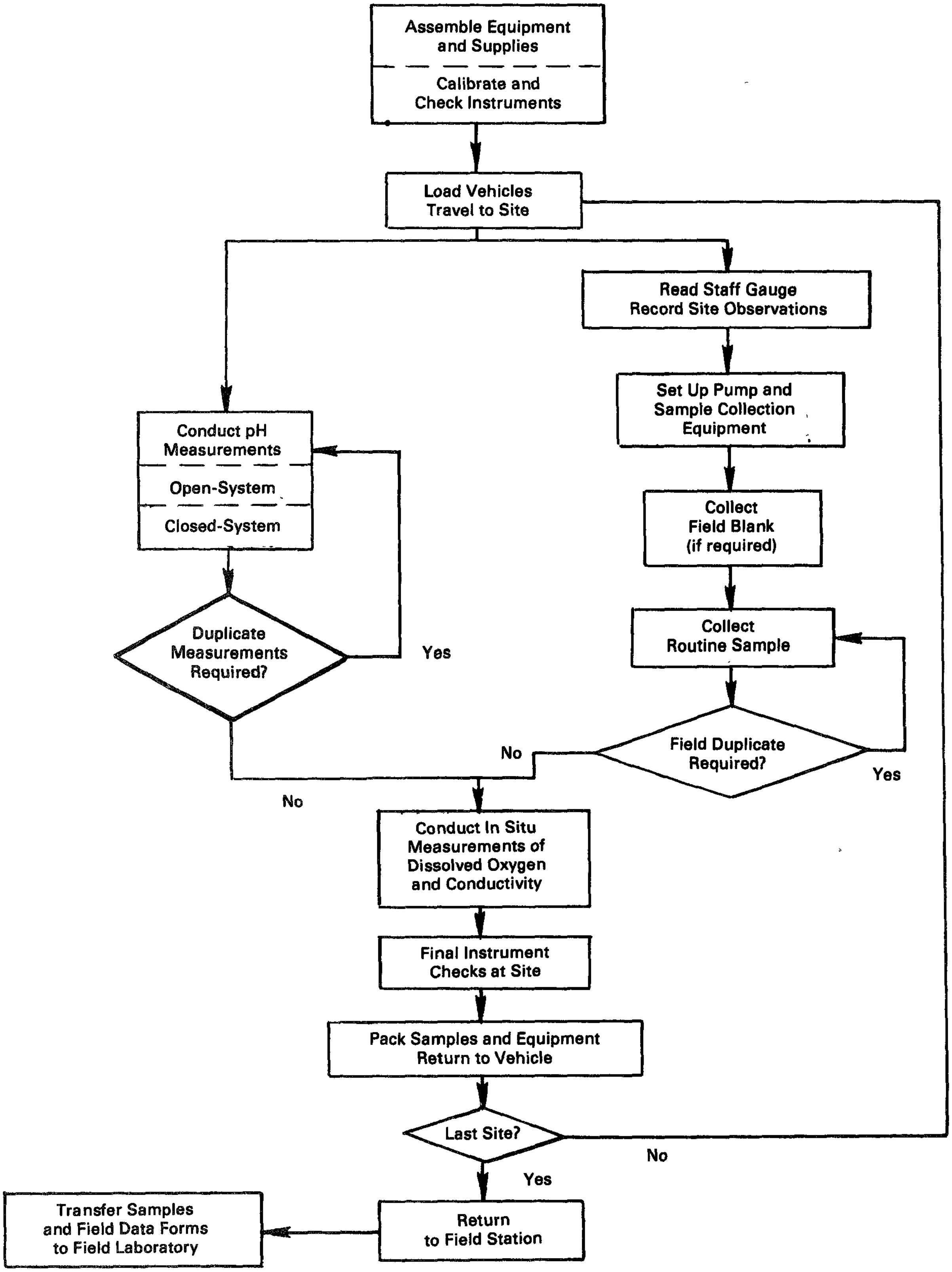
Figure 3-2. Daily field station activities in the Phase I-Pilot Survey.



blank" sample at the first site visited. Reagent grade deionized water (meeting ASTM Type I specifications), prepared daily with a Millipore Milli-RO/ Super Q System in the mobile laboratory, was pumped from the four-liter Cubitainers carried to the site into clean sample containers. One team chosen at random also filled a second set of sample containers (Cubitainer, syringes, and 500 ml bottle) with stream water from the pump immediately after the routine sample had been collected. This second sample was labeled as a "field duplicate" sample.

One of the most critical *in situ* measurements was pH. At the beginning of the study, there was concern that $CO_2$ present under highly supersaturated conditions in streamwater would de-gas rapidly from water samples held in open containers during the measurement, thus preventing a stable pH reading. In order to determine whether de-gassing might present a problem, two measurements of pH were conducted at streamside on different aliquots of sample. One measurement was made on an aliquot collected in a beaker. This aliquot was exposed to

Figure 3-3. Daily activities of the field sampling teams during the Phase I-Pilot Survey.



the atmosphere during collection and measurement, and was operationally defined as an open-system measurement. The second measurement was made on a sample collected in a 60 ml syringe and a flow-through sample chamber (described in Hillman et al., 1985). This arrangement allowed pH to be determined on aliquots that were not exposed to the atmosphere during collection and measurement. This was operationally defined as a closed-system measurement.

In both cases, pH was measured using a portable Beckman pHI-21 meter (automatic temperature compensated) equipped with a Ross combination electrode (Orion models 81-52 or 81-04). Field instruments were calibrated each day before use at the field station using commercially available high ionic strength buffer solutions (pH 7.00 and 4.00). A pH 4.00 ($10^{-4}$ N $H_2SO_4$) Quality Control Check Sample (QCCS) was used to check the calibration of the meter at each stream site. The meter was recalibrated if it failed to read between pH 3.90 and 4.10. At any site where a field duplicate sample was collected, duplicate open and closed pH measurements were made on a second sample collected from the stream (beaker or syringe). Protocols for both pH measurements are described in Knapp et al. (1987).

Specific conductance was measured using a YSI Model 33 meter. A $10^{-3}$ N KCl solution (specific conductance = 147 $\mu$S $cm^{-1}$ at 25°C) was used to check the factory calibration of the meters prior to each day's sampling. The calibration was checked at each stream site using a $10^{-4}$ N KCl solution (specific conductance = 74 $\mu$S $cm^{-1}$ at 25°C) as a QCCS. Failure to meet acceptable values for these checks (64-84 $\mu$S $cm^{-1}$) required recalibration of the meter. Following the QCCS, the probe was attached to the sampling boom and immersed into the stream in an area of flowing water. Measurements were taken at a depth of approximately 10 cm (mid-depth if the site depth was $< 10$ cm). Conductance and water temperature were recorded when the conductance reading changed less than 5 $\mu$S $cm^{-1}$ over a 1-minute period. A check was made using the QCCS after each *in situ* measurement.

Dissolved oxygen (DO) was measured using YSI Model 54 or 57 meters. The calibration was checked at the field station at the beginning and end of each day with a QCCS of water, saturated with bubbled air. Acceptable values of these checks were within $\pm$ 0.5 mg $O_2$/l of the calibration value. The meters were calibrated at each site using a chamber fabricated from a metal tube and rubber stoppers, containing water-saturated air. The DO probe was inserted into the chamber and the chamber was submerged in the stream for 15-20 minutes to provide a water-saturated atmosphere within the chamber. The meter was calibrated at each site based on the theoretical partial pressure of oxygen at ambient temperature and elevation. After calibration, the probe was removed from the chamber, attached to the sampling boom, and immersed into an area of flowing water to a depth of approximately 10 cm. Dissolved oxygen concentration and water temperature were recorded when the oxygen reading changed less than 0.5 mg $L^{-1}$ over a 1-minute period.

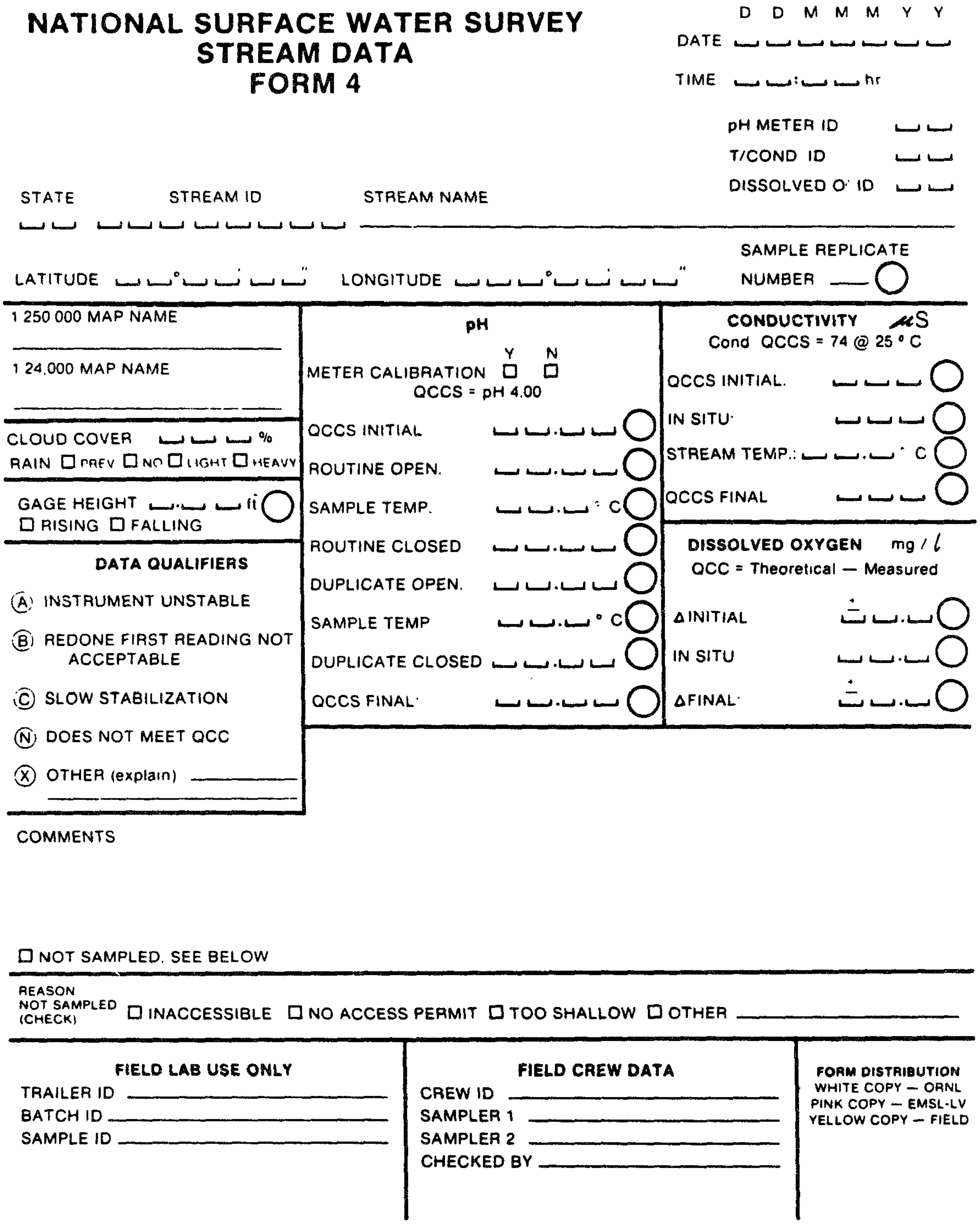
Additional measurements and observations recorded for each site included water stage, weather conditions, and any problems associated with sample collection or measurements. All data and observations were recorded in logbooks at streamside. Observations and final measurement values were later transcribed to a standardized field data form (Form 4, Figure 3-4). Failure to meet QC checks for any measurement was noted on the field form. Any changes in local watershed characteristics since the previous visit were recorded, and the site dossier was updated. A complete list of equipment and supplies used by the field teams is presented in Knapp et al. (1987).

### *3.3.3 Field Laboratory Operations*

A field laboratory was used for the Phase I-Pilot Survey in order to meet the 12-hour holding time requirement for preliminary analyses and the preservation/aliquoting steps. This field laboratory was housed in a trailer originally designed for the ELS and provided a "clean" environment for analyses and preparation of aliquots for analysis of chemical variables critical to the NSWS. Field laboratory analyses included pH, DIC, specific conductance, true color, turbidity, and aluminum fractionation. The specifications for this laboratory are described in Morris et al. (1986). The daily activities at the field laboratory are summarized in Figure 3-5.

The site coordinator received audit samples from an independent laboratory (Drousé et al., 1986) and streamwater samples from the field crews daily. Each sample was assigned an ID number, and all samples received and processed at the field laboratory on a given day constituted a field batch, which also was given a unique ID number. All containers associated with a given stream or audit sample were labeled with the appropriate batch and sample ID numbers. Once a batch was organized and labeled, the bulk water and syringe samples were transferred to the laboratory supervisor for processing and analysis. Aliquots for total suspended solids were transferred to the environmental science laboratory at Southwestern Technical College for

**Figure 3-4. NSS Data Form 4: Stream Data.**



NATIONAL SURFACE WATER SURVEY
STREAM DATA
FORM 4

DATE D D M M M Y Y
TIME __ __ : __ __ hr

pH METER ID __ __
T/COND ID __ __
DISSOLVED O' ID __ __

STATE __ __ STREAM ID __ __ __ __ __ __ __ __ STREAM NAME ____________

LATITUDE __ __ ° __ __ ' __ __ " LONGITUDE __ __ __ ° __ __ ' __ __ "

SAMPLE REPLICATE NUMBER ___ ○

1 250 000 MAP NAME ____________

1 24,000 MAP NAME ____________

CLOUD COVER __ __ __ %
RAIN ☐ PREV ☐ NO ☐ LIGHT ☐ HEAVY

GAGE HEIGHT __ . __ __ ft ○
☐ RISING ☐ FALLING

**DATA QUALIFIERS**

- Ⓐ INSTRUMENT UNSTABLE
- Ⓑ REDONE FIRST READING NOT ACCEPTABLE
- Ⓒ SLOW STABILIZATION
- Ⓝ DOES NOT MEET QCC
- Ⓧ OTHER (explain) ____________

**pH**

METER CALIBRATION Y ☐ N ☐
QCCS = pH 4.00

| | | |
|---|---|---|
| QCCS INITIAL | __ __ . __ __ | ○ |
| ROUTINE OPEN. | __ __ . __ __ | ○ |
| SAMPLE TEMP. | __ __ . __ ° C | ○ |
| ROUTINE CLOSED | __ __ . __ __ | ○ |
| DUPLICATE OPEN. | __ __ . __ __ | ○ |
| SAMPLE TEMP | __ __ . __ ° C | ○ |
| DUPLICATE CLOSED | __ __ . __ __ | ○ |
| QCCS FINAL | __ __ . __ __ | ○ |

**CONDUCTIVITY** µS
Cond QCCS = 74 @ 25 ° C

| | | |
|---|---|---|
| QCCS INITIAL | __ __ __ | ○ |
| IN SITU | __ __ __ | ○ |
| STREAM TEMP. | __ __ . __ ° C | ○ |
| QCCS FINAL | __ __ __ | ○ |

**DISSOLVED OXYGEN** mg / l
QCC = Theoretical — Measured

| | | |
|---|---|---|
| Δ INITIAL | ± __ __ . __ | ○ |
| IN SITU | __ __ . __ | ○ |
| Δ FINAL | ± __ __ . __ | ○ |

COMMENTS

☐ NOT SAMPLED, SEE BELOW

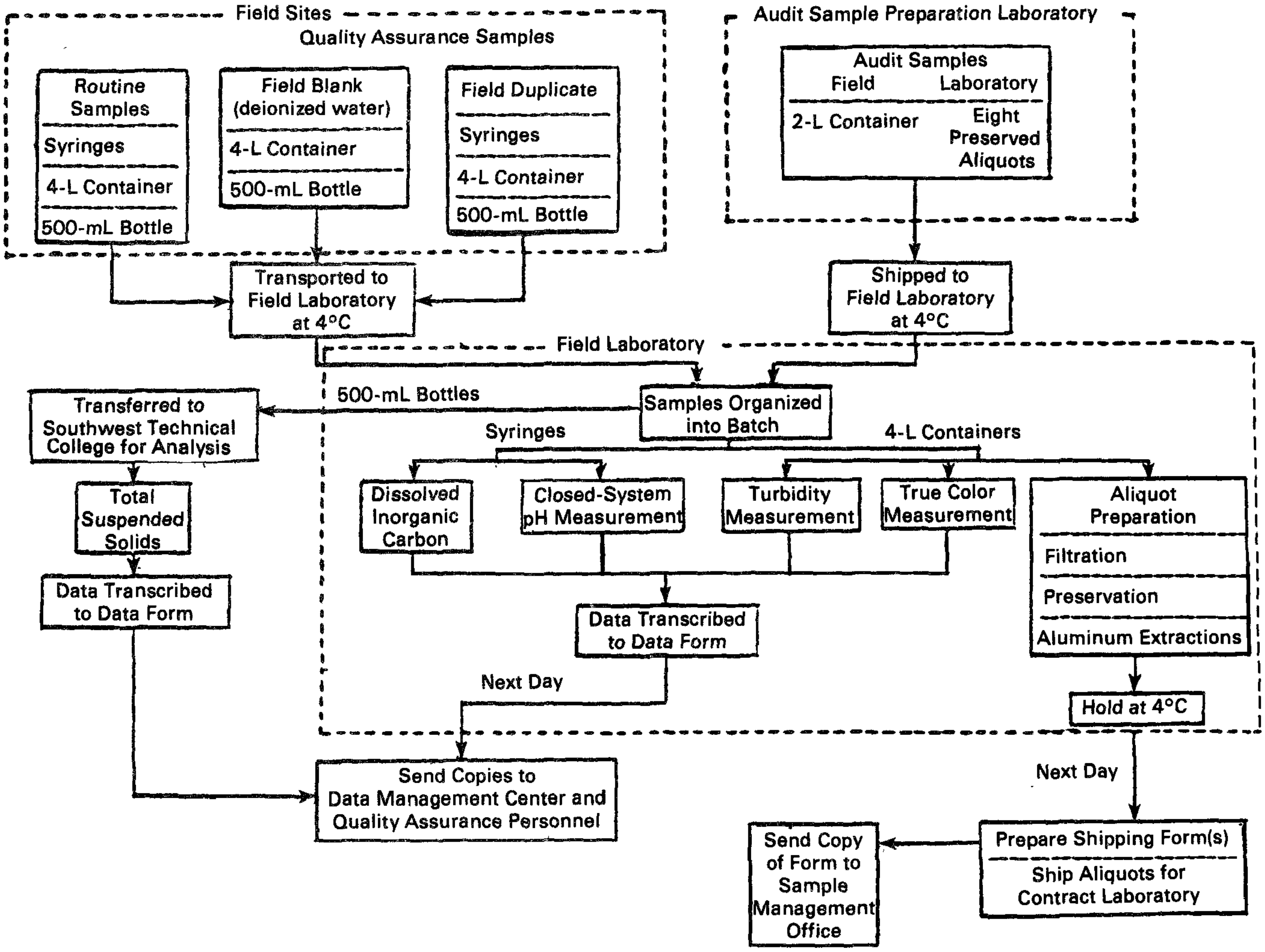
REASON NOT SAMPLED (CHECK) ☐ INACCESSIBLE ☐ NO ACCESS PERMIT ☐ TOO SHALLOW ☐ OTHER ____________

**FIELD LAB USE ONLY**
TRAILER ID ____________
BATCH ID ____________
SAMPLE ID ____________

**FIELD CREW DATA**
CREW ID ____________
SAMPLER 1 ____________
SAMPLER 2 ____________
CHECKED BY ____________

**FORM DISTRIBUTION**
WHITE COPY — ORNL
PINK COPY — EMSL-LV
YELLOW COPY — FIELD

Figure 3-5. Daily activities at the field laboratory during the Phase I-Pilot Survey.



analysis. Details of the field laboratory analytical and sample processing protocols are presented in Hillman et al. (1985).

One syringe sample from each stream or audit sample was allowed to reach ambient temperature for pH determination. All other containers were stored at approximately 4°C until analysis or processing. The laboratory supervisor conducted the DIC and pH determinations. One analyst prepared fractions for subsequent analysis of total extractable and non-exchangeable aluminum, and the other analyst prepared the other six aliquots from each bulk water or audit sample indicated in Table 3-2. All aliquoting was conducted in a laminar flow hood to avoid contamination. The third analyst conducted turbidity and true color determinations, and preserved the aliquots as they were prepared by adding concentrated acid and/or refrigerating them.

One sample in each batch was designated as a "trailer duplicate" for purposes of analyzing duplicate precision for mobile laboratory analyses. Two aliquots of this sample from each syringe were analyzed for DIC and pH, respectively. Two subsamples were prepared from the bulk sample and analyzed for turbidity and true color. All quality assurance protocols for these analyses and processing steps are described in Drousé et al. (1986).

After all aliquots had been prepared and preserved, they were sealed, bagged individually, and the data transcribed to a standardized form. Aliquots were held at approximately 4°C overnight. The following morning, aliquots were packed with standardized shipping forms into insulated containers with enough chemical refrigerant packs to maintain samples at approximately 4°C during transport. Aliquots were shipped to the contract analytical

Table 3-2. **List of NSS Aliquots, Containers, and Preservatives***

| | Aliquot (Container) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 (250 ml) | 2[a] (10 ml) | 3[a] (250 ml) | 4[a] (125 ml) | 5[a] (500 ml) | 6[a] (125 ml) | 7 (125 ml) | 8[a] (10 ml) |
| Preservative and Description | Filtered, pH <2 with $HNO_3$ | Filtered MIBK-HQ Extract | Filtered, no Preservative | Filtered, pH <2 with $H_2SO_4$ | Unfiltered no Preservative | Filtered, pH <2 with $H_2SO_4$ | Filtered pH <2 with $HNO_3$ | Filtered MIBK-HQ Extract |
| Parameters | Ca (180) | Total Extractable Al (7) | $Cl^-$ (28) | DOC (14) | pH (14) | Total P (28) | Total Al (180) | Non-exchangeable extractable Al (7) |
| | Mg (180) | | $F^-$ (28) | $NH_4$ (28) | BNC (14) | | | |
| | K (180) | | $SO_4^{2-}$ (28) | | ANC (14) | | | |
| | Na (180) | | $NO_3^-$ (7) | | Specific Conductance (14) | | | |
| | Mn (180) | | $SiO_2$ (28) | | DIC (14) | | | |
| | Fe (180) | | | | | | | |

*Maximum permitted holding times from date of sampling are shown in days in parentheses with each variable.
[a]Stored at 4°C in the dark.

laboratory via overnight courier service. Copies of the field and field laboratory data forms were sent to the data management center at ORNL and to quality assurance personnel at EMSL-LV. Copies of the shipping forms were sent to the NSS sample management office (Viar and Company, Alexandria, Virginia).

## 3.4 Evaluation of Equipment and Methods

Selection of equipment and protocols initially proposed for use in the Phase I-Pilot Survey was based on consultation with experienced researchers, previous experience in NSWS projects, and procurement constraints. The three tasks identified for investigation included: (1) evaluation of meters for suitability in the field; (2) evaluations of different techniques; and (3) study of the possible effects of extending sample holding times beyond 12 hours. Details of the equipment and methods evaluation are presented in Knapp et al. (1987).

### *3.4.1 Equipment Evaluation*

Field meters were evaluated on the basis of field tests, laboratory tests, ease of use, portability, and overall durability. The Beckman pHI-21 pH meter equipped with an Orion Ross 81-04 pH electrode etched with 50% NaOH prior to use was used for all streamside pH measurements. Enclosing the meter in a plastic bag and devising a special carry case similar to that used for small cameras greatly increased the suitability of the instrument for field use. The YSI Model 33 S-C-T meter, although not temperature compensating, was used for making field conductivity measurements. YSI Model 54 and 57 meters with membrane-type probes were used for measuring dissolved oxygen. All meters were found to be satisfactory, and were recommended for use in Phase I.

### *3.4.2 Methods Evaluations*

Field methods were developed based upon recommendations of instrument manufacturers and researchers and on similarity to methods described in the ELS methods manual (Hillman et al., 1986b). Modifications of these methods were evaluated during field sampling. Some modifications were developed and adopted immediately (e.g., pH) and some were evaluated and rejected. The following sections summarize the evaluations of several field methods. Details of the procedures as adopted for Phase I can be found in Hagley et al. (1986).

#### 3.4.2.1 Filtration Methods

Streamside filtration of samples was attempted in an effort to avoid potential deterioration of samples before delivery to the mobile laboratory. In a field evaluation conducted over several days, a filtration apparatus (Nalgene cartridge filtrator) which used disposable filters (Gelman 47 mm diameter, 0.45 μm pore size Metricel) was fitted into the Tygon pump line. The filtration apparatus was used on both the suction and the discharge side of the pump in an evaluation conducted over a period of three days by teams collecting samples from a total of 16 streams. Drawbacks included a high potential for sample contamination during filter replacement or filter rupture, unacceptably long filtration times, and a requirement for additional rinse water and supplies. It was concluded that in-line filtration at streamside was not practical.

### 3.4.2.2 Streamside pH Measurements

Two methods of streamside pH measurement were performed at each stream throughout the Phase I-Pilot Survey. A closed-system method using a syringe was designed to measure the pH of a sample without atmospheric contact. An open-system method, developed by the U.S. Geological Survey, was also evaluated. Early in the study, an experiment was conducted to evaluate the equivalence of these two methods and to compare each pH measurement technique on samples collected using a pump versus grab samples collected directly from a stream. Three replicate samples of each treatment combination (method x collection device) were measured at each of three streams. A two-way analysis of variance detected no significant differences ($p = 0.05$). Several experimental devices designed to make *in situ* measurements without developing a streaming potential also were tested and showed no statistically significant differences from either open or closed-headspace streamside measurements (Knapp et al., 1986).

Following the completion of field data collection, the open and closed field pH measurements were compared with the mobile lab pH measurement (variable PHSTVL) to determine the degree of equivalence among the three techniques. All analyses were based on samples collected during the summer period, during which all field protocols had been finalized. Paired t-tests, unweighted for each inclusion probability, indicated no significant difference between the two streamside measurements, and a statistically significant but unimportant difference of 0.03 units between the streamside and mobile laboratory closed pH measurements ($p = 0.05$). (Water equilibrated with 300 ppm v/v $CO_2$ at the contract analytical laboratory showed a significantly higher pH value than the closed headspace measurements, owing most likely to the $CO_2$ supersaturation common in small streams).

Linear regressions were performed to compare the ability to predict the field laboratory closed pH value on the basis of either of the field methods (Figure 3-6). The slopes of the regression lines were virtually identical and not significantly different from unity (0.995). Although the closed field pH was a slightly better predictor of field lab pH based on a smaller mean standard error of the estimate, the open field pH measurement was chosen because of its logistic simplicity. It is important to note that the open and closed field pH techniques gave very similar results; a bias adjustment of 0.03 units yielded virtually identical population distributions. However, it is not known which pH measurement technique (open or closed) is more accurate. The choice of the field lab closed measurement to express most of the Phase I-Pilot Survey population estimates was based primarily on consistency with the NLS data (Linthurst et al., 1986).

### 3.4.2.3 Aluminum Methods

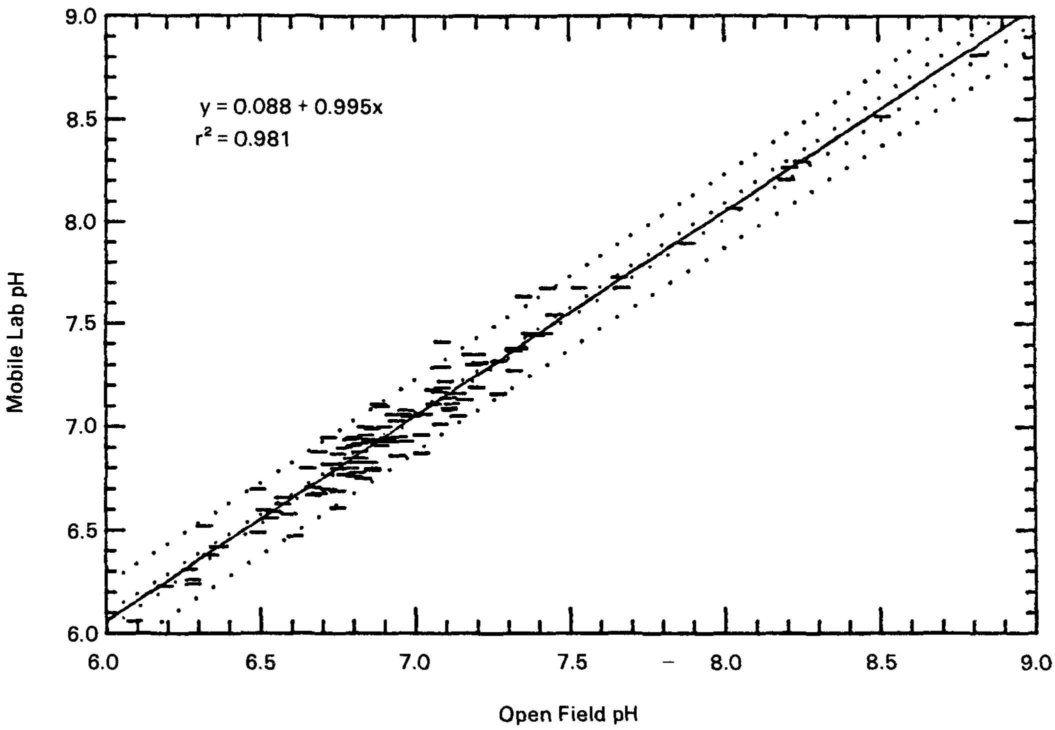
The Phase I-Pilot Survey employed a previously untested (in the NSWS) protocol for fractionation of MIBK extractable (monomeric) aluminum into non-exchangeable (organic) and exchangeable (inorganic) forms. The exchangeable fraction was calculated as the difference between total extractable aluminum and the non-exchangeable fraction which are measured directly. The determination of non-exchangeable aluminum involved passing aliquot #8 (Table 3-2) through a cation exchange column prior to complexation with 8-hydroxyquinoline and extraction into methyl isobutyl ketone (MIBK). Total extractable aluminum was determined similarly, except the aliquot was not passed through the exchange column. Details of the procedure are described by Hillman et al., (1986a).

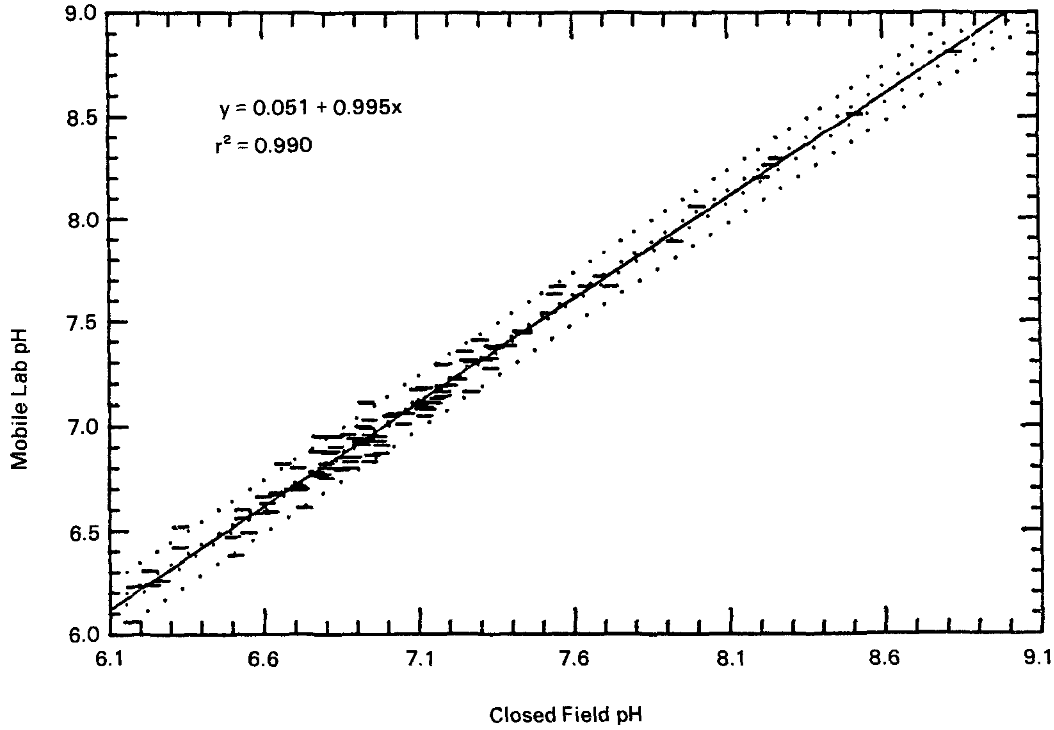
The ion exchange resin (Amberlite 125) had to be conditioned before use so that the pH of the resin column was within 0.5 pH unit of the expected sample pH. Columns were conditioned by adjusting a solution of $10^{-5}$ N NaCl to the desired pH with HCl or NaOH. This solution was passed through the resin column, collected, and the pH measured. This process was repeated until the desired column pH was achieved.

Following preparation of the column, a 125 ml aliquot of sample was filtered into a 250 ml Pyrex beaker that had been washed with 5% $HNO_3$ and rinsed with deionized water. Portions of the filtered aliquot were used to rinse a 50 ml polycarbonate centrifuge tube. The remainder was pumped through the ion-exchange column (30 ml/min). The first 30 ml of sample from the column were discarded. The next 20 ml were collected and analyzed for pH, and the following 25.0 ml volume was collected in the centrifuge tube. The column was then flushed with the buffer solution, and an aliquot of the buffer was collected from the column. The pH of this aliquot was measured to ensure that the column was conditioned properly for the next sample. The aliquot in the centrifuge tube was complexed and extracted into MIBK.

Adjusting the pH of the NaCl solution was often very time-consuming, and the solution was not stable over time. Allowing the solution to equilibrate with the atmosphere overnight before adjusting the pH sometimes improved stability, however. During

**Figure 3-6.** Comparison of three pH methods used in the Phase I-Pilot Survey. Confidence bounds (90 and 95%) about the regressions are shown.





laboratory operation, 3 to 4 different columns had to be prepared daily to cover the range of sample pH values, and there was no standard solution of non-exchangeable extractable aluminum that could be used as an audit sample to check on the accuracy of the procedure. A new, automated monomeric aluminum speciation and measurement technique using pyrocatechol violet has been instituted in Phase I to overcome some of these difficulties (Dougan and Wilson, 1974; Rogeberg and Henriksen, 1985).

### *3.4.3 Holding Time Studies*

The 12 hour holding time protocols established for the National Lake Survey (in which helicopters were used to collect and transport samples) set significant limits on the area that could be served by a mobile laboratory because of driving time constraints. A set of pilot experiments were conducted on five streams in the Southern Blue Ridge to evaluate the stability of syringe and Cubitainer samples over periods of 5, 12, 24, and 48 hours. Although the experiment yielded little indication of changes in any of the parameters, the number of audit samples included was insufficient to establish the degree of within-treatment analytical variability or among-treatment analytical bias.

Two experiments were designed to overcome these obstacles: (1) a laboratory study aimed at establishing the $CO_2$-impermeability of the syringes under markedly sub- or super-saturated conditions; and (2) a field test of Cubitainer samples collected on a number of lakes and streams in the Eastern U.S. These experiments are documented thoroughly by Burke and Hillman (1986) and Stepanian et al. (1986), respectively, and the results are briefly summarized here.

#### 3.4.3.1 Syringe Experiment

In the syringe experiment, syringes filled with 1 mg $L^{-1}$ $Na_2CO_3$ solution at $pCO_2$ levels of 0x, 1x, 10x, and 100x atmospheric levels (atm) were held for 1 to 8 days at 4°C and 25°C. Companion experiments were conducted to test the ability of the experiment to detect $CO_2$ equilibration in open systems that were similarly sub- or super-saturated and blanks, 10 ppm $CO_2$, and pH 4 $H_2SO_4$ QCCS samples. Open containers containing 0 and 100 x atm $pCO_2$ equilibrated within 24 hours. Conversely, none of the samples showed significant changes in DIC or pH over 7 to 8 days when held in syringes at 4°C and 11°C (Table 3-3). Syringes did gain or lose DIC when held at room temperature, however, apparently due to increased permeability of the polypropylene syringe walls. Experiments with actual lake samples at 0.1-0.2 x atm $pCO_2$ produced similar results (Burke and Hillman, 1986).

**Table 3-3. Dissolved Inorganic Carbon Concentrations (mg $L^{-1}$ ± 1 s.d.) in Samples Initially Sub- or Supersaturated with $CO_2$ and held for 7-8 Days**

| $pCO_2$ | Temp (°C) | Time (Days) 0 | Time (Days) 7-8 |
|---|---|---|---|
| 0 × atm | 10 | 1.548 ± 0.023 | 1.514 ± 0.036 |
| 0 × atm | 23—26 | 1.548 ± 0.023 | 1.757 ± 0.023 |
| 1 × atm | 11 | 2.134 ± 0.003 | 2.078 ± 0.037 |
| 1 × atm | 23—27 | 2.134 ± 0.003 | 2.286 ± 0.036 |
| 10 × atm | 8 | 2.840 ± 0.038 | 2.857 ± 0.068 |
| 10 × atm | 22—26 | 2.840 ± 0.038 | 2.927 ± 0.088 |
| 100 × atm | 4 | 12.41 ± 0.12 | 12.02 ± 0.15 |
| 100 × atm | 22—26 | 12.41 ± 0.12 | 9.44 ± 0.22[a] |

[a] Variance of 24-30 repeated measures on test samples in a treatment ≤ analytical variance of quality control check (QCCS) samples analyzed along with the treatments ($\alpha = 0.05$).

Based on these experiments, it was determined that the holding protocol for DIC and pH held in syringes at 4°C could safely be increased to 24 hours. Although no experiments were performed on aluminum, it has been assumed that syringe aliquots can also be held for at least 24 hours prior to aluminum extraction. It is assumed that pH changes driven by $CO_2$ degassing are the most significant cause of alteration in aluminum speciation in samples held for at least 5 to 6 hours prior to extraction.

#### 3.4.3.2 Cubitainer Experiment

In the Cubitainer holding time experiment, two 19-liter samples were collected in June, 1985, from three lakes in New York, three streams in Pennsylvania, two streams in Maryland, and one stream each in South Carolina and Tennessee. These water bodies represent a wide range of water chemistry types. Samples were transported at 4°C by air within 12 hours of collection to the field laboratory, where they were each split into eight aliquots. Two aliquots were processed immediately (12 hours), while the remainder were held at 4°C, and duplicates processed after 24, 48, and 84 hours, respectively. Duplicate QA audit samples from Big Moose Lake, New York, were analyzed with each batch. All analyses were performed according to regular NSS protocols.

The results of the Cubitainer holding time experiment are presented in Table 3-4. Two criteria were utilized in assessing the significance of observed changes. First, all data that are below the limit of detection for that variable were excluded (see Table 4-9). For the remaining sample pairs, the percentage increase or decrease between each analyte concentration at 12 hours holding time and the 24, 48, or 84 hours holding times was calculated. Each percentage then was compared with the maximum root mean square

**Table 3-4. Changes in Constituent Concentrations in Duplicate Field Samples and Big Moose Lake QA Audits Held at 4°C for 12, 24, 48, and 84 Hours Prior to Stabilization***

| Chemical Variable | Pairs (n) | Mean Percent Change in Field Samples | | | System Precision | Mean Percent Change in Audit Samples | | |
|---|---|---|---|---|---|---|---|---|
| | | 12–24 hr | 12–48 hr | 12–84 hr | RMS RSD (%)[a] | 12–24 hr | 12–48 hr | 12–84 hr |
| ANC | 9 | 1.1 | 1.7 | 0.5 | 5.0 | [c] | [c] | [c] |
| Sulfate | 10 | −2.3 | −2.0 | −2.8 | 3.3 | −2.6 | −1.1 | 2.8 |
| Nitrate | 10 | −4.9 | −5.2 | −4.5[b] | 5.9 | −12.7 | −17.0 | −1.9 |
| Chloride | 10 | −2.0 | −1.4 | −3.4[b] | 2.2 | −0.5 | 2.7 | 1.1 |
| Silica | 10 | 1.2 | 0.2 | 0.6 | 8.0 | 0.2 | −0.2 | 0.0 |
| Fluoride | 10 | 0.0 | −1.2 | −2.2[b] | 2.1 | 0.7 | −4.6 | −0.7 |
| Calcium | 10 | 3.1[b] | 3.6 | 0.8 | 2.3 | 2.6 | 5.3 | 0.5 |
| Magnesium | 10 | 1.2 | 0.5 | 1.4 | 1.1 | 1.9 | 2.1 | 1.8 |
| Sodium | 10 | −0.2 | −0.3 | −1.4[b] | 1.1 | 0.8 | −0.1 | −0.7 |
| Potassium | 10 | 2.4 | 3.0 | 0.7 | 3.8 | 0.9 | 1.6 | −0.8 |
| DIC (equil) | 9 | 2.5 | 8.5 | 7.9 | 9.8 | [c] | [c] | [c] |
| pH (equil) | 10 | 0.0 | −0.02 | −0.02 | 0.1 | 0.0 | 0.0 | 0.0 |
| DOC | 9 | 0.4 | −5.5 | 4.8 | 6.2 | −0.7 | 2.3 | 5.0 |
| Ammonium | 4 | 0.1 | 14[b] | 13[b] | 10 | 2.8 | 1.4 | −1.4 |
| Total P | 3 | −3.7 | 14[c] | 4.4 | 5.1 | [c] | [c] | [c] |
| Total Al | 6 | 39[b] | 9.7 | 12 | 20 | 28 | 8.3 | 12 |
| Extractable Al | 6 | −2.5 | 12 | 3.8 | 12 | 4.8 | 25 | −8.2 |
| Iron | 9 | 20 | 25 | −36 | 25 | 3.0 | 5.9 | −20 |
| Manganese | 9 | 4.4 | −21[b] | −16 | 8.9 | 5.6 | 3.9 | 1.1 |

*Underlined values exceed the RMS %RSD for routine/duplicate precision.

[a] Root mean square percent residual standard deviation.

[b] Exceeds interbatch bias as determined by changes in the audits.

[c] No bias estimate could be calculated.

percent residual standard deviation (RMS % RSD) for routine duplicate sample pairs analyzed during the Phase I-Pilot Survey (Table 4-9). If the percentage difference between the analyses at two different holding times was less than the routine/duplicate differences typically expected to occur within the same batch, then differences resulting from > 12 h holding times were indistinguishable from routine sampling and analytical error. Several variables show discernible differences, but only four variables exhibited potentially distinguishable changes between 12 and 24 hours (nitrate, calcium, magnesium, and total aluminum).

The foregoing analysis does not include the effects of interbatch analytical bias, however. A measure of interbatch analytical bias was obtained by analyzing duplicate QA audit samples from Big Moose Lake, New York, with each batch of samples. This QA audit has been shown to be chemically stable for the variables of interest over holding periods of several months (Table 4-3; Drousé et al., 1987). Percentage changes in each variable were calculated for the QA duplicates for the four holding time intervals and are also shown in Table 3-4. If the chemical analytes are truly stable in the audit samples, then these changes represent the degree of interbatch analytical bias in the holding time experiment (again, concentrations below the limit of detection were excluded).

Of the discernible analyte changes based on the estimated within-batch precision, most were accompanied by at least the same degree of interbatch bias. The differences that exceeded the apparent interbatch bias are asterisked in Table 3-4. Only two variables, calcium and total aluminum, appear to show possible changes between 12 and 24 hours. The 3% change in calcium is barely detectable above the analytical precision and is of no practical interpretive significance. The large percentage changes in total aluminum, as with iron, manganese, and total phosphorus after 48 hours, probably result in part from sampling errors associated with the colloidal nature of these constituents in streams. A great deal of precision is neither expected nor needed for these variables in streams. Ammonium is the only other constituent seen to change in 48 hours. Although the increase may be a result of organic nitrogen mineralization, the increases also are barely greater than the analytical variance.

It should be noted that the choices of 1 RMS RSD and various other decision criteria in this analysis are rather arbitrary, and no rigorous statistical testing is implied. Instead, this interpretation should be thought of as a screening procedure by which to focus attention on the variables most likely to have experienced changes after 12 hours. Also, the experiment does not assess the probability of chemical changes during the 12 hours between sample collection and analysis. Any regional survey activity must be predicated on the stability of samples for this period, or on the assumption that any changes that do occur are minimal, quantifiable by calibration, or of no interest (e.g., speciation changes for some variables may not affect the types of interpretations to be expected from synoptic data sets). Secondly, it is very difficult to perform a holding time experiment such as the one described above that incorporates a reasonable range of geographic variability with a high degree of statistical discriminatory power. Thus far, the data have been analyzed using at least three different approaches, including various group means and treatment of the audit data (Overton, personal comm.; Stapanian et al., 1986), including a multivariate statistical Hoteling-Lawley trace approach.

All analysts have concluded that there is no important effect of increasing the sample holding times to as much as 48 hours. This is not to say that no sample will change in this time, but that the frequency and magnitude of such changes are probably acceptable in terms of the data quality objective of the project.

## 3.5 Summary of Field Operations

The Phase I-Pilot Survey was completed as scheduled on July 17, 1985. In completing the sampling activities, the three field crews traveled approximately 45,000 miles by vehicle, averaging 270 miles per day to access 1 to 3 stream sites. Most stream sites were accessible by vehicle alone. A few sites required additional transport by horseback or boat. The longest hike required to a site was 16 miles round trip. A total of 339 reach sites were sampled during the survey, 724 samples were processed by the field laboratory, and 668 samples were shipped to the contract analytical laboratory. Only one shipment of samples was delayed during the entire operation.

The field operations plan implemented during the Survey worked very well and was not modified during the study. The preliminary reconnaissance activities and contacts with local cooperators were integral to the success of the field operations plan, and served to minimize unexpected problems associated with site access and daily sampling itineraries. The few problems that were encountered were caused by outdated maps and these were quickly rectified. Training for field sampling personnel in the future will provide more details on the selection criteria for a suitable sampling location at a given stream site. Additional training in field hydrology will ensure that staff gauges are placed correctly at all locations.

Experience in the field demonstrated that, in most cases, equipment initially selected for use in the Survey was adequate. A sensitive, portable conductivity meter will not be needed because conductivity will also be measured at the field laboratory on a research-grade instrument. Comparisons of the two streamside pH protocols indicate that the more difficult "closed" measurement is not needed, because $CO_2$ de-gassing is apparently sufficiently slow in unstirred natural waters. Results from the holding time experiments indicate that the holding time protocols can probably be safely increased to at least 24 hours, provided aluminum samples are held in the $CO_2$-tight syringes.

# 4. Quality Assurance and Data Management

## 4.1 Introduction

The water quality data gathered in the National Stream Survey constitute a large and important research data base that requires a high degree of quality assurance (QA) and quality control (QC). Maintaining a high degree of QA/QC involves two separate but highly integrated tasks. The first task is to establish a QA/QC program to ensure that all samples are collected and analyzed in a consistent manner and to establish the accuracy and precision of the reported values with a known degree of confidence. Second, a data management program must be designed to store and track the data, identify and eliminate entry errors, and keep a record of such changes. Ultimately, the product of these tasks will be well-documented data files that are readily accessible to project scientists and extramural users.

## 4.2 Quality Assurance/Quality Control Operations

This section provides an overview of the QA/QC activities in field sampling, field laboratory, and contract analytical laboratory operations. Elements of the QA/QC program include contract laboratory performance evaluations, on-site auditing of field and contract laboratories, specification of all sample handling protocols, and utilization of a variety of QA/QC samples. Detailed discussion of these elements can be found in the Project QA Plan (Drousé et al., 1986).

### *4.2.1 Selection of Contract Analytical Laboratories*

The objective of the analytical laboratory selection process was to award contracts to the smallest number of laboratories possible in order to minimize potential interlaboratory bias, while ensuring that each laboratory chosen could analyze the required number of samples within the specified holding time and quality performance criteria. The Contract Laboratory Program (CLP) established to support the EPA's hazardous waste monitoring activities was used in laboratory procurement. The contract process required: (1) preparation of a statement of work (SOW) that defined the analytical and QA/QC requirements in a contractual format; (2) preparation and advertisement of an Invitation for Bids (IFB) to solicit contractor support; and (3) evaluation of the lowest bidders to ensure that qualified laboratories were selected.

An SOW was prepared to document the analytical methods and the QA/QC requirements that are defined in the Analytical Methods Manual (Hillman et al., 1986b) and Project QA Plan (Drousé et al., 1986), and to specify these requirements in a contractual format. An IFB was advertised in the *Commerce Business Daily* in December 1984. Approximately 180 laboratories responded and were sent copies of the SOW. The lowest bidders were sent pre-award performance evaluation (PE) samples. These laboratories were required to analyze high- and low-concentration PE samples and to report results within 15 days of sample receipt. The data reports were evaluated for quality and completeness.

Two laboratories scoring 88 percent subsequently were visited by an EPA team to verify their qualifications and capabilities to meet the contractual requirements. Both laboratories passed the PE sample analysis and on-site evaluations and were awarded contracts to provide analytical support to the Phase I-Pilot Survey. Only the New York State Department of Health (NYSDOH) laboratory received samples during the survey, however, because they were the lowest bidder and possessed ample capacity to analyze all of the samples.

### *4.2.2 Training*

Data quality depends on the ability of the project personnel to properly collect, process, and analyze samples, and training is essential in ensuring consistent application of all operational and quality assurance procedures. Field laboratory personnel underwent a five-day training period in Las Vegas, Nevada, in all technical aspects of laboratory operations.

### *4.2.3 Daily Quality Assurance Contact*

During sampling and analysis, the QA staff communicated daily with the field station and the contract laboratory to monitor logistics, methods, and QA/QC activities. These communications were crucial and effective in identifying and resolving issues affecting data quality at an early stage (see Section 4.6.2). Each communication was logged either on a field communication form or in a bound laboratory notebook.

### *4.2.4 Field and Contract Laboratory Audits*

On-site evaluations of the contract laboratory and the field station were conducted during the survey to assure that sampling and analysis activities were being performed as planned. The contract laboratory was visited once before sampling started and once during field activities. The purpose of the first on-site visit was to assure that the analytical laboratory had the capability to perform the required analyses. During the second on-site evaluation, QA/QC data were reviewed and several issues were identified and resolved. For example, it was discovered that NYSDOH was analyzing pH and DIC at different times, and was experiencing problems with the air-equilibrated pH measurement. All observations were summarized in an on-site laboratory evaluation report.

Auditors also conducted an in-depth review of field laboratory operations and interviewed the sampling teams. During the on-site evaluation, the auditors observed that the trailer was near a road where a large amount of dust was present, resulting in elevated total aluminum values in some samples. The auditors recommended moving the field laboratory to a nearby dust-free location. Samples processed after relocation of the trailer indicated no further contamination. Also as a result of the review, calibration activities were relocated to a heated building to avoid slow meter response times on cold mornings.

### *4.2.5 Field Sampling Quality Control Procedures*

The QC procedures consisted of calibrating all instruments before and after each sampling trip and monitoring any changes between calibrations. The procedures are described in detail in Knapp et al. (1987) and are discussed in Chapter 3 of this report. The calibration check for temperature was to compare the field meter reading to that determined using an NBS-traceable thermometer. The reading had to be within 2°C to meet QC criteria. A QCCS having a theoretical pH value of 4.00 was analyzed prior to and following all streamside pH determinations. If any QCCS reading deviated from the theoretical pH by more than ± 0.1 pH unit, the instrument was recalibrated and the pH of the QCCS was remeasured. If the reading still did not meet the specifications, then a data qualifier was recorded on the Stream Data Form 4 (Figure 3-4). The *in situ* specific conductance measurement was verified by checking the factory calibration of the conductivity meter by measuring QCCSs of 147 $\mu S\ cm^{-1}$ and 74 $\mu S\ cm^{-1}$. The allowed error for the QCCSs were $\pm$ 15 $\mu S\ cm^{-1}$ and $\pm$ 10 $\mu S\ cm^{-1}$, respectively. The QC check for dissolved oxygen consisted of calibrating the meter with water-saturated air, and then measuring the dissolved oxygen in a sample taken from a carboy of water saturated by bubbling with compressed air. The readings had to be within 0.5 mg $L^{-1}$. There were no QC checks for staff gauge and other stream site data (Table 2-3).

All streamside and in situ measurements and QC data were recorded on Stream Data Form 4 (Figure 3-4). This multipart form was checked for completeness and internal consistency at the field station. One part of each form was sent to Oak Ridge National Laboratory (ORNL) for entry into the NSS raw data base. A second part of the form was sent to the QA group in Las Vegas where it was checked to identify and correct transcription errors and to ensure that QCCS criteria were met. All forms were sent by overnight mail.

### *4.2.6 Field Laboratory Quality Control Procedures*

The primary functions of the field laboratory were to chemically stabilize aliquots of field samples and to perform limited analyses for those variables that are relatively unstable. The objectives of preservation were to inhibit biological and chemical activity and prevent changes due to volatility, precipitation, and adsorption. Preservatives for each aliquot are described in Table 3-2. Filtration through a 0.45-$\mu m$ membrane filter removed suspended material, including large colloids, and provided subsamples that contained only dissolved analytes and smaller colloidal material. Aliquots 1, 4, 6, and 7 were preserved with strong acid to prevent loss of dissolved analytes through precipitation or chemical/biological reactions. Storage at 4°C was required to reduce biological activity in all aliquots except 1 and 7 and MIBK or volatilization in aliquots 2 and 8.

After sample preparation and preservation steps, holding times were monitored to assure that the samples were analyzed before any significant degradation had occurred. The maximum permitted holding times are shown in parentheses after each variable in Table 3-2.

### *4.2.7 Quality Assurance/Quality Control Samples*

The QA program utilized a variety of QA/QC samples to assure that the sampling and analytical activities were performed according to the QA Plan and the data quality objectives. Every effort was made to keep the number and costs of QA/QC samples within logistic and budgetary constraints while providing adequate information to the QA staff. Because little information was available on the chemical stability of low ionic strength waters, EPA protocols for analysis of water and wastewater samples were used (U.S. EPA, 1983).

### 4.2.7.1 Quality Control Samples

All QC activities related to field laboratory measurements of DIC, pH, true color, and turbidity are described in the QA Plan (Drousé et al., 1986). QC sample type, source applications, and frequency of use are shown in Table 4-1 and described further below.

*Calibration Blank*—Analysis of a calibration blank was required for each batch of samples. This blank (ASTM Type I deionized water) was analyzed after the initial calibration to check for drift in the measured signal and for contamination. The observed concentration was required to be less than or equal to twice the detection limit required by the SOW contract.

*Reagent Blank*—A reagent blank was required for dissolved $S_iO_2$ and total aluminum analyses because additional reagents were added in the digestion step prior to analysis. The reagent blank was essentially a calibration blank that had undergone the digestion steps prior to analysis.

*Matrix Spike*—A matrix spike was required for each batch of samples. A matrix spike is a routine sample to which a known quantity of analyte at a concentration of approximately twice the indigenous level or ten times the detection limit (whichever was greater) was added. The purpose of the matrix spike was to verify the accuracy of the analysis in a matrix typical of the samples being analyzed. The contract laboratory met the limits for spike recovery for every batch and no matrix interferences were observed.

*Laboratory Duplicate*—A contract laboratory duplicate was required for each batch of samples. The duplicate analyses provide estimates of within-batch analytical precision, which must be met for the samples in each batch to meet the QA limits established for these variables.

*Quality Control Check Sample*—Each QCCS was a commercially or laboratory-prepared sample that was obtained from a source different from that used for the calibration standards for the analyte. It was analyzed to verify calibration at the beginning, after every ten samples, and at the end of each batch. The observed concentrations were required to be within specified control limits. A low concentration QCCS also was analyzed for some variables to determine and verify the detection limits for these analytes.

### 4.2.7.2 Quality Assurance Samples

External QA samples were used to judge the overall performance of the sampling and analytical activities and to establish the quality of the data with known confidence limits. Table 4-2 lists types, sources, and applications of QA samples used in the Phase I-Pilot Survey. These samples were processed through the field station and were "double blinds" to the contract laboratories (i.e., the laboratory did not know that they were QA samples and did not know their composition).

*Field Blank*—A field blank was a deionized water sample (meeting specification for ASTM Type I reagent-grade water) that was carried to the stream and processed through the sampling pump as though

**Table 4-1. Types, Sources, and Applications of Quality Control Samples Used in the Phase I-Pilot Survey (Drousé, 1987)**

| Sample Type | Description/Source | Application | Frequency |
|---|---|---|---|
| Quality Control Check Sample (QCCS) | Standard; source other than calibration standard | Indicates accuracy and consistency of calibration | Before, after every ten, and after final sample analysis |
| Contract Laboratory Blank[a] | Reagent-grade water (zero analyte concentration) | Indicates signal drift and sample contamination | One per batch |
| Trailer Duplicate[a] | Stream sample; split | Indicates within-batch precision | One per batch |
| Contract Laboratory Duplicate[a] | Stream sample; split | Indicates within-batch precision | One per batch |
| Matrix Spike | Sample plus known quantity of analyte | Indicates sample matrix effect on analysis | One per batch |

[a] Samples serve both as QA and QC samples.

Table 4-2. **Types, Sources, and Applications of Quality Assurance Samples Used in the Phase I-Pilot Survey (Drousé, 1987)**

| Sample Type | Description/Source | Application | Frequency |
|---|---|---|---|
| Field Blank | Reagent-grade water treated as a stream sample | Estimate system decision limit and quantitation limit | One per day |
| Contract Laboratory Blank[a] | Reagent-grade water (zero analyte concentration) | Estimate nonparametric detection limit | One per batch |
| Field Duplicate[a] | Duplicate stream sample | Estimate overall within-batch precision | One per day |
| Trailer Duplicate[a] | Stream sample; split | Estimate analytical within-batch precision | One per batch |
| Contract Laboratory Duplicate[a] | Stream sample; split | Estimate analytical within-batch precision | One per batch |
| Field Audit | Synthetic samples and natural lake samples | Estimate overall among-batch precision; estimate laboratory bias | As scheduled |
| Contract Laboratory Audit | Synthetic samples and natural lake samples | Estimate analytical among-batch precision; estimate laboratory bias | As scheduled |

[a]Samples serve both as QA and QC samples.

it were a routine sample. One field blank was collected by each sampling team on each operating day.

These samples were intended to identify any contamination problems that may have occurred in the overall sampling and analytical processes. Field blank data were used to establish estimated decision limits, quantitation limits, and background values expected for each variable.

*Field Duplicate*—A field duplicate was a second sample collected at the stream site by the same sampling team immediately after the routine sample was collected. Field duplicate data were used to estimate overall within-batch precision for the sampling and analytical processes. One field duplicate was collected on each sampling day.

*Trailer Duplicate*—A trailer duplicate was a spike of a routine sample processed in the mobile laboratory. One trailer duplicate was processed for each batch. The trailer duplicate was used to establish the analytical precision of the analyses performed in the field laboratory.

*Audit Samples*—Two types of audit samples were used as QA checks on field and contract laboratory operations. Field audit samples were used to establish overall field and contract laboratory performance. Laboratory audit samples were used to establish the performance of the contract laboratory. The use of both types of samples enabled field laboratory problems to be distinguished from analytical laboratory problems.

Field audit samples were received in 2-liter aliquots from Radian Corporation (Austin, Texas, laboratory) and were processed as routine stream samples by the field laboratory. Laboratory audit samples were received at the field station already prepared as aliquots 1 through 8 from Radian, which were then sent to the contract laboratory for analysis. Laboratory audit samples thus were not subject to any analytical errors arising at the field laboratory.

Two natural samples and two low-concentration synthetic samples were also used during the Survey (Table 4-3). The natural samples (from Big Moose Lake in the Adirondack Mountains of New York and from Bagley Lake in the State of Washington) represented two types of low ANC and low ionic strength surface waters expected to be encountered in the Survey. Following collection, these samples were filtered through a 0.45-$\mu$m filter and stored at 4°C until use. Synthetic audit samples were prepared just prior to being sent to the field laboratory. A high-concentration synthetic sample was not utilized because concentrations of analytes in streams in the Phase I-Pilot Survey area were anticipated to be quite low.

### 4.2.8 Data Review

The results of the various chemical analyses were reported on appropriate field and laboratory reporting

Table 4-3. **Composition of Big Moose Lake (FN4) and Bagley Lake (FN5) Natural Audit Samples**

| | Field Audit Sample Concentration[a] | |
|---|---|---|
| Variable | Big Moose Lake[b] | Bagley Lake[c] |
| Al, organic ext. | 0.123 | 0.002 |
| Al, total ext. | 0.284 | 0.005 |
| Al, total | 0.418 | 0.037 |
| ANC, ($\mu$eq L$^{-1}$) | −25 | 156 |
| BNC ($\mu$eq L$^{-1}$) | 133 | 41 |
| Ca | 1.96 | 1.96 |
| $Cl^-$ | 0.469 | 0.22 |
| Conductance ($\mu$S/cm) | 33 | 18 |
| DIC, air equilib. | 0.167 | 1.62 |
| DIC, initial | 0.320 | 1.74 |
| DOC | 7.53 | 0.63 |
| $F^-$, total dissolved | 0.076 | 0.029 |
| Fe | 0.134 | 0.003 |
| K | 0.659 | 0.37 |
| Mg | 0.367 | 0.24 |
| Mn | 0.092 | 0.001 |
| Na | 0.628 | 1.06 |
| $NH_4^+$ | 0.038 | 0.026 |
| $NO_3^-$ | 2.35 | 0.085 |
| P, total | 0.006 | 0.005 |
| pH, acidity | 4.63 | 7.04 |
| pH, alkalinity | 4.63 | 7.02 |
| pH, air equilib. | 4.72 | 7.41 |
| $SiO_2$ | 4.45 | 10.8 |
| $SO_4$ | 6.46 | 0.937 |

[a] All variables are measured in mg/l unless otherwise indicated.

[b] Mean concentration of 37 analyses of Big Moose Lake sample processed at the field laboratory.

[c] Mean concentration of 9 analyses of Bagley Lake sample processed at the field laboratory.

forms, each of which was checked for accuracy before entry into the data base. Prior to describing these procedures in detail, however, it is helpful to understand the NSS data flows and data base structure. The NSS data-base management system is described in the following section.

## 4.3 Data Base Management

NSS data-base management activities are patterned after procedures developed for the National Lake Survey (Kanciruk et al., 1986). All NSS data sets are maintained at Oak Ridge National Laboratory (ORNL) on IBM 3033 mainframe computers using the SAS software package (SAS Institute, Inc., 1983, 1985). Data sets are also periodically transferred to the National Computer Center (NCC) at Research Triangle Park, North Carolina, via magnetic tape, where they can be accessed by NSS scientists at the Las Vegas and Corvallis laboratories.

### *4.3.1 Data Structure and Flow*

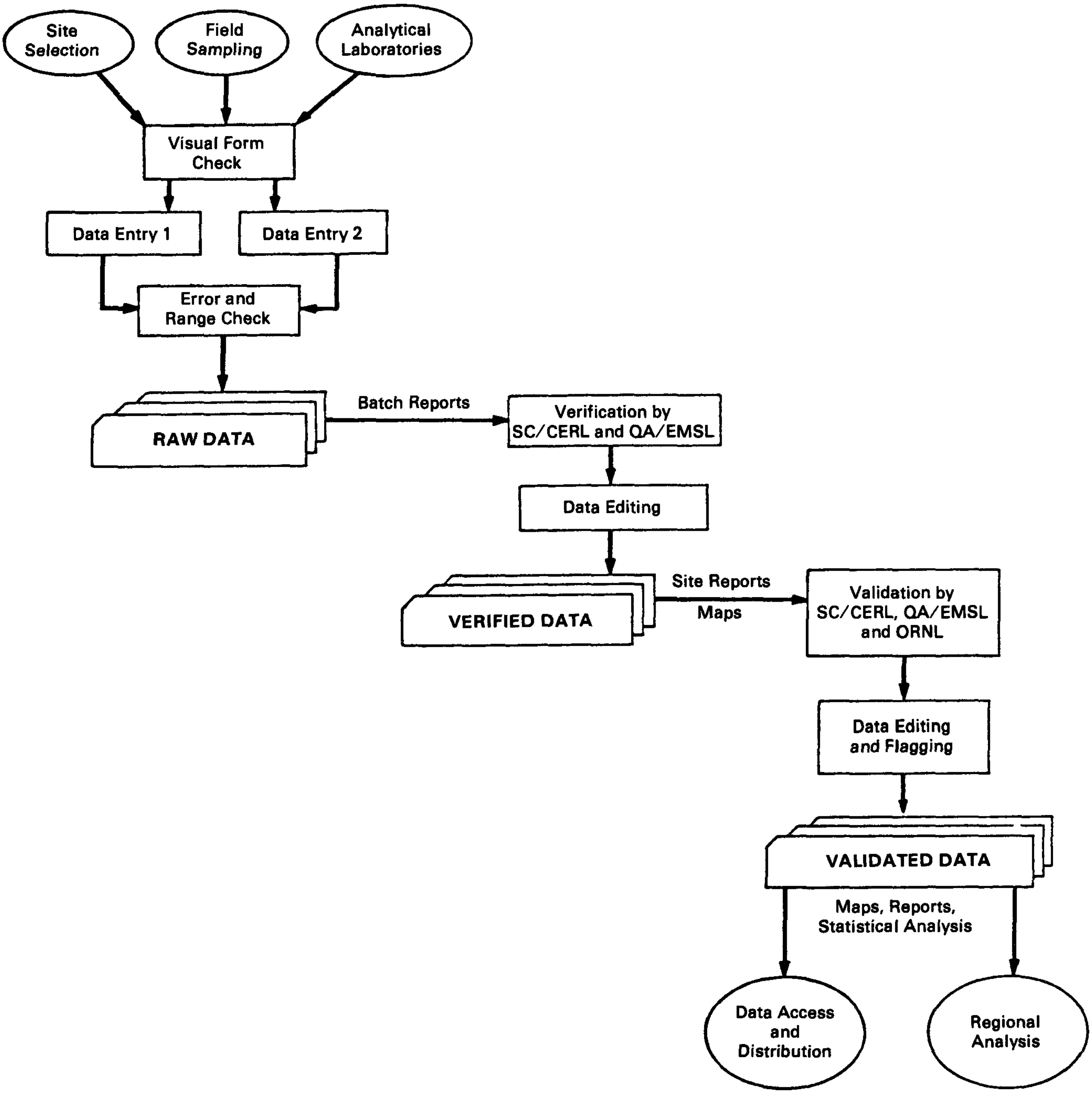
The basic structure and data flow employed during the Phase I-Pilot Survey are schematized in Figure 4-1. Three data bases, "raw," "verified," and "validated," represent increasing levels of data scrutiny. Data initially were entered into a raw data set from the various field and laboratory reporting forms. When enough data became available, a data tape was sent to NCC, where it could be accessed by the QA team. Changes to the raw data set included insertion of data qualifiers (tags and flags) and substitutions for incorrect values discovered by the QA team at EMSL-LV. Changes were sent to ORNL via a "change" tape, which was used to update the existing raw data. When more raw data became available, the process was repeated.

The verified data base was in turn used in the process of validation, wherein additional data qualifiers and substitutions were made based on examination of distributions of variable values among samples by the technical staff at ERL-C. This process also was iterative, and involved the generation of additional change tapes. The use of such tapes allowed any changes to be tracked for any raw datum in the data base.

### *4.3.2 Primary NSS Data Sets*

The raw data set contains data that received a preliminary review by ORNL and EMSL-LV staff to ensure that they conformed to proper formats, were complete and legible, and were within plausible ranges (Rosen and Kanciruk, 1985). The raw data set was used internally by the management team to screen data for problems, to perform trial data

**Figure 4-1. *NSS data structure and flows.***



analyses, to test and debug computer codes and programs, and to make design adjustments when needed. The raw data was continually updated as new data were received from the field and as errors were corrected.

At the verified level, data were reviewed and any errors in transcription, keying, or processing were corrected. Error checking as part of the verification process included intra-sample analyses such as cation-anion balances and chemical equilibrium checks as described below. Verified data are assumed to represent the correct values that were measured and recorded in the field or contract laboratory. As in the raw data set, the verified data set was revised several times during the verification process. Verification changes were initiated by the QA group at EMSL-LV and the required corrections were made by ORNL. Following entry, the data set was reverified to search for entry errors that occurred during the data set editing process.

The validated set contains data which were subjected to the highest level of review. In contrast to verification, the emphasis of validation was on inter-sample comparisons. Validation routines were performed as described below, and data were flagged or deleted from the validated data file. Data in this validated file will be archived in STORET (1985) as well as in the official NSWS data base.

Each raw, verified, and validated data set contains 11 data files that correspond to the individual field and laboratory forms on which the data were reported (Table 4-4). This data structure provides a logical basis for data entry and tracking that is necessary for large data bases such as the NSS data base.

### 4.3.3 Enhanced Data Files

An "enhanced" or "interpreted" data set (printed out in Appendix D) was subsequently created from the validated data set for specific purposes. In this enhanced data set, data for routine/duplicate sample pairs were averaged, any missing values from the validated data set were replaced by averaging or calibration of other chemical variables, and data associated with episodes were identified. This enhanced data set is a clean and compact set for performing population distribution estimates and certain mapping and statistical analyses. The enhanced data set will also be released to external scientists upon request.

### 4.3.4 Data Change and Qualifiers

Three types of data qualifiers are used in the data base: tags, flags, and missing value codes (see Sale et al., 1986 for values assigned to data qualifiers). Tags are assigned based on field observations made during sample collection (e.g., an erratic field meter). Flags are assigned during data verification and validation to indicate questionable values or values that did not meet QA/QC standards. Missing value codes are entered directly into the data base to indicate the reason for a missing datum (e.g., sample lost). Numeric changes and data qualifiers assigned in the verification or validation processes are sent to ORNL in the form of change records (i.e., "tuples;" see Section 4.4.5). These change records are then applied to a copy of the raw data set to generate

**Table 4-4. Data Set Members for the Raw, Verified, and Validated Versions of the NSS Phase I-Pilot Survey Data Base**

| Member Name | Description | Number of Variables | | | Number of Observations |
|---|---|---|---|---|---|
| | | Data | Tags | Flags | |
| F04 | Field measured variables from Form 4 | 49 | 21 | 19 | 339 |
| F05 | Trailer measured variables from Form 5 | 25 | 9 | 9 | 724 |
| F07 | Site and watershed characteristics from Form 7 | 56 | 13 | 0 | 117 |
| F11 | Analytical chemistry from contract lab from Form 11 | 35 | 29 | 29 | 668 |
| F13 | Titration data from Form 13 or diskette | 22 | 12 | 12 | 45K |
| F18 | Detection limits (QA/QC) from contract labs and Form 18 | 49 | 39 | 26 | 51 |
| F19 | Holding times (QA/QC) from contract labs and Form 19 | 79 | 50 | 50 | 668 |
| F20 | Blanks (QA/QC) from contract labs and Form 20 | 418 | 411 | 411 | 51 |
| F21 | Spikes (QA/QC) from contract labs and Form 21 | 232 | 227 | 227 | 51 |
| F22 | Duplicates (QA/QC) from contract labs and Form 22 | 332 | 325 | 325 | 51 |
| F71 | Site location variables from various sources | 31 | 0 | 0 | 117 |

a series of partially verified data sets. A permanent file of all change records is maintained for post-processing audits. This three-tiered system of independent checks (Figure 4-1) is essential to achieving the NSS data quality objectives and producing the high-quality data base required for NSS analyses.

## 4.4 Data Verification

Data verification involves the identification and correction, flagging, or elimination of data of unacceptable quality on the basis of intra-batch QA criteria. Verification involved: (1) reviewing the available QA/QC data from the field and contract laboratories; (2) reviewing any comments or questions associated with the batch or sample under evaluation; (3) performing QA checks for data consistency and chemical reasonableness; (4) reviewing QA sample data; (5) obtaining confirmation, correction, or reanalysis data from the laboratories; and (6) providing the verified data for entry into the ORNL data base. Computer programs were developed to automate this procedure as much as possible. A team of auditors evaluated each data package on a sample-by-sample basis using the procedures outlined below.

### *4.4.1 Review of Field Data Forms*

Verification began with the receipt of the data forms from the field. The auditor reviewed each form to check the following items:

1. Stream ID—The Stream Data Form (Form 4) was compared with the Batch QC Field Data Form (Form 5) to identify transcription errors.
2. Trailer Duplicate—Form 5 had to have a duplicate Stream ID that matched a routine stream sample ID, and the field precision criteria had to be met.
3. Calibration Data—pH and conductivity calibration data on Form 4 were compared to the data from the field calibration forms to ensure that initial calibration criteria were met, or that the appropriate data qualifiers were recorded.
4. Streamside pH—The Form 4 pH values (open and closed) were compared to the field laboratory pH value on Form 5.
5. Field Laboratory pH and DIC—Form 5 values for field audit samples were compared to acceptance criteria. Routine/duplicate pairs and trailer duplicates were evaluated for within-batch precision.
6. pH and DIC QCCS Data—Form 5 QCCS data were reviewed to ensure that criteria were met.

Data anomalies were reported to the field laboratory coordinator for corrective action. Data reporting errors were reported to ORNL to be corrected before entry into the raw data set. Telephone communications were documented in a bound notebook, and data changes were annotated on the appropriate form.

### *4.4.2 Initial Review of Sample Data Package*

As they were received, the sample data packages were reviewed for completeness, internal QC compliance, and proper use of data qualifiers. A checklist was used by the EMSL-LV auditor to assure consistency in the review of all data packages. Any problems were reported to the appropriate contract laboratory manager for corrective action. Comments provided by the laboratory with the data package also were reviewed to determine any impact on data quality or need for follow-up action by the laboratory.

### *4.4.3 Review of Quality Assurance/Quality Control Data*

Following entry of the data into the raw data set at ORNL, a magnetic tape containing the data was sent to NCC. The QA personnel then were able to access the data by telecommunication. The verification process utilized a series of computer programs that comprise the AQUARIUS QA/QC system (Fountain and Hoff, 1985). The programs listed in Table 4-5 identify or flag results that were classed as "exceptions" (i.e., that did not meet the expected QA/QC limits). The AQUARIUS system automated much of the routine QA review process, which enabled the auditor to concentrate more effort on the substantive tasks of correcting or flagging questionable data. The auditor used the output from these programs (along with original data and field notebooks) to complete the NSWS Verification Report called for in the QA Plan. The form of the Verification Report was a work sheet designed to systematically guide the auditor through the verification process by explaining how to: (1) flag data; (2) track data resubmissions and requests for reanalysis and confirmation; (3) list the steps that led to identification of QA exceptions; and (4) summarize modifications to the raw data set (change records).

Each sample was verified individually. Stream sample analytical results had to meet checks for anion-cation percent ion balance difference (% IBD) and for percent conductivity difference (% CD) in order not to generate an "exception," unless the discrepancy could be explained by either the presence of organic species (as indicated by the Protolyte Analysis Program) or by an obvious and correctable reporting error. The Protolyte Analysis

**Table 4-5.** **Exception Generating Programs Within the AQUARIUS Data Review and Verification System (Fountain and Hoff, 1985)**

| Program | Data Type[a] |
|---|---|
| Audit Sample Summary | (FL, LL, FN) |
| Lab/Field Blank Summary | (B, LB) |
| Field Duplicate Precision Summary | (R, D, Pairs) |
| Instrumental Detection Limit Summary | (All Species) |
| Holding Time Summary | (All Species) |
| Conductance Check Calculations | (All Species) |
| Anion/Cation Balance Calculations | (All Species) |
| Batch QA/QC Summary | (All Exceptions) |
| Comparison of Form 4 and Form 5 | (pH and DIC) |
| Comparison of Form 5 and Form 11 | (pH and DIC) |
| Protolyte Analysis | (DIC, DOC, pH, ANC, and BNC Data Evaluation) |
| Audit Sample Window Generation | |
| Raw Data Listing | |
| QA/QC Flag Summary | |
| Reagent/Calibration Blanks and QCCS | |
| Calculation of Laboratory Penalties | |
| Matrix Spike Summary | |
| Modified Gran Analysis | |

[a]FL = Field Low Audit.
LL = Laboratory Low Audit.
FN = Field Natural Audit.
B = Blank.
D = Duplicate.
LB = Laboratory Blank.
R = Routine.

Program flagged field and contract laboratory measurements of pH, DIC, ANC, BNC, and DOC when carbonate equilibria, corrected for organic protolytes, were not in internal agreement. Additional data qualifiers were added to a given variable when the QA samples within the same analytical batch (field blanks, field duplicates, or audit samples) did not meet the acceptance criteria. Additional data qualifiers were added if internal QC checks such as matrix spike recovery, calibration and reagent blank analyses, internal duplicate precision, required instrument detection limit, QCCS percent recovery, and required holding times were not met. In all cases, each flag generated by AQUARIUS was evaluated by the auditor for reasonableness and consistency before it was entered into the data set.

### *4.4.4 Follow-Up with Contract Laboratories*

Completion of the verification steps in sections 4.4.2 and 4.4.3 required follow-up with the contract laboratory to confirm or correct reported data and to reanalyze samples, if required. This follow-up was the most difficult and time-consuming step in the verification process, particularly when requests to the laboratory were not specified in the original statement of work. Typically, responses to requests for confirmation or correction of reported data were completed within two to four weeks. Re-analyses were completed only if specified holding times had not been exceeded.

### *4.4.5 Preparation and Delivery of Verification Tapes*

After the previous steps were completed, the data were used to construct the verified data set. This process required a consistent and trackable method for transferring the change records to ORNL. The process chosen used data base entries called "tuples." A tuple consists of an ordered set of seven variables (batch ID, sample ID, variable, old flag, new flag, old value, new value) which identifies a change to the data set. Tuples can be generated automatically by AQUARIUS or manually by the auditor (e.g., changes and deletions). Tuples are stored in separate data files until the tuple listing is ready to be sent to ORNL. At that time, a computer program combines all of the tuple areas and appends the combined tuple list to the data set (flag, tag, or value changes) only if the batch ID, sample ID, variable name, and old value match. The combined tuple list was written to a magnetic tape and mailed to ORNL from NCC. ORNL then processed the tuple list and returned it to NCC via a magnetic tape. Any illegal tuples ("no-go's") which could not be applied to the data set had to be reexamined by the QA staff. This procedure was repeated approximately five times before the final verified data set was generated.

## 4.5 Data Validation

The process of data validation was intended to assure that data generated during the Phase I-Pilot Survey accurately described the physical and chemical characteristics of the study area. Validation, an iterative process performed in conjunction with data verification, highlights "unusual" values, which subsequently are investigated for entry, transcription, or analytical errors. Suspect values are checked against all data forms and the verified data set, and then flagged or changed, as appropriate.

Validation of the Phase I-Pilot Survey data consisted of:

1. Frequency analyses
2. Univariate analyses
3. Multivariate scoping
4. Bivariate/multiple linear regression analyses
5. Multivariate analyses
6. Episodes screening
7. Reverification/validation checks and data correction/flagging

### *4.5.1 Frequency Analyses*

In order to develop an appropriate strategy for validation, it was necessary to determine first the basic structure of the Phase I-Pilot Survey data set. The SAS PROC FREQuency procedure (SAS Institute, 1985) was used to produce one, two, three, four, and five-way frequency/cross tabulation analyses of the verified data. The analyses were ordered on various combinations of stream ID, batch ID, sample ID, sample code, and individual chemical variables, each of which provided information on the structure and completeness of the data base. As in verification, this procedure can uncover errors such as duplicate sample entries within a batch of samples, missing stream IDs, invalid or incorrect stream IDs or sample codes, and transcription errors. Once the data base structure was determined and preliminary corrections were made, more advanced statistical procedures were applied.

### *4.5.2 Univariate Analyses*

The first approach to outlier detection was to consider each chemical variable individually, searching for values that were extreme with respect to all other observations in the data set. Univariate analysis of the data consisted of: basic summary statistics with plots, and computation of univariate fences. Univariate summary statistics, together with histograms or stem and leaf diagrams, probability plots, box plots, and the five extreme high and low values were computed for all observed routine and duplicate values of each variable. In addition to identifying extreme values, these techniques provided useful information on the underlying data distributions and variability. For example, many of the major anion and cation concentrations demonstrated log-normal distributions, which required data transformations prior to conducting multivariate tests. Seven data combinations were evaluated using univariate statistics: all data, all spring data, all summer data, spring downstream data, spring upstream data, summer downstream data, and summer upstream data.

A unique feature of the Phase I-Pilot Survey compared to previous NSWS designs is the multiple observations at each stream reach through time. These multiple observations permitted computation of univariate statistics for all samples (regular and duplicate) collected from each reach. Univariate fences (Velleman and Hoaglin, 1981) were computed for each stream using custom SAS programming and the SAS PROC UNIVARIATE (SAS Institute, 1985) procedure. The fence procedure compares univariate quartiles for each chemical variable computed under SAS PROC UNIVARIATE definition one: weighted average of Xnp. An inner quartile range (i.e., the difference between the first and third quartiles) was used to establish various "hinges:"

Inner lower hinge = Q1 - (1.5 x QDIFF)
Outer lower hinge = Q1 - (3.0 x QDIFF)
Inner upper hinge = Q3 + (1.5 x QDIFF)
Outer upper hinge = Q3 + (3.0 x QDIFF)

where Q1 = 25th percentile, Q3 = 75th percentile, and QDIFF = Q3 - Q1. Any data value falling inside the inner hinges, between the inner and outer hinges, or outside the outer hinges was so noted and identified for further checking.

### *4.5.3 Multivariate Scoping*

To examine relationships among two or more sets of variables in the validation process, it was first necessary to specify which sets of variables should be explored. Many such relationships could be based on previous experience or upon formal geochemical models. This process is most suitable for bivariate analysis, but the 4,600 potential bivariate pairs in the data set make this approach to validation inefficient. A more efficient procedure was to perform multivariate regressions using several related parameters, rotating the dependent variable and comparing predicted to observed values in order to detect outliers.

Although multivariate suites could also be based on geochemical models, we chose to take an empirical approach. Correlation coefficients were computed for all chemical variables measured during the Survey. Highly correlated variables then were placed into 14 suites of variables (Table 4-6). Twelve suites

**Table 4-6. Variable Suites Obtained from Multivariate Scoping**

| | | |
|---|---|---|
| 1. ANC (alkalinity) | vs. | Calcium<br>Specific Conductance<br>Magnesium<br>Silica<br>pH (field lab) |
| 2. Aluminum (total) | vs. | Ammonium<br>Turbidity<br>True Color |
| 3. Calcium | vs. | Specific Conductance<br>Total Dissolved fluoride<br>Sulfate<br>Silica |
| 4. Chloride | vs. | Specific Conductance<br>Sodium |
| 5. Specific Conductance | vs. | Total Dissolved Fluoride<br>Potassium<br>Magnesium<br>Sodium<br>Silica<br>Sulfate |
| 6. Aluminum (organic extract) | vs. | Potassium<br>Magnesium<br>Silica<br>Total Extractable Aluminum |
| 7. Potassium | vs. | Magnesium |
| 8. Ammonium | vs. | Turbidity<br>True Color<br>BNC |
| 9. Silica | vs. | pH (field lab)<br>Magnesium |
| 10. Turbidity | vs. | True Color |
| 11. pH (field lab) | vs. | pH (initial and air-equilibrated) |
| 12. DIC (field lab) | vs. | DIC (initial and air-equilibrated) |
| 13. Calcium | vs. | Magnesium<br>Potassium<br>ANC<br>Specific Conductance<br>Silica<br>Sulfate<br>pH (field lab) |
| 14. BNC (Acidity) | vs. | Aluminum (total)<br>Ammonium<br>Turbidity<br>True Color<br>Dissolved Organic Carbon |

were used in regression analyses (bivariate or multiple linear), and two suites were used in the SAS Principal Components Analysis and PROC FASTCLUSter analysis.

### *4.5.4 Bivariate/Multivariate Linear Regression Analyses*

Although the concentrations of neither of two variables in a single sample may be outliers within their respective univariate distributions, the ratio of the pair may reveal one of the values to be an outlier. Scatter plots were used to examine relationships between pairs of observed and predicted values for a given variable using simple and/or multiple linear regression analysis. For suites 1 through 4 and 6 through 12 (Table 4-6), simple linear or multiple linear regression analyses were performed, in which each variable was modeled as the dependent variate on all other variables in the suite. Only specific conductance was modeled as the dependent variate for suite 5. Outliers were identified by a combination of visual inspection of regression plots of observed versus predicted dependent variates, and by use of a studentized residual threshold. Observations were identified as outliers if the absolute value of the studentized residual [(actual - predicted) / (residual standard deviation)] was greater than 4. Each regression was repeated three times with outliers identification and removal of outliers after each iteration.

### 4.5.5 *Multivariate Analyses*

In contrast to multiple linear regression, in which a single dependent variate is modeled on two or more theoretically (or practically) related independent variables, multivariate analysis enables examination of several variables simultaneously. Suites 13 and 14 (Table 4-6) were examined using cluster analysis and principal components analysis. Cluster analysis is a classification technique for identifying similarities or dissimilarities among observations. Each observation is compared to others in the set and is assigned to a group or cluster using a measure of similarity. The PROC FASTCLUS procedure in SAS (SAS Institute, 1985), a non-hierarchical divisive method that is sensitive to outliers, was used in the validation process. Principal components analysis forms factors from linear combinations of the original variables, such that the first factor reflects most of the dispersion in the data. Each successive factor explains less variance. If the original data are approximately normally distributed, the resulting factors are also approximately normal, and a plot of any two components results in an elliptical cluster with outliers displaced from the ellipse.

### 4.5.6 *Episodes Screening*

The purpose of episodes screening was to identify chemical values attributable to rain storms that occurred immediately before or during field sampling, in order to exclude these data from population estimate computations. The purposes of this exclusion are explained in Section 2.2.2. Preliminary data screening precipitation data from the three NOAA meteorological stations in the study area, field (Data Form 4; Figure 3-4) records of precipitation and cloud cover, date and time of sampling, staff gauge height and direction of change (if any), and turbidity data. Four screening criteria were devised:

1. Precipitation $>$ 0.1 inch on the same date at a meteorological station.
2. Indication of rain on field Data Form 4 (light, heavy, or previous).
3. Gauge height $>$ 0.25 ft over other spring measurements.
4. Turbidity increase (4x if baseline value is $>$ 10 NTU, 2x otherwise).

For a particular sample to be flagged as an episode, three of the four criteria had to be met. Eight spring episode samples were identified as a result of the screening process and substituted by calibration in the enhanced data set.

Summer episodes and upstream episodes were difficult to detect using the screening technique described above, due to the lack of readily comparable staff gauge or turbidity data. Several alternatives involving comparisons using spring downstream data were explored, most of which failed to provide clear decision criteria. During the validation process described in the following section, samples with multiple chemical outliers were flagged as potential episodes, and cross-checked against criterion 1 or 2 above. Satisfying either criterion caused an episode flag to be generated. All of these flagged values were carried into the enhanced data set, because no substitute numbers were available, but the values have been treated as missing in some of the statistical comparisons, as noted in Chapter 5.

### 4.5.7 *Reverification/Validation and Data Correction/Flagging*

The end product of the six validation steps was a master matrix of samples containing outliers. This matrix was ordered by stream ID, sampling point location (upstream and downstream), and time of sampling (any of four spring and one summer sampling intervals); outliers were identified by chemical variable, and coded by a symbol denoting the particular test (or tests) that identified that observation as an outlier. Each code also specified whether the routine and/or duplicate value (if available) was flagged.

The validation matrix was sent to the QA/QC group for reverification. All questionable values were reexamined for data entry or other errors. The reverified data then were subjected to a sample-by-sample examination by the NSS technical management team that resulted in a series of validation flags (Table 4-7).

Substitution (U) flags were set for variables under three conditions:

1. Downstream episodes: datum replaced with average of remaining two spring downstream samples (U1).
2. Datum flagged for which a duplicate analysis was not flagged: regular sample datum replaced by duplicate or duplicate datum dropped (U2-U4).
3. Datum was impossible (e.g., extractable aluminum was higher than total aluminum) but no duplicate was available: datum was replaced by calibration using a bivariate or multivariate model developed as part of the validation process (Section 4.5.4) (U2-U4).

Very few data were substituted under the last rule.

Validation (K) flags were used when data were identified as outliers during validation, but not during

Table 4-7. NSS Validation Flags

| | |
|---|---|
| *Substitution Flags* | |
| U1 | Downstream Spring Episode |
| U2 | Univariate Outlier |
| U3 | Multivariate Outlier |
| U4 | Univariate and Multivariate Outlier |
| *Validation Flags* | |
| K1 | Episode—(No substitute value available) |
| K2 | Univariate Outlier |
| K3 | Multivariate Outlier |
| K4 | Univariate and Multivariate Outlier |
| *Verification/Validation Flags* | |
| W2 | Univariate Outlier—(no substitute value available) |
| W3 | Multivariate Outlier—(no substitute value available) |
| W4 | Univariate and Multivariate Outlier—(no substitute available) |

the verification process. Generally, it is assumed that these data represent "unusual" but not necessarily incorrect numbers. Summer or upstream episode samples, for which no substitute values were available, represent a special case (K1) of such situations. Other examples may indicate transient pollution or contamination of sample containers.

Verification/validation (W) flags were generated when data were identified in *both* validation and verification procedures. These data may well be incorrect, but no clearly superior substitute values were available. Virtually all such cases involved small discrepancies in the validation models, or involved chemical concentrations close to the detection limit for the variable. In general, it was assumed that the averaging process employed in constructing the enhanced data base would decrease the impact of most small analytical errors on population distribution estimates.

Once validation was completed, a final list of validation change tuples was produced and sent to ORNL, accompanied by instructions for building an enhanced data set. This data set is the final product of verification and validation, although intermediate raw and verified (but final) data sets also are produced. In the complete version of the enhanced data base, episode values have been given a sample code of "EA" if substitute values are available, or "E" if substitute values are not available (e.g., spring upstream, summer upstream, or summer downstream observations). Routine/duplicate observation pairs are averaged and given a sample code, "DA." Appropriate verification and validation changes have been made in the enhanced data set, but all tags, flags, and comments were dropped. These QA/QC data remain available in the final validated data set.

## 4.6 Data Management and Quality Assurance Results

The success of the Phase I-Pilot Survey data management and QA program can be judged on several counts, including the efficient performance of the system in recording and tracking data, the efficiency of the verification and validation processes in identifying and treating suspect values, and the degree of accuracy and precision attained in the analytical data themselves. These issues are addressed in the following section.

### *4.6.1 Data Base Management Performance*

One measure of data base management performance for the Phase I-Pilot Survey is the length of time required to complete the various data bases described in Section 4.3.2. The corresponding dates are:

| | | |
|---|---|---|
| 17 July 1985 | -- | Field sampling complete |
| 30 August 1985 | -- | Raw data base complete |
| 30 October 1985 | -- | Verified data base complete |
| 30 January 1986 | -- | Validated data base complete |
| 30 March 1986 | -- | Enhanced data set complete |

These dates reflect completion of the "first draft" of each data set. Reverification changes (none of which involve numeric data changes) were finalized on 30 May 1986.

The eight-month period required to produce a near-final enhanced data set was not unexpectedly long considering that more than 22 x $10^3$ numerical chemical data alone are represented in the data base, in addition to flags, tags, site, and geographic data. Raw data were generally available in machine-readable form within seven weeks of collection for preliminary analyses. Several data transfer protocols are being initiated in Phase I that are expected to shorten some communications delays, and many of the validation procedures that had to be developed specifically for the Phase I-Pilot Survey can be transferred with minor modifications to Phase I.

### *4.6.2 Verification/Validation Performance*

Because a strict QA/QC program was adhered to throughout the period of operations, any problems that were encountered were detected and resolved quickly through the daily QA contact. Examples of issues that were addressed as a result of such calls included:

1. incorrect calculations in reporting inorganic and organic extractable aluminum and chloride data;
2. use of contaminated matrix modifier (lanthanum chloride) for calcium analysis by flame AA that resulted in high calcium values;
3. indications of negative bias in manganese analysis by evaluation of audit sample data;
4. use of an analytical method for nitrate analysis that was not specified by the IFB contract;
5. illegible data reported by the contract laboratory;
6. a brief aluminum contamination episode at the field laboratory due to presence of large amount of dust;
7. temporary contamination of aliquot #3 at the field laboratory; and
8. inconsistent temperature correction and reporting of *in situ* conductivity and QCCS data.

The preliminary QA/QC sample data, obtained during daily communications, provided guidance for QA staff to identify and solve most of the issues that arose, resulting in minimal impacts on the final data set. Several protocol changes were implemented during the Survey, and others were made after the Survey as a result of data evaluation. All changes were incorporated into the final QA Plan for Phase I (Drousé et al., 1986).

Table 4-8 presents the final results of the verification and validation processes. The verification data include all routine, duplicate, trailer duplicate, audit, and blank samples; validation data address all but audits and blanks. There were a total of 20,613

**Table 4-8.** **Results of Verification/Validation: Numbers of Observations Flagged and Numeric Changes Made (and percent of total observations) in the NSS PIPS Data Base (excluding episode flags)**

| Chemical Variable | Total Number of Observations | Number (Percent) of Observations Flagged in Verification | Number (Percent) of Numeric Changes from Verification | Number (Percent) of Observations Flagged in Validation | Number (Percent) of Numeric Changes from Validation |
|---|---|---|---|---|---|
| Acidity | 668 | 206 (30.8) | 0 (0) | 6 (0.9) | 0 (0) |
| Al (extractable) | 668 | 97 (14.5) | 2 (0.3) | 15 (2.2) | 2 (0.3) |
| ANC | 668 | 130 (19.5) | 1 (0.1) | 2 (0.3) | 1 (0.1) |
| Al (organic) | 668 | 86 (12.9) | 13 (1.9) | 7 (1.0) | 9 (1.3) |
| Al (total) | 668 | 374 (56.0) | 7 (1.0) | 9 (0) | 0 (0) |
| Ca | 668 | 176 (26.3) | 0 (0) | 5 (0.7) | 0 (0) |
| Cl | 668 | 201 (30.1) | 3 (0.4) | 0 (1.3) | 2 (0.3) |
| Color | 724 | 0 (0) | 0 (0) | 6 (0.9) | 0 (0) |
| Conductivity (lab) | 668 | 45 (6.7) | 1 (0.1) | 1 (0.1) | 0 (0) |
| Conductivity (in situ) | 339 | 10 (2.9) | 7 (2.1) | 2 (2.9) | 0 (0) |
| DIC (equilibrated) | 668 | 150 (22.5) | 4 (0.6) | 0 (0) | 0 (0) |
| DIC (initial) | 668 | 214 (32.0) | 11 (1.6) | 0 (0) | 0 (0) |
| DIC (field lab) | 724 | 70 (9.7) | 0 (0) | 0 (0) | 0 (0) |
| DOC | 668 | 113 (16.9) | 15 (2.2) | 5 (0.7) | 1 (0.1) |
| Fe | 668 | 112 (16.8) | 1 (0.1) | 10 (1.5) | 0 (0) |
| F (total) | 668 | 89 (13.3) | 1 (0.1) | 2 (0.3) | 0 (0) |
| K | 668 | 48 (7.2) | 2 (0.3) | 2 (0.3) | 0 (0) |
| Mg | 668 | 27 (4.0) | 0 (0) | 3 (0.4) | 0 (0) |
| Mn | 668 | 306 (45.8) | 287 (43.0) | 1 (0.1) | 1 (0.1) |
| Na | 668 | 31 (4.6) | 1 (0.1) | 5 (0.7) | 0 (0) |
| $NH_4$ | 668 | 38 (5.7) | 0 (0) | 10 (1.5) | 1 (0.1) |
| $NO_3$ | 668 | 275 (41.2) | 72 (10.8) | 3 (0.4) | 6 (0.9) |
| pH (field-closed) | 339 | 0 (0) | 0 (0) | 3 (0.9) | 0 (0) |
| pH (field-open) | 339 | 0 (0) | 0 (0) | 2 (0.6) | 0 (0) |
| pH (acidity) | 668 | 311 (46.6) | 0 (0) | 5 (0.7) | 1 (0.1) |
| pH (alkalinity) | 668 | 0 (0) | 0 (0) | 3 (0.4) | 0 (0) |
| pH (equilibrated) | 668 | 0 (0) | 0 (0) | 45 (6.7) | 45 (6.7) |
| pH (field lab) | 724 | 42 (5.8) | 0 (0) | 1 (0.1) | 0 (0) |
| P | 668 | 166 (24.9) | 1 (0.1) | 5 (0.7) | 1 (0.1) |
| $SiO_2$ | 668 | 120 (18.0) | 8 (1.2) | 2 (0.3) | 0 (0) |
| $SO_4$ | 668 | 165 (24.7) | 2 (0.3) | 5 (0.7) | 2 (0.3) |
| Turbidity | 724 | 0 (0) | 1 (0.1) | 8 (1.1) | 0 (0) |

individual observations subjected to verification. *In situ* dissolved oxygen and stream temperature data, although not included in these statistics, were examined manually and were found to be realistic. Of all the data, 17.5% (3,602 observations) were flagged, but only 2% (440 observations) were changed numerically. The majority of the numeric changes resulted from chemical reanalyses, as discussed in Section 4.4.4. Most of these numeric changes were less than 1% of the original values reported.

Since audits and blanks accounted for 5,027 of the 20,613 observations subject to verification (ca. 25%), validation addressed the remaining 15,586 values. Of this number, only 1% (173 observations) were flagged during validation, and less than 0.5% (72) were actually changed. Forty-five of the 72 numeric changes involved the first seven batches of equilibrated-pH values, for which calibrated values were substituted based on mobile and laboratory pH observations. The verification/validation results indicate that very few values were found to be in error and subsequently changed.

### *4.6.3 Data Quality*

The success of the Phase I-Pilot Survey ultimately will be judged on the ability of the data to produce robust population distribution estimates for the primary NSS variables of interest. Error in these estimates can arise from two primary sources: sampling error and analytical error. The first source is a function of the variability of the natural environment and the sampling design. The second is largely a function of the degree to which sampling and analytical protocols are capable of providing accurate data with acceptable levels of precision. The statistical data in this section can be used to answer some of these questions. Some of the QA results that have a bearing on the interpretation of the data in Chapter 5 are summarized in this section. Drousé (1987) provides a more detailed treatment, including the degree to which contractual analytical targets were met.

#### 4.6.3.1 Detection Limits

During the Survey, 71 field blanks were processed, and the data provide an overall estimate of the normal background contamination that occurred during sampling and analysis. Table 4-9 shows the nonparametric decision limit for each variable based on a statistical evaluation of the verified blank data. This value represents the concentration limit, above which the analyte can be detected with a known degree ($p = 0.5$) of confidence.

For most of the variables, the prespecified targets of the NSS QA Plan were met (Drousé, 1987). However, data for the following variables indicated background sources of contamination that caused the decision limit to be appreciably higher than the required detection limit:

1. Ammonium—although the detection limit exceeded the prespecified target for ELS lakes, concentrations in streams below 21 $\mu$g $L^{-1}$ (1.1 $\mu$eq $L^{-1}$) are unlikely to be of interpretive significance.

2. Total aluminum—contamination may result from digestion reagents or dust in the field or contract laboratories. Again, 0.062 $\mu$g $L^{-1}$ is probably an acceptable detection limit in streams, where some colloidal aluminum may pass through the 0.45-$\mu$m filters, but has little interpretive significance.

3. DIC—the background level in a blank exposed to air was approximately 0.2 to 0.3 mg $L^{-1}$, which affects the results for samples that have low DIC as a result of $CO_2$ undersaturation or low ANC.

4. DOC—blank background levels were approximately 0.1 to 0.3 mg $L^{-1}$, apparently from $CO_2$ contamination. This value is above the concentration of DOC of most Southern Blue Ridge streams sampled during the study.

5. Total P—0.008 mg $L^{-1}$ should be adequate for interpreting most stream data with respect to acid deposition, although many unpolluted streams will have P concentrations below this value.

6. Nitrate—Contamination is suspected by $HNO_3$ vapors in the hood where aliquots are prepared. This detection limit is not unacceptably high, but reducing it is desirable, given the potential importance of the anion in terms of acid deposition.

In summary, most detection limit goals were achieved in the laboratory. However, in interpreting the data, the data user must take the results from the field blanks into consideration. If the background value from sample collection and handling is higher than the laboratory (system) detection limit, obtaining extremely low detection limits in the laboratory is meaningless. The decision limit and system detection limits must be considered as the real limits for data interpretation.

#### 4.6.3.2 Precision

Sampling and analytical variance, apart from temporal (> 1 hour) variations in stream chemistry, can arise in the survey from three major sources:

**Table 4-9. System Decision Limits and Precision Estimates[a] Based on Interbatch Analysis of Field Audits and Intrabatch Analyses of Field, Trailer, and Laboratory Duplicates (Drousé, 1987)**

| Variables | Non-parametric System Decision Limit ($P_{95}$)[b,c] | Field Audits (FN4)[d] | Field Duplicates | Lab Duplicates |
|---|---|---|---|---|
| Al, organic ext. | 0.002 | 32 | 39 | 5.1 |
| Al, total ext. | 0.002 | 23 | 12 | 5.1 |
| Al, total | 0.062 | 11 | 20 | 12.8[g] |
| ANC ($\mu$eq $L^{-1}$ | – | [h] | 5 | – |
| BNC ($\mu$eq $L^{-1}$) | – | 14 | 9.5 | – |
| Ca | 0.04 | 3.0 | 2.3 | 1.2 |
| $Cl^-$ | 0.06 | [h] | 2.2 | 1.6 |
| Conductance ($\mu$S $cm^{-1}$) | 0.92 | 0.99 | 0.8 | 0.5 |
| DIC,, air equilib. | 0.36 | [h] | 7.1 | 2.3 |
| DIC, initial | 0.20 | [h] | 9.8 | 2.5 |
| DOC | 0.54 | 6.6 | 6.2 | 2.3 |
| $F^-$, total dissolved | 0.005 | 2.7 | 2.1 | 1.2 |
| Fe | 0.004 | 10 | 25 | 18.2 |
| K | 0.009 | 2.1 | 3.8 | 1.1 |
| Mg | 0.004 | 1.5 | 1.1 | 0.8 |
| Mn | 0.002 | 5.4 | 8.9 | 6.0 |
| Na | 0.011 | 1.5 | 1.1 | 0.8 |
| $NH_4^+$ | 0.021 | [h] | 10 | 7.7 |
| $NO_3^-$ | 0.028 | 7.0 | 5.9 | 3.6 |
| P, total | 0.008 | [h] | 5.1 | 5.1 |
| pH, acidity | – | 0.05[e] | 0.086[f] | 0.03[f] |
| pH, alkalinity | – | 0.05[e] | 0.083[f] | 0.02[f] |
| pH, air equilib. | – | 0.03[e] | 0.11[f] | 0.03[f] |
| $SiO_2$ | 0.062 | [h] | 8 | 1.6[g] |
| $SO_4$ | 0.040 | 2.8 | 3.3 | 1.9 |
| pH (field lab) | – | – | 0.05 | 0.03 |
| DIC (field lab) | – | – | 4.00 | 3.36 |
| True Color (PCU) | – | – | 21.5 | 11.7 |
| Turbidity (NTU) | – | – | 14.9 | 10.4 |

[a] Root-mean-square of % relative standard deviation based on pairs with $\bar{x} > 10$ times standard deviation of field blank.

[b] All variables are measured in mg/l unless otherwise indicated.

[c] $P_{95}$ = the 95th percentile of 71 field blank measurements.

[d] Big Moose Lake (FN4).

[e] Absolute standard deviation.

[f] Root-mean-square of standard deviation.

[g] $\bar{x} > 10$ times standard deviation of the reagent blank.

[h] $\bar{x} < 10$ times standard deviation of the field blank.

(1) a field component associated with short term temporal variability in stream chemistry, (2) an analytical component associated with subsampling an aliquot of water and random variation in instrument response within an analytical batch, and (3) an analytical component associated with batch-to-batch variation in instrument calibration and response. The relative importance of these sources of variation can be assessed by comparative statistical evaluations of analyses of field audits, field duplicates, and laboratory and trailer duplicates. The relative degree of precision in these analyses also is shown in Table 4-9.

Precision of the various sets of analyses, with the exception of pH, are expressed as root mean squares of percent relative standard deviations of all samples or sample pairs above the system quantitation limit. The system quantitation limit, represented by ten times the standard deviation of the corresponding blank concentrations, assures that individual samples considered in the analysis have sufficiently high analyte concentrations that their expected precision is constant. This practice insures that samples with analyte concentrations near the detection limit do not provide a false picture of the interbatch or duplicate precision.

For most variables, interbatch variance, as estimated from repeated measurements of the Big Moose Lake field audits, exhibits the lowest degree of precision. However, except for metal species, the relative standard deviation is typically less than 10%. Within-batch duplicate precision was better for most variables, with pairs exhibiting the highest precision associated with species that travel in colloidal form in streams, and thus may be expected to exhibit some degree of sampling variability when compared with even single sample aliquots of lake water. Laboratory duplicate precision was better still, as expected, and represents the highest degree of precision that could likely be achieved in a project such as the NSS.

### *4.6.4 Summary*

The QA/QC and data management program functioned well in the Phase I-Pilot Survey and produced a data set of known and acceptable quality in time to meet project objectives. Much was learned, however, about how to avoid or minimize future QC problems and delays in data transfers and verification and validation procedures. The new protocols were implemented in the Phase I Research Plan (U.S. EPA, 1985b; Drousé et al., 1986).

# *5. Population Estimates and Stream Classification*

## 5.1 Introduction

The primary objectives of the National Stream Survey are (1) to provide population estimates of streams that are currently acidic (low pH) or potentially at risk from acid deposition (low ANC), and (2) to classify streams for further intensive studies. Future studies will aim at determining temporal (e.g., episodic) variability, biotic conditions, and long-term trends, and will require that the results can be extrapolated to some larger target population of streams with known confidence. The approach to these objectives taken in the Phase I-Pilot Survey was to "overdesign" a synoptic survey of streams focused on a relatively small geographic area. That is to say, more samples were taken during the Pilot Survey than were expected to be necessary, in order to establish the minimum acceptable sampling design needed to meet the NSS objectives on a regional basis in Phase I. This chapter illustrates, on the basis of Phase I-Pilot Survey data, the types of results that could be expected from a full scale synoptic survey of streams and establishes the minimum number of samples required to meet the Phase I project objectives.

The results presented here thus fall into two categories: population distribution estimates and stream classifications. We first consider alternative methods for calculating and displaying population estimates. Results from the three spring sampling replicates and the summer sampling are compared in order to determine the effect of sampling date and replication on population estimates and stream classifications. Chemical data from upstream and downstream nodes are compared in order to establish the desirability of sampling two points on each reach during Phase I field work. Following these discussions relating to survey design and data analyses, we consider the ways in which the Phase I data will likely be interpreted in order to provide incremental information inputs to the assessment process. This discussion necessarily focuses on the Southern Blue Ridge as an example. Some caveats and pitfalls also are noted and discussed.

The chapter then turns to the issue of classification, the second major goal of the NSS. Examples of classification based both on subjective (geographical and geochemical) and objective (cluster analysis) interpretations are presented. Some examples of how the resulting classification might be used to interpret historical data collected at the special interest sites in the Phase I-Pilot Survey also are discussed. It is important to note that any future classification schemes must depend on the specific nature of the intended research.

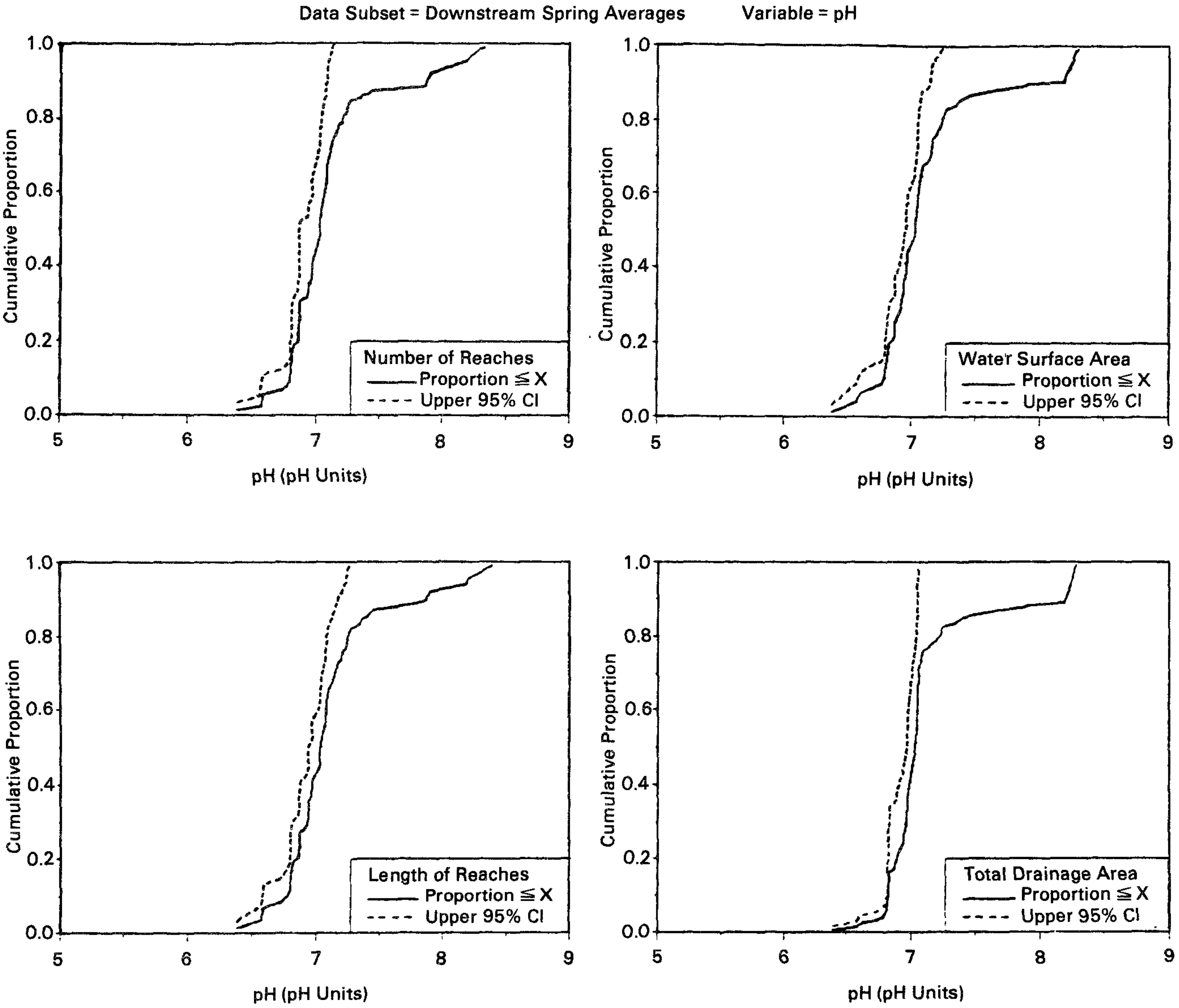
## 5.2 Population Estimates

Just as population distributions for geographic characteristics were estimated from the first and second stage samples (Table 2-2), the distributions of chemical variables also can be estimated based on the chemical data collected from the reaches in the second stage sample. The generation of cumulative population distribution curves for each chemical variable satisfies the first two primary objectives of the NSS (Section 1.3). Graphical and tabular outputs showing the distribution estimates for six primary NSS variables (pH, ANC, sulfate, nitrate, chloride, and extractable aluminum) are shown in Figures 5-1 through 5-6. The six variables presented here are of particular interest because they indicate present levels of acidity (pH) or potential susceptibility (ANC); they are critical determinants of toxicity commonly associated with atmospheric acidification (extractable aluminum); or they involve anions (sulfate and nitrate) that are commonly, though not uniquely, associated with atmospheric acids. Chloride was included as a possible indicator of nonpoint source pollution (from agricultural runoff, road de-icing, or wastewater effluent disposal) in these streams. The region is too far from the ocean to exhibit significant chloride deposition from marine aerosols. While few interpretations can be based on single variables alone, the distribution of these variables within and among streams in the probability sample is useful in evaluating the utility and modifying the design of future NSS Phase I activities. Similar distribution estimates for the remaining NSS chemical variables can be found in Appendix A of this report (Figures A.1-A.23).

### *5.2.1 Graphical Displays*

The distribution estimates in Figures 5-1 - 5-6 are based on the mean value for each constituent at the downstream sampling node of each reach over the three spring visits. Water samples collected

**Figure 5-1.** Population distribution estimates for average spring downstream pH conducted at the mobile laboratory on samples held in syringes closed to the atmosphere in the NSS Phase I-Pilot Survey.



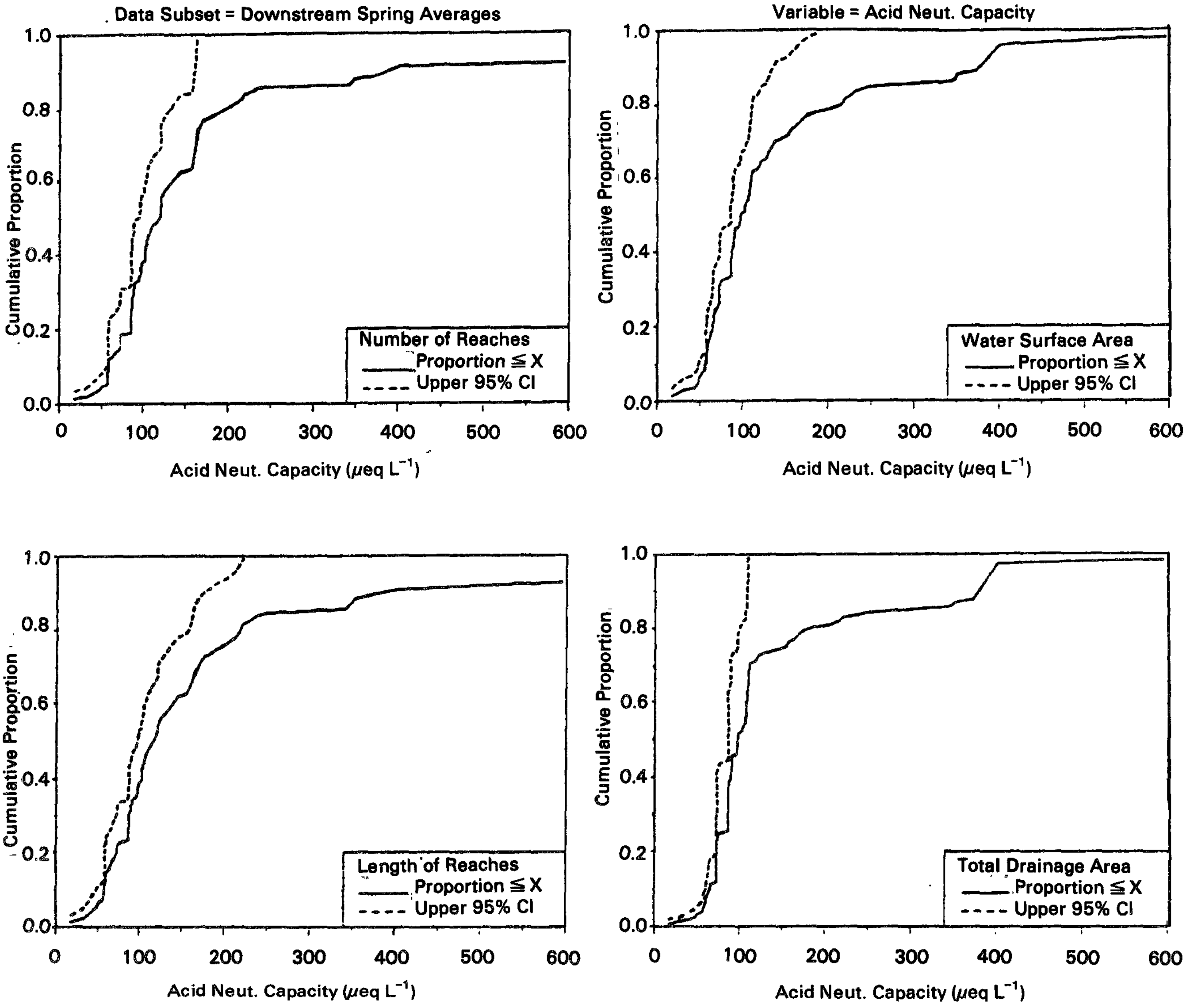
Data Subset = Downstream Spring Averages    Variable = pH

| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (pH Units) | 6.86 | 6.84 | 6.85 | 6.89 |
| 40 %ILE (pH Units) | 6.97 | 6.97 | 6.97 | 6.99 |
| Median (pH Units) | 7.03 | 7.03 | 7.03 | 7.03 |
| 60 %ILE (pH Units) | 7.06 | 7.06 | 7.08 | 7.05 |
| 80 %ILE (pH Units) | 7.21 | 7.23 | 7.24 | 7.22 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics (pH Units) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 6.38 | 8.43 | 7.12 | 0.42 |

**Figure 5-2.** **Population distribution estimates for average spring downstream acid neutralizing capacity ANC in streams in the NSS Phase I-Pilot Survey.**

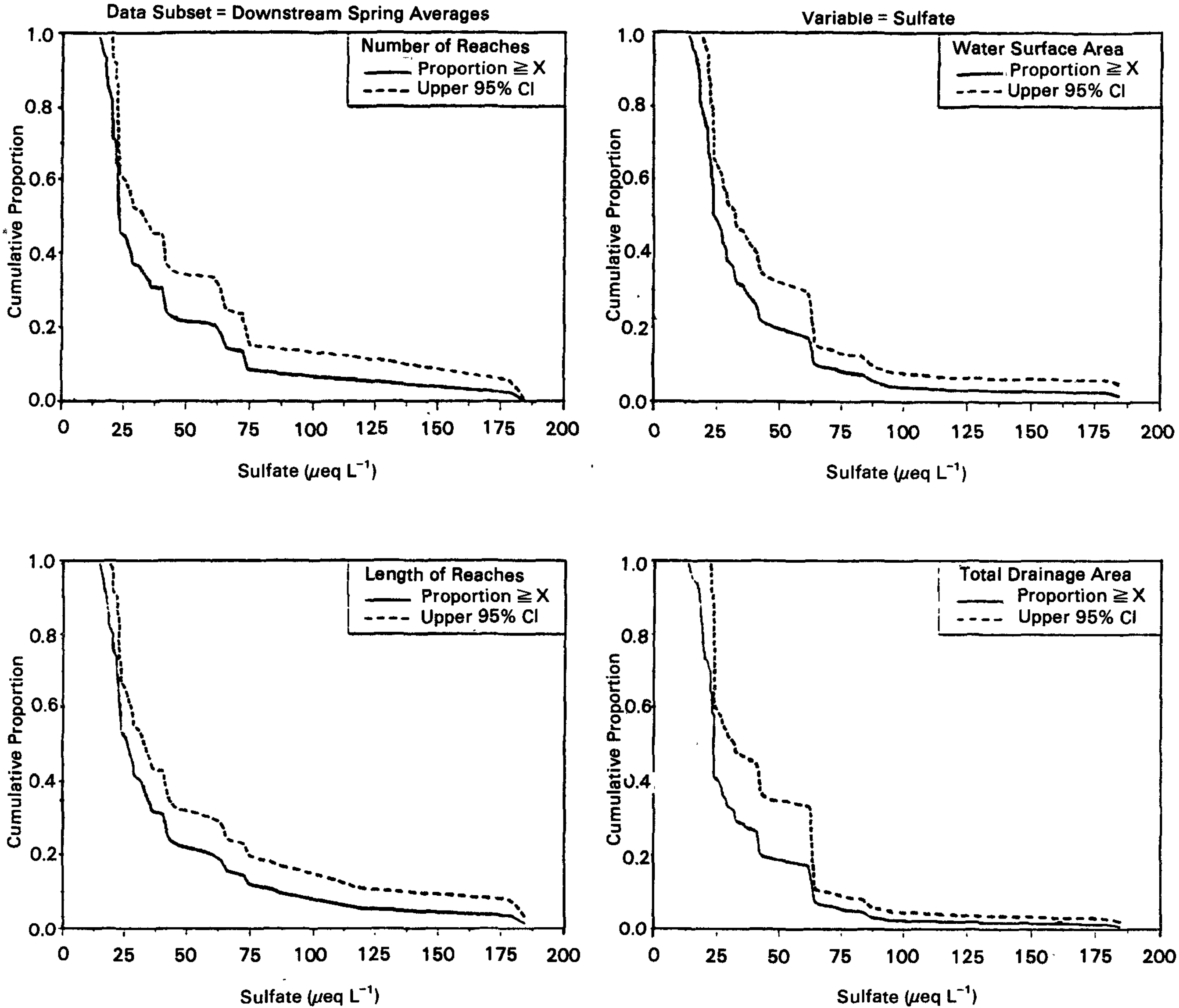


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu$eq $L^{-1}$) | 86.64 | 65.03 | 72.67 | 72.84 |
| 40 %ILE ($\mu$eq $L^{-1}$) | 102.59 | 87.73 | 102.48 | 89.41 |
| Median ($\mu$eq $L^{-1}$) | 119.61 | 98.58 | 115.53 | 98.03 |
| 60 %ILE ($\mu$eq $L^{-1}$) | 134.26 | 110.03 | 138.41 | 108.09 |
| 80 %ILE ($\mu$eq $L^{-1}$) | 197.69 | 216.11 | 217.53 | 181.45 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics ($\mu$eq $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 16.18 | 1710.5 | 252.02 | 399.14 |

Figure 5-3. **Population distribution estimates for average spring downstream sulfate concentrations in streams in the NSS Phase I-Pilot Survey.**

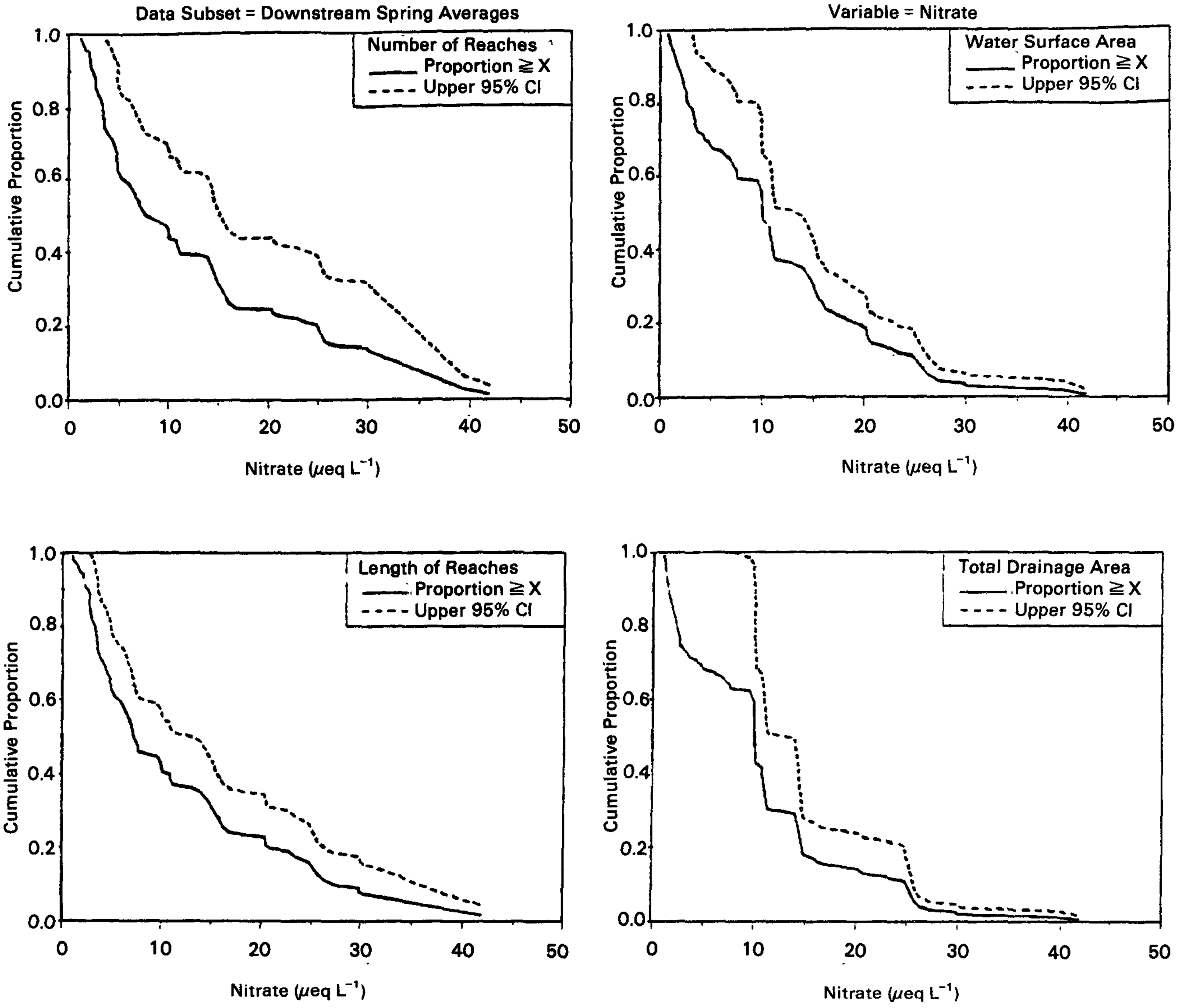


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu$eq $L^{-1}$) | 18.56 | 18.05 | 18.28 | 18.13 |
| 40 %ILE ($\mu$eq $L^{-1}$) | 22.37 | 22.67 | 22.66 | 22.52 |
| Median ($\mu$eq $L^{-1}$) | 22.87 | 23.47 | 25.22 | 23.31 |
| 60 %ILE ($\mu$eq $L^{-1}$) | 27.52 | 28.61 | 29.15 | 24.77 |
| 80 %ILE ($\mu$eq $L^{-1}$) | 58.86 | 43.62 | 55.83 | 41.57 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics ($\mu$eq $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 12.87 | 184.43 | 38.38 | 32.75 |

**Figure 5-4.** **Population distribution estimates for average spring downstream nitrate concentrations in streams in the NSS Phase I-Pilot Survey.**

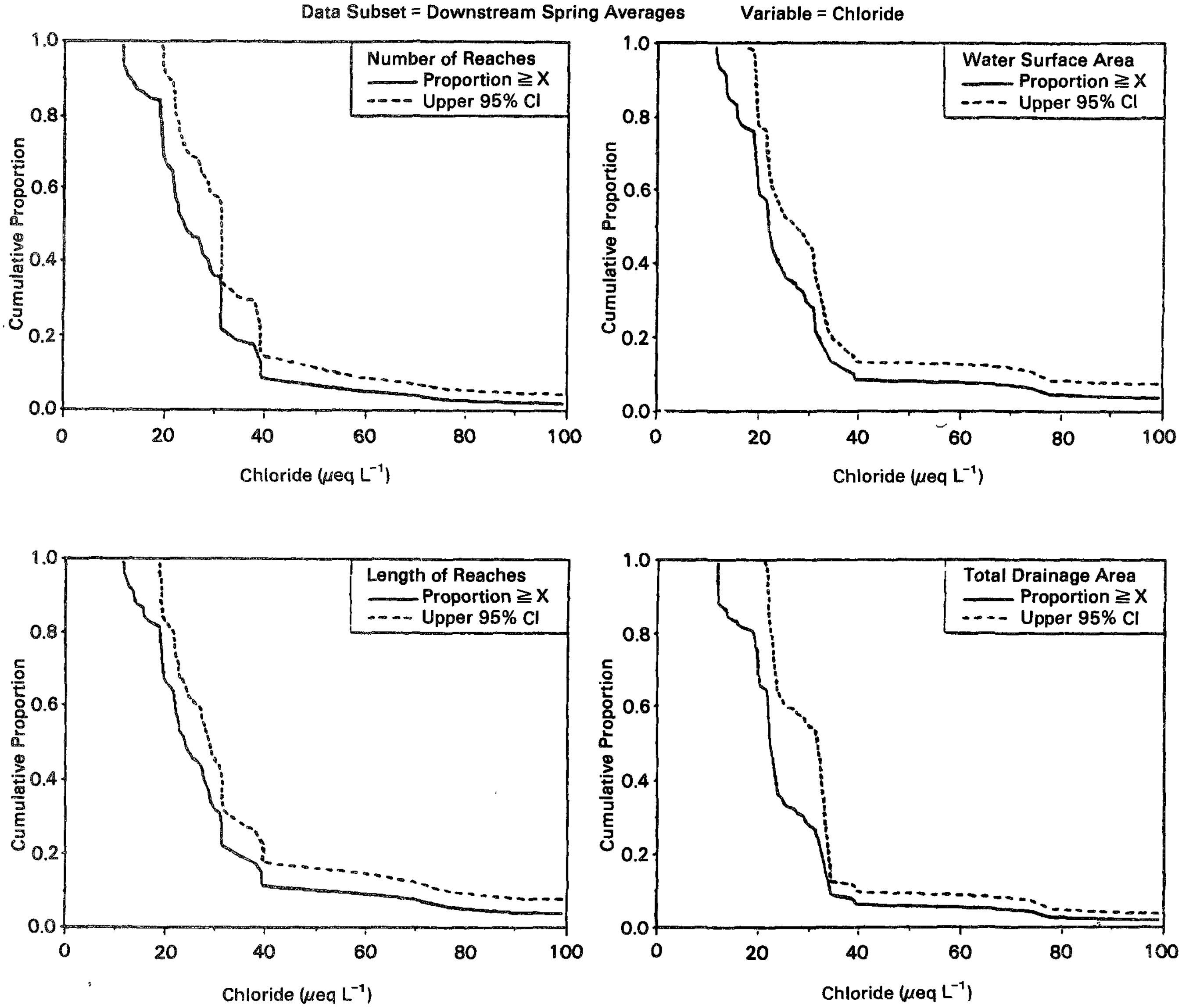


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu$eq $L^{-1}$) | 2.99 | 2.65 | 2.86 | 2.01 |
| 40 %ILE ($\mu$eq $L^{-1}$) | 4.89 | 7.51 | 4.98 | 9.57 |
| Median ($\mu$eq $L^{-1}$) | 7.55 | 9.91 | 6.98 | 9.89 |
| 60 %ILE ($\mu$eq $L^{-1}$) | 10.85 | 10.84 | 10.09 | 10.82 |
| 80 %ILE ($\mu$eq $L^{-1}$) | 23.38 | 16.63 | 20.36 | 13.77 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics ($\mu$eq $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 0.66 | 41.83 | 12.08 | 10.55 |

**Figure 5-5.** Population distribution estimates for average spring downstream chloride concentrations in streams in the NSS Phase I-Pilot Survey.

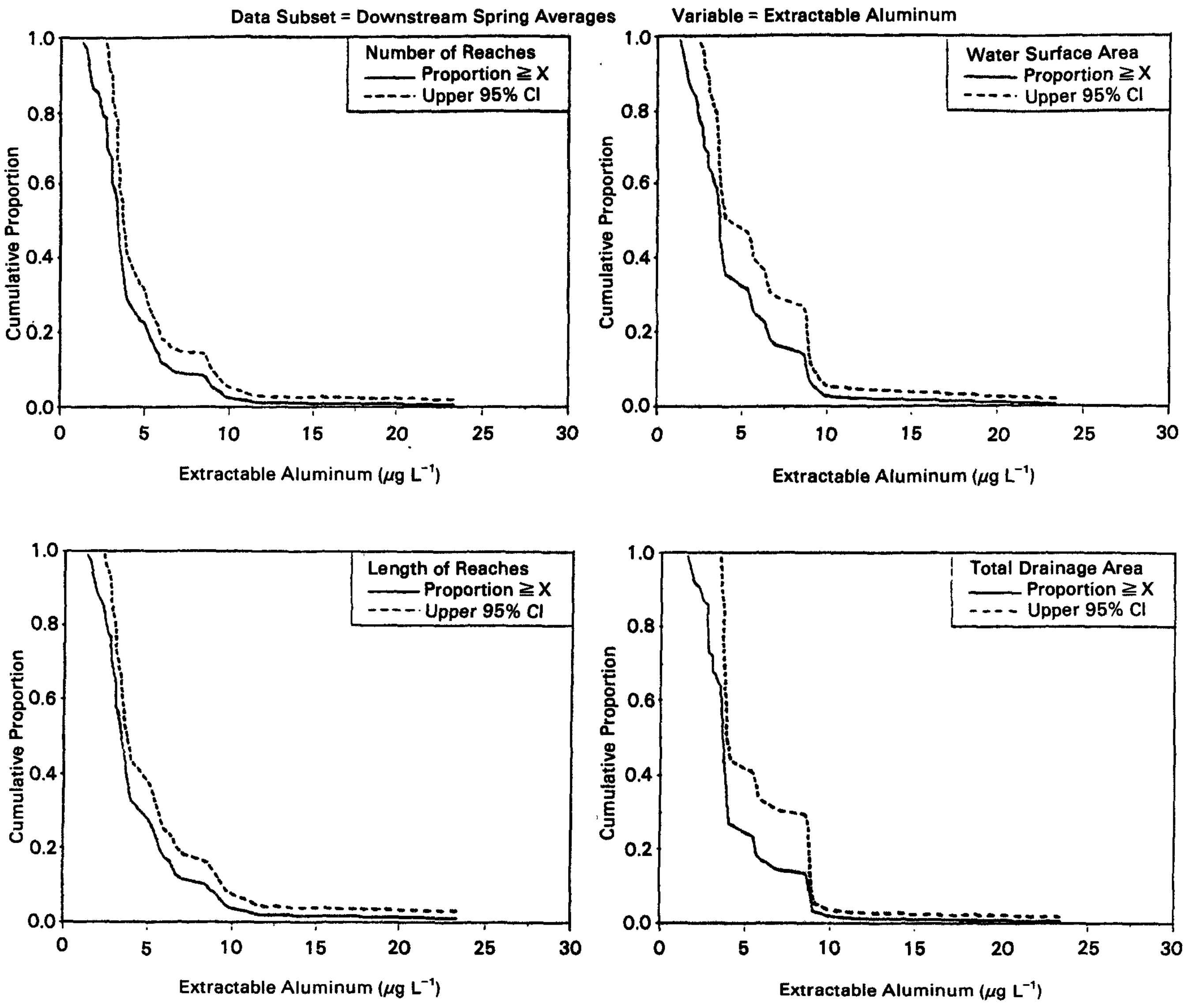


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (μeq L$^{-1}$) | 18.87 | 15.47 | 18.04 | 18.64 |
| 40 %ILE (μeq L$^{-1}$) | 21.48 | 19.40 | 21.49 | 21.09 |
| Median (μeq L$^{-1}$) | 23.21 | 21.66 | 23.49 | 21.87 |
| 60 %ILE (μeq L$^{-1}$) | 27.63 | 23.22 | 27.09 | 22.55 |
| 80 %ILE (μeq L$^{-1}$) | 31.34 | 31.27 | 31.40 | 31.29 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics (μeq L$^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 11.29 | 622.03 | 29.06 | 33.14 |

**Figure 5-6.** **Population distribution estimates for average spring downstream extractable aluminum concentrations in streams in the NSS Phase I-Pilot Survey.**



| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu g\ L^{-1}$) | 2.33 | 2.33 | 2.33 | 2.58 |
| 40 %ILE ($\mu g\ L^{-1}$) | 3.00 | 3.20 | 3.00 | 3.37 |
| Median ($\mu g\ L^{-1}$) | 3.24 | 3.50 | 3.24 | 3.47 |
| 60 %ILE ($\mu g\ L^{-1}$) | 3.51 | 3.67 | 3.67 | 3.67 |
| 80 %ILE ($\mu g\ L^{-1}$) | 4.93 | 6.18 | 5.51 | 5.44 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 37 | 84 |

| Sample Weighted Statistics ($\mu g\ L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 1.20 | 23.33 | 3.93 | 2.70 |

during seven rainfall events that occurred during the third sampling period have been excluded.

The curves represent the target reach population distribution estimates for the various water chemistry variables in terms of *number* of reaches (upper left), stream *length* (lower left), stream *surface area* (upper right), and a preliminary *discharge index* based solely on *drainage area* (lower right). The four types of distributions in Figures 5-1 - 5-6 are interpreted similarly. Values on the vertical axes in the graphs represent the proportion of the total target reach attribute (reach number, length, surface area, or discharge index) within the survey area estimated to have a value for any particular chemical variable greater than or equal to the corresponding value of that variable along the x axis (less than or equal to for pH and ANC). The pH and ANC plots were ordered differently because it is the lower values that are of greater environmental concern, rather than the higher values.

The dashed lines above the cumulative distribution curves represent the 95% upper confidence bound for the estimate. The NSWS estimates thus are viewed from a "worst case" standpoint, i.e., the maximum percentage of lakes or streams in the respective target populations that could reasonably be expected to be below some particular value for pH or ANC. An alternative viewpoint might be based on the minimum 95% confidence bound, i.e., the minimum percentage that could be expected to exhibit a particular pH or ANC concentration. A lower one-sided 95% bound would appear symmetrical to the upper bound about the cumulative distribution curve.

The tabular data at the bottom of each figure include values for the four quintiles and the median of each distribution. These figures permit rapid quantitative comparisons and provide an estimate of the total resource in the target population based on the second stage sample. For example, Figure 5-1 indicates that 20% of the 2021 reaches in the Southern Blue Ridge target population are estimated to have "index" pH values below 6.86 (the first quintile), while half were below 7.03 (the median). If the proportions are based on kilometers of reach, 20% of the 8963 km of streams in the target population were characterized as having a pH less than 6.84, and so on. Sample means and standard deviations, weighted to account for the non-uniform inclusion probabilities of each reach, are also shown. Actual, unique, and effective sample sizes (Overton, 1985) also are included in each figure. The actual sample size is the number of reaches in the second stage sample; the unique sample size is the number of uniquely occurring values for each variable, and the effective sample size is the number of grid points (including non-target reaches) associated with the second stage sample.

### 5.2.2 *Alternative Measurement Variables*

The representation of alternative distributions based on four different reach attributes is provided to stimulate discussions on the relative merits of these (or other) forms of expressing the distributions of the chemical variables for future Phase I results. *Frequency* distribution curves indicate the proportion of the total number of reaches which were above or below some reference value and are relatively easy to understand. Frequency distributions, however, treat reaches of different length and discharge equally. For this reason they may present, for example, a misleading picture of low ANC waters if ANC is correlated with reach length, drainage area, discharge, or position in the discharge network.

Expressing the estimates as *length* distributions (lower left frame) gives a better picture of the total resource, but still treats large and small streams of the same length equally. The length distribution estimate, as presented in the figures, assumes that the value of the chemical variable is uniform throughout the length of the reach, and equal to the value at the lower node. The extent to which this approximation may be reasonable is evaluated below. An alternative is to collect data at more than one point on the reach and to interpolate the results to a number of segments within each target reach.

A crude aquatic habitat area index was calculated by multiplying reach length by mean stream width measured at the two sampling nodes. The resulting index ("water surface area") was used to construct the areal distribution curves in the upper right frames of Figures 5-1 - 5-6. These areal distribution curves indicate the proportion of combined reach water surface area above or below some reference value of a chemical variable. Fisheries managers frequently refer to "weighted usable area" as a measure of the amount of aquatic habitat available to any particular species. Weighted usable area is often calculated on the basis of velocity, depth, substrate, and other physical variables (e.g., Bovee and Cochnauer, 1977). While it can be seen that such a measure would quantify the "usable" portion of the total aquatic surface area indexed in the Pilot Survey, the calculation of that habitat portion for the sample of 54 streams was beyond the scope of work in the Survey.

The lower right frames in the distribution estimate figures display preliminary *discharge index* distributions, which were calculated solely on the basis of total watershed area ($a_1 + a_2$) of the target reaches (and are thus labeled). When multiplied by an appropriate net precipitation index value, discharge index values estimate the discharge at the downstream nodes of target reaches. Total watershed area (discharge index) distribution curves indicate, on the basis of watershed area, the proportion of target reaches above or below a given reference value of a chemical variable.

The total population of target reaches within the Pilot Survey area includes drainages ranging from 1 to 155 km$^2$, with smaller drainages nested within larger ones. The estimated total watershed area of 51,215 km$^2$ for the target reaches in Pilot Survey area, therefore, includes drainage areas counted more than once and should not be construed to represent the total land area drained by the network of target reaches. Once adjusted for runoff, the total discharge index would provide an estimate of the sum of the discharges at the downstream nodes of all target reaches in the population, summing the discharge of all reach segments within a hierarchical network of target reaches.

While a stream *discharge index* is not a particularly good measure of available fish habitat, the preliminary discharge index distributions, once refined, would provide a useful picture of the chemical composition of water moving through the target stream population. The best interpretation of the curves as they are presently shown is that they estimate the instantaneous, discharge-weighted distribution of the chemical variables *over the downstream nodes* of all target reaches in the population, *assuming* that discharge is proportional to drainage area only. The discharge index distribution estimates will be revised upon completion of a predictive model for net precipitation that takes into account spatial differences in precipitation, evapotranspiration, and runoff. The accuracy of such a revised discharge index (or the uncorrected index as presently expressed) would be reduced in drainage networks where groundwater is delivered across topographic drainage divides (Toth, 1963).

Another useful target reach attribute would be the concentration of some chemical variable (C) in runoff contributed to a reach by direct drainage between an upper and lower sampling location. For headwater reaches (R = 1), this concentration would be equal to that in the water at the downstream node. For downstream reaches (R > 1), an appropriate concentration variable ($C_{a_1}$) would be calculated using a mass balance between the upstream and downstream nodes, as estimated by the measured chemical concentrations and measured or estimated (indexed) discharges:

$$C_{a_1} = \frac{(Q_D \cdot C_D) - (Q_U \cdot C_U)}{(Q_D - Q_U)} \qquad [5\text{-}1]$$

where Q and C refer to discharge and concentration, respectively, and the subscripts U and D refer to the upstream and downstream nodes, respectively. Such estimates could only be calculated for the Phase I-Pilot Survey summer sampling period and thus are not included in the distribution figures.

Comparisons of the curves and quintile values for each of the variables in Figures 5-1 - 5-6 show very similar distributions. Apparently, there is very little effect of the choice of a particular distribution index on the interpretation of each of the six NSS chemical distributions. Distribution estimates based on the discharge index show the greatest differences, but this may be caused by the incomplete nature of the index. The similarity of the curves suggests that, at least on a region-wide basis, there was little (if any) correlation between concentrations of the NSS primary variables and stream length or drainage area, which was subsequently confirmed using univariate and multivariate regression analyses. Elevation is thus far the only geographic variable tested that has shown any significant relationship to pH or ANC concentrations, and even this relationship proved too weak to be of any predictive or descriptive value in partitioning these distributions into *a priori* categories of interest.

### *5.2.3 Reference Values*

A potentially useful way of expressing population estimates is with respect to the proportion or number (length, area, etc.) of reaches which are above or below some particular chemical reference value. A reference value could represent a criterion value established on the basis of toxicological studies (e.g., a $TLC_{50}$ for inorganic monomeric aluminum) or a legal standard. No widely accepted criteria are presently available for evaluating the quality of waters with respect to acidification by atmospheric deposition, but reference values can also be based on common usage. For example, waters with negative ANC values are acidic by definition, and those below 50 $\mu$eq L$^{-1}$ are often cited as being highly susceptible to acidification (Pfeiffer and Festa, 1980; Linthurst et al., 1986, Table 5-2). Alternatively, reference values may simply partition a population into useful categories. Such categories may be artificial, such as (logarithmically) evenly spaced pH increments (e.g., 4.0, 4.5, 5.0, 5.5), or they may represent natural groupings (clusters) of geochemically similar waters, as explained below. Although any partitioning scheme provides an important starting point for most detailed analyses, care must be exercised in interpreting population distributions based on criteria associated with any single chemical variable.

Examples of such partitioning of distribution estimates for the Phase I-Pilot Survey streams are

Table 5-1. **Phase I-Pilot Survey Length Distribution Estimates Associated with Reference Values Based on Natural Univariate Groupings of Streams (except where noted for ANC)***

| Variable | Reference Value | Population Estimate*<br>Proportion (%) | <br>Total Length (km) | <br>Upper 95% C.I. (km) |
|---|---|---|---|---|
| pH | ≤6.7 | 7.4 | 662 | 1244 |
| | ≤7.6 | 87.0 | 7800 | 9373 |
| | ≤8.1 | 92.0 | 8247 | 9816 |
| ANC (µeq $L^{-1}$) | ≤25 | 1.2 | 108 | 283 |
| | ≤50[a] | 6.3 | 561 | 980 |
| | ≤115 | 48.0 | 4304 | 5637 |
| | ≤200[a] | 74.4 | 6666 | 8353 |
| | ≤250 | 84.5 | 7573 | 9155 |
| Sulfate (µeq $L^{-1}$) | ≥40 | 30.8 | 2761 | 3820 |
| | ≥80 | 10.7 | 957 | 1625 |
| | ≥120 | 3.7 | 331 | 710 |
| Nitrate (µeq $L^{-1}$) | ≥10 | 40.7 | 3648 | 4899 |
| | ≥20 | 22.9 | 2054 | 3088 |
| | ≥35 | 2.9 | 259 | 557 |
| Chloride (µeq $L^{-1}$) | ≥50 | 9.5 | 852 | 1356 |
| | ≥100 | 2.4 | 215 | 455 |
| | ≥200 | 0.9 | 77 | 190 |

*All estimates based on spring average reach chemistry at the downstream sampling nodes.

[a] Values provided to allow comparison with commonly cited sensitivity criteria (Table 5-2 in Linthurst et al., 1986).

shown in Table 5-1. The reference values used in Table 5-1 were derived by ordering sample sites according to measured values of each chemical variable (ordination) and searching for natural gaps in the data (the interpretive value of this procedure will become clear below). Because of the absence of low pH values, there appears to be little value at this time in partitioning these distributions into *a priori* categories of interest. Extractable aluminum concentrations were too low to make partitioning meaningful and are not represented in Table 5-1. Commonly cited ANC reference values (50 and 200 µeq $L^{-1}$) are included to allow comparisons with other data bases. Because the measurement variables do not have a strong effect on the distribution estimates, only those based on reach length are reported here. New reference values that would aid in comparing the Southern Blue Ridge with other NSWS target populations will be computed for future data reports.

### 5.2.4 Sample Timing and Frequency

During the design phases of the NSS, concern was expressed that temporal chemical variability may be so high during the spring that more than one sampling visit would yield widely diverging population estimates. Temporal variability could include both hourly/daily components due to hydrologic events, and weekly/monthly components due to vegetational (e.g., leafout) and climatic (e.g., soil warming) effects. In order to determine the effect of these variance components on the outcome of a synoptic survey, three biweekly spring samples and one summer sample were collected during the Phase I-Pilot Survey without regard to present or antecedent meteorologic conditions.

Rainfall events were observed to cause temporal variability in NSS target population streams. Table 5-2 demonstrates the effect of seven hydrologic events on two primary NSS variables, pH and ANC. In each case, identifying the occurrence of the event was predicated on the occurrence of previous precipitation, an increase in stream stage, and an increase in turbidity and total aluminum indicative of increased runoff in the watershed (Section 4.5.6). ANC decreased by an average of 23 percent (range -17% to -35%) and pH decreased by almost 0.2 units (range -0.01 to -0.37 units) during the events. Summer events were also typically characterized by reduced pH and ANC concentrations, but the effects were difficult to quantify precisely without a summer benchmark against which to compare stage heights during suspected events. The average spring ANC depression due to hydrologic events would be sufficient to move a given stream approximately 20 percentile units, relative to its position on the curves in Figure 5-2, and thus could have a substantial impact on stream classification, as explained below.

Once the episodic effects were removed, the remaining temporal variance had little effect on the

**Table 5-2.** **Effects of Rainfall Events* on ANC and pH at Seven Downstream Phase I-Pilot Survey Sampling Sites**

| Stream ID | ANC[a] ($\mu$eq $L^{-1}$) | pH[a] (Units) | Δ Stage (Ft) |
|---|---|---|---|
| 7702 | 967<br>-21% | 8.22<br>-0.29 | +0.25 |
| 7819 | 201<br>-19% | 7.02<br>-0.14 | +0.51 |
| 7831 | 274<br>-22% | 7.00<br>-0.12 | +0.55 |
| 8809 | 75<br>-17% | 6.78<br>-0.01 | +0.28 |
| 8902 | 41<br>-35% | 6.67<br>-0.17 | +0.51 |
| 8904 | 132<br>-29% | 6.76<br>-0.37 | +0.63 |
| 8906 | 52<br>-28% | 6.25<br>-0.24 | +0.30 |
| Mean (± 1 SD) | -23 ± 6% | -0.19 ± 0.12 Units | |

*Events are predicated on at least three of the following 7.5 cm change in stage, evidence of precipitation on Data Form 4, precipitation within 1 day at the nearest NOAA meteorological station, or an increase in turbidity and total aluminum.

[a] ANC and pH represent values measured during episodes, and percentages represent depressions below corresponding mean spring values.

shape of the distribution estimates over the three spring sampling periods. Figures 5-7 - 5-9 display cumulative frequency curves based on the four different sampling intervals, with the seven spring episodes removed from the data base as explained in Section 4.5.6. For all variables, the length distribution estimates based on the three spring samples are virtually superimposed. The total extractable aluminum concentrations are sufficiently close to the analytical decision limit (Table 4-8) that differences probably include a substantial component of analytical error (variance). Week-to-week variation in stream chemistry during the spring apparently has minimal effect on the distribution of these species in streams of the target population, if the large rainfall events can be separated from typical spring flow conditions.

Seasonal variation, however, was sufficient to alter the distribution estimates for some of the NSS primary variables. Summer distributions were virtually identical to spring distributions for pH, sulfate, chloride, and total extractable aluminum. ANC increased substantially from spring to summer, especially in streams with ANC $< 250$ $\mu$eq $L^{-1}$. Nitrate distributions were similar during both sampling intervals, except for streams near the low ($< 10$ $\mu$eq $L^{-1}$) end of the distribution.

We also approached the question of differences among the sampling periods by calculating paired-t statistics for the six primary variables. Table 5-3 presents results based on reaches with ANC less than 250 $\mu$eq $L^{-1}$, unweighted for reach inclusion probability. High ANC reaches were excluded to avoid possible differences in geochemical patterns correlated with land use or geology. No calculations were performed for extractable aluminum, because a majority of the values were below the quantitation limit; pH calculations were performed on the log-transformed value rather than on hydrogen ion activity.

Chloride and pH were the only variables to increase significantly between the three spring sampling intervals, but the quantitative changes are small and probably unimportant from a water quality assessment perspective. The 12% increase in chloride, followed by a subsequent 11% decline, probably reflects the unusually dry conditions during the second (SP2) sampling interval. ANC exhibited a substantial 36% increase between the average spring and summer sample, and pH increased by 0.04 units. The limitation of the t-test, which is a test only for difference in the means, is illustrated by nitrate, which exhibits a differential shift in different parts of the distribution (Figure 5-8).

### *5.2.5 Spatial Aspects of Reach Chemistry*

The relatively rapid downstream flow which is characteristic of streams yields a set of sampling problems different from those encountered in the study of lakes. Sampling at a point in the center of an unstratified lake is widely accepted as providing a useful index value for the central water column chemistry. A single point sample at the downstream node of a stream reach, however, may not provide a particularly good representation of the chemistry of the entire reach lying above it. Chemical composition may change along the reach due to instream processes (e.g., primary production), confluence with streams not represented on 1:250,000-scale maps, and lateral inflows from springs and seeps feeding the reach. In describing a population of stream reaches, it is often the length (or some transformation such as habitat area) of reaches characterized by some particular chemical value that is of interest. Any variation along the reach should be accounted for at a level of resolution appropriate to the population estimate.

During the Phase I-Pilot Survey, 23 reaches were sampled at their upstream and downstream nodes

Figure 5-7. **Comparison of population length distribution estimates for pH and ANC from the three spring and one summer sampling intervals.**

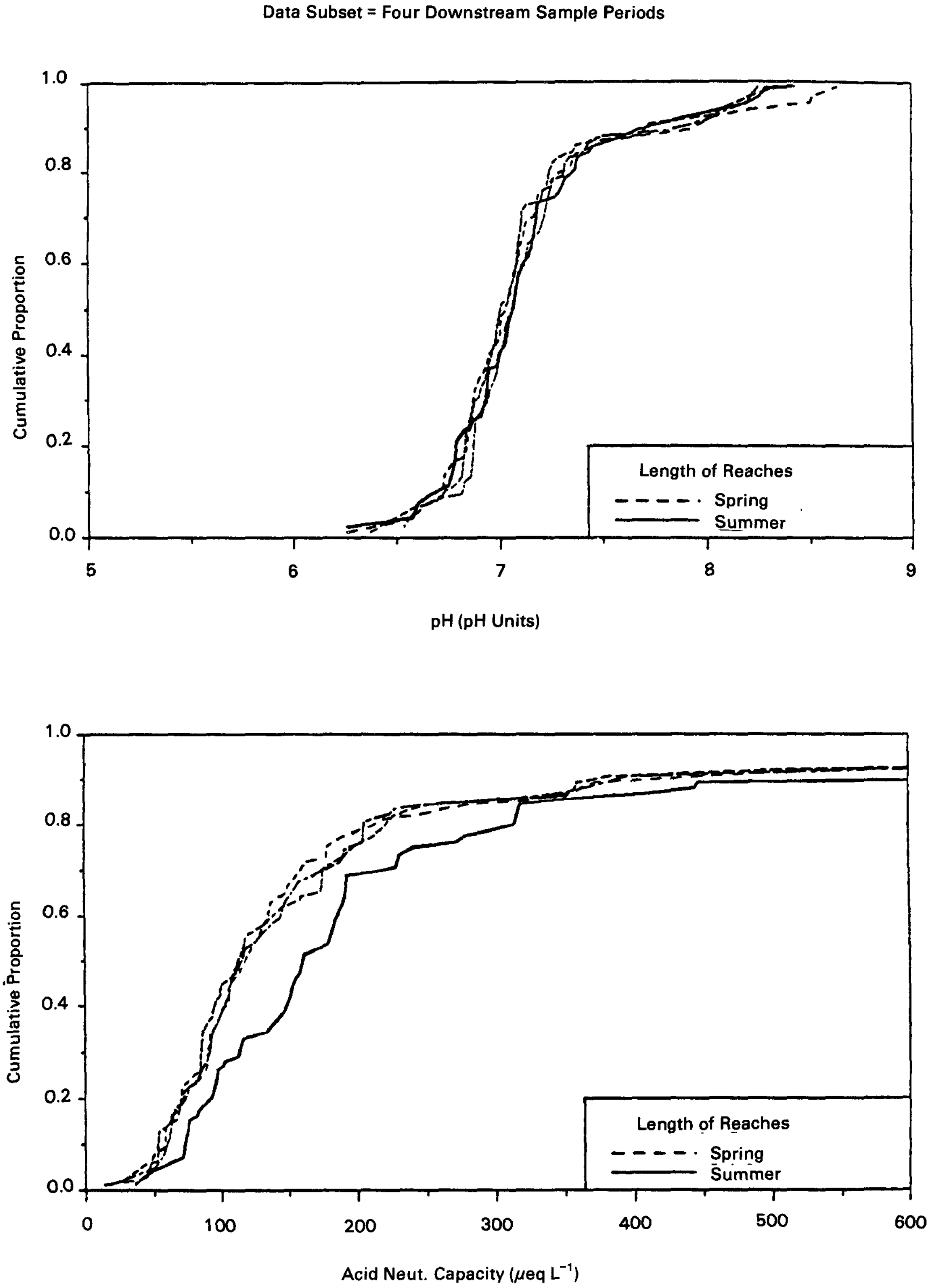
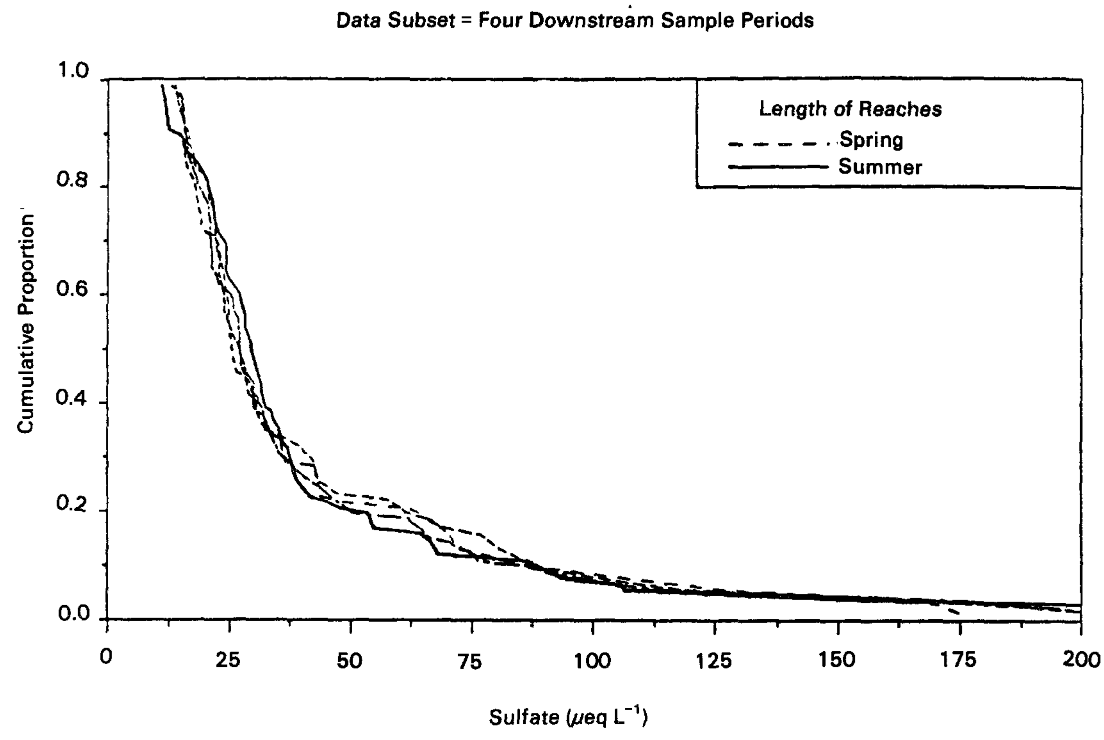


**Figure 5-8.** **Comparison of population length distribution estimates for sulfate and nitrate from the three spring and one summer sampling intervals.**



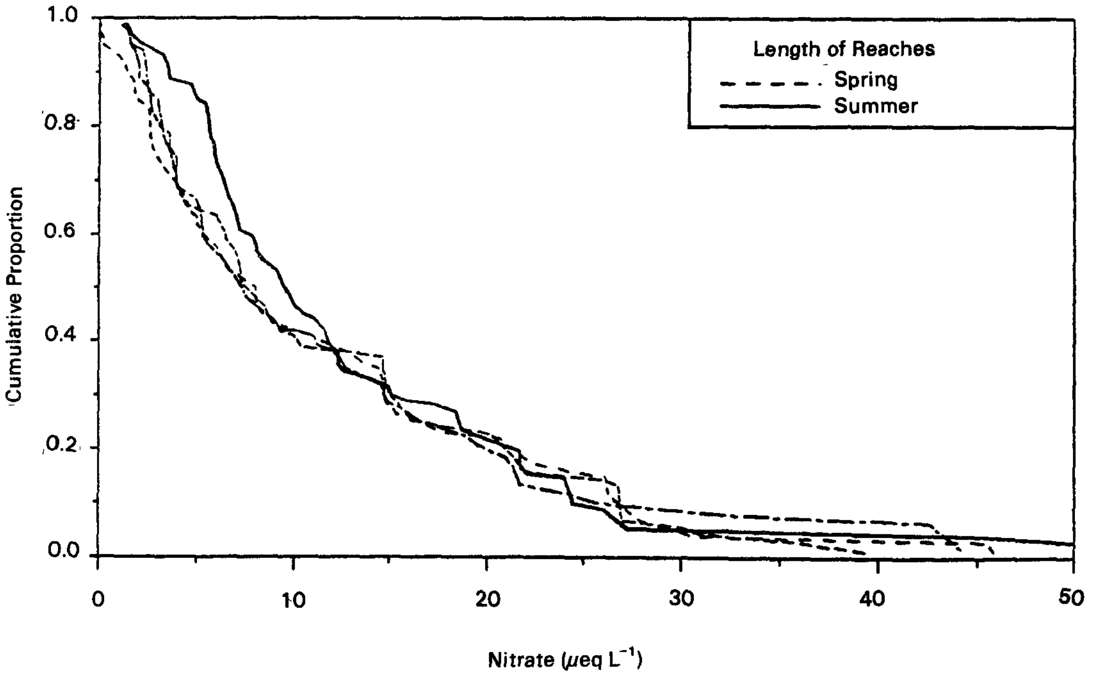


Figure 5-9. **Comparison of population length distribution estimates for chloride and extractable aluminum based on the three spring and one summer sampling intervals.**

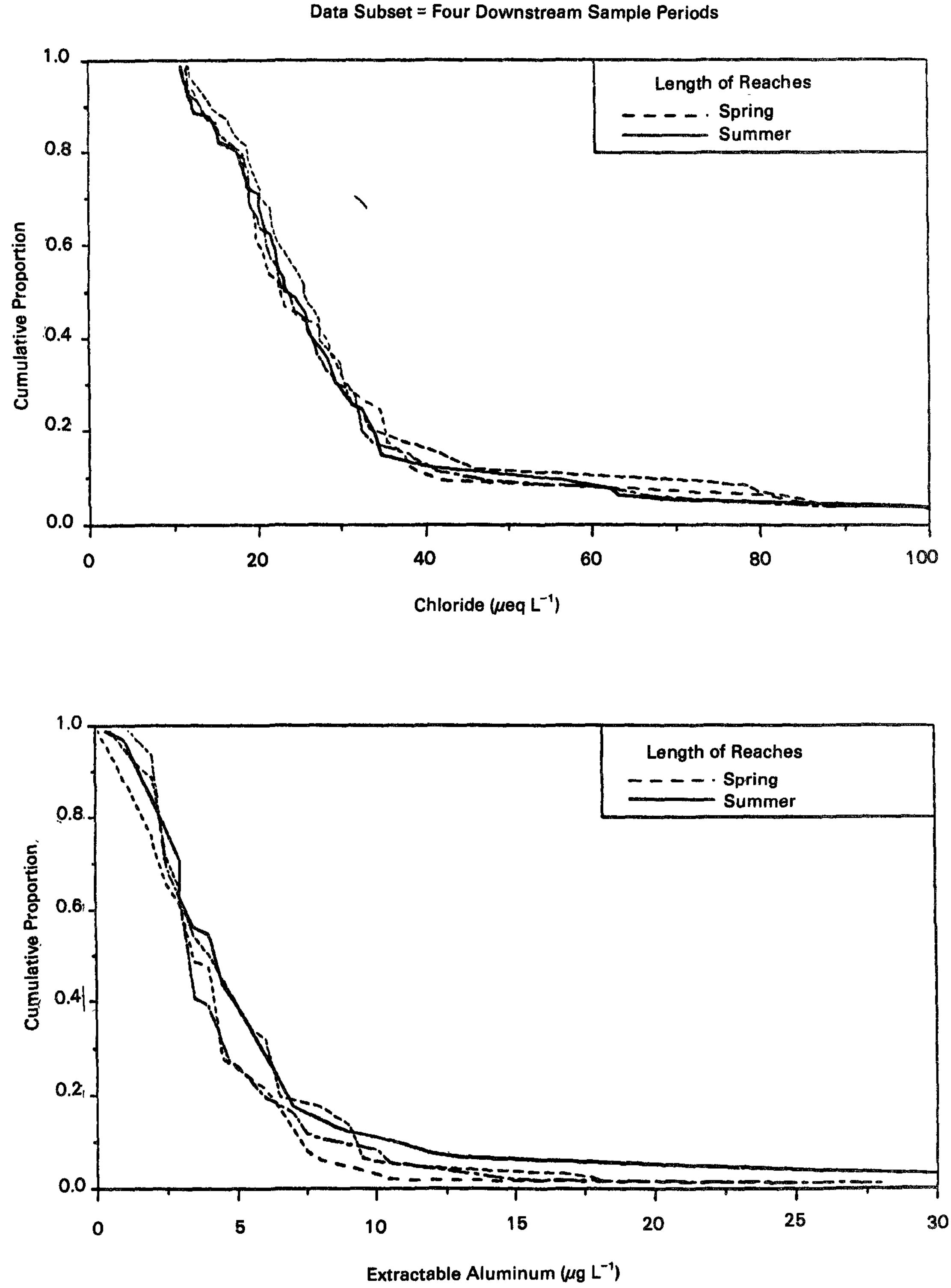


**Table 5-3. Statistically Significant (p = 0.05) Differences Between Mean Concentrations of Primary Variables Between Spring (SP1, SP2, SP3) and Between Summer (SU) and Average Spring (SP) Sampling Intervals (downstream nodes) for Streams with $< 250\ \mu eq\ L^{-1}$ ANC**

| Chemical Variable | Mean Concentration Difference[a]<br>SP2 − SP1<br>n = 38 | SP3 − SP2<br>n = 39 | SU − $\overline{SP}$<br>n = 34 |
|---|---|---|---|
| ANC | NS | NS | +36% |
| pH | NS | +0.05 units | +0.04 units |
| Sulfate | NS | NS | NS |
| Nitrate | NS | NS | NS |
| Chloride | +12% | −11% | NS |

[a] Comparisons are not weighted according to reach inclusion probability; episodes have been excluded.
NS = not significant at p = 0.05.

during the third spring sampling interval, and all sites were sampled at both nodes during the summer. The purpose was to determine:

1. Whether chemistry at the opposite nodes of a single reach was substantially different.
2. Whether downstream chemistry could be adjusted to reflect the entire reach chemistry on the basis of a limited number of upstream samples.

The answer to objective (1) was approached much as the question of temporal variability was in the previous section.

Figures 5-10 through 5-12 show frequency distribution estimates for the six primary variables based on the chemistry at the upstream versus the downstream sampling nodes during the summer sampling interval. With the exception of sulfate and extractable aluminum, substantially lower values of all variables were observed at the upstream sites. The curves indicate only that the frequency distribution estimates are affected by the sampling position along the reach during the summer sampling interval. An insufficient number of streams was sampled at both nodes to construct meaningful comparative spring distribution estimates.

It should be noted that the upstream node chemistry could be used to indicate the chemical properties of an unspecified target population of streams draining smaller watersheds than those represented by the actual NSS target population. The distribution estimates based on upstream chemical data in Figures 5-10 - 5-12 represent this unspecified population of streams. Median values (expressed as proportions) for pH, ANC, nitrate and chloride would be lower for this unspecified population. The NSS geographic site data describe the drainage areas (a3) for this population of smaller streams, but no information on the length of streams in this population is presently encoded. We are presently investigating alternatives for making distribution estimates for these lower order streams.

The effect of sampling position can also be seen in Table 5-4 using paired-t comparisons for the sites not exhibiting episodes on the last spring and summer sampling dates. Again, sites with spring ANC averages $> 250\ \mu eq\ L^{-1}$ were excluded and aluminum has been excluded due to the low concentrations observed. Virtually all primary variables showed statistically significant within-stream spatial differences, many of which were numerically large enough to affect interpretation of the data. The tabulated data also show that the spatial sampling effects demonstrated in Figures 5-10 through 5-12 were not restricted to the summer sampling period.

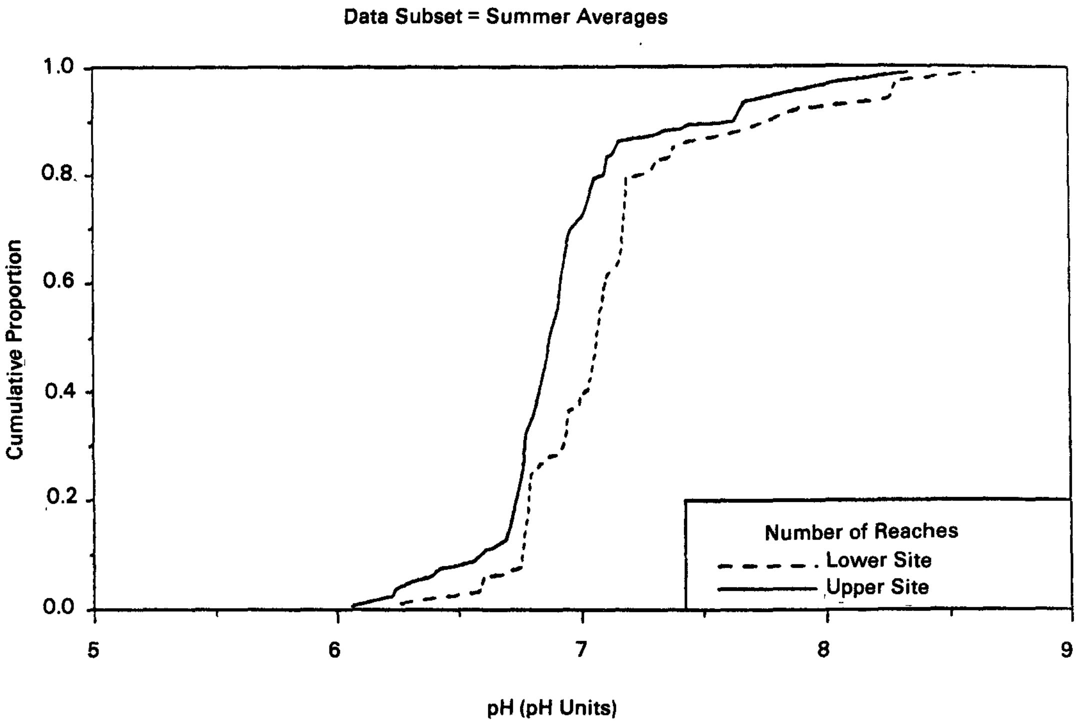
Given that the chemistry at the upstream and downstream nodes of the reaches in the target population were clearly different, it remained to be determined whether one value could be inferred by calibration on the basis of the other. Simple linear regression equations were calculated and bivariate plots were investigated visually for both spring and summer data, with and without episodes removed, both including and excluding high ($> 250\ \mu eq\ L^{-1}$) ANC reaches. Whereas most of the summer relationships were highly significant, the 95% confidence intervals about the predicted values were on the order of ± 50% or more and this restricts the utility of prediction of upstream values using downstream chemical data.

### *5.2.6 Interpretation for Regional Assessments*

One of the primary objectives of Phase I of the NSS is to provide population distribution estimates of the number of acidic (low pH) and potentially susceptible (low ANC) streams in each NSS subregion. Ways in which the population estimates can be constructed and used to estimate the characteristics of the target populations were presented and discussed in Section 5.2.2. Although not a specific objective of the NSS, a relevant issue is how the resulting estimates could be interpreted to provide incremental information useful in a regional assessment. In this section we will demonstrate, by example, some potential uses of the data, as well as some caveats and potential pitfalls in the interpretation process.

It is apparent from Figure 5-1 - 5-6 and Table 5-1 that the Phase I-Pilot Survey characterized a very high proportion of target stream reaches and target stream length as possessing low acid neutralizing capacity (ANC). Half of the reaches and half of the

Figure 5-10. Comparisons of frequency distribution estimates for pH and ANC in Phase I—Pilot Survey streams based on upstream versus downstream sampling locations during the summer sampling interval.



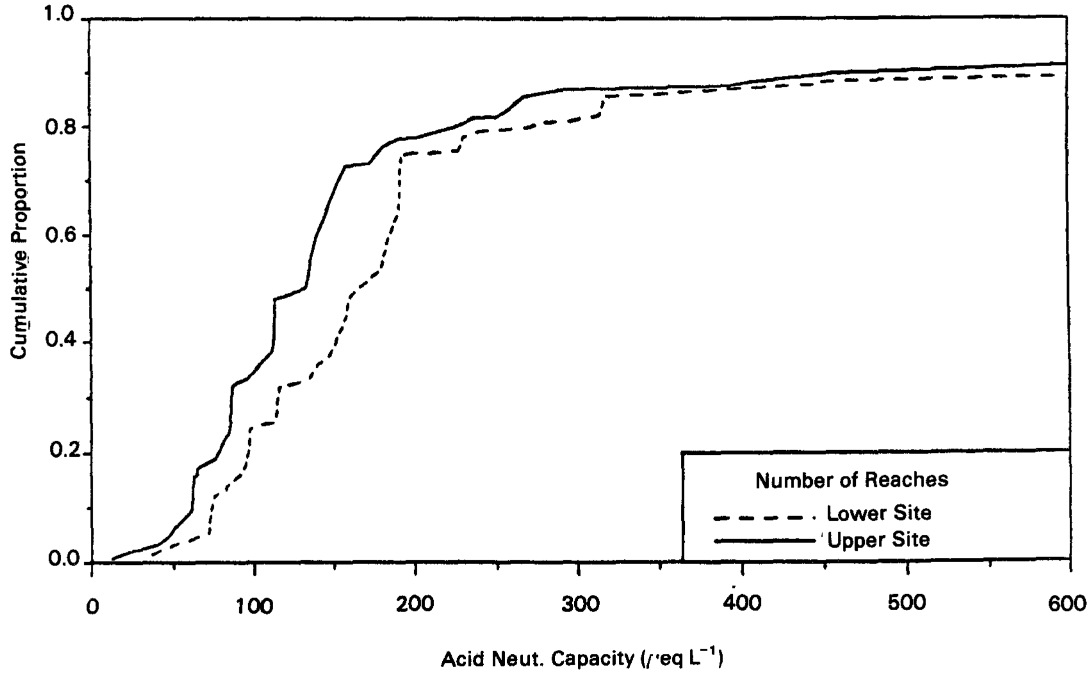


**Figure 5-11.** Comparisons of frequency distribution estimates for sulfate and nitrate concentrations in Phase I-Pilot Survey streams based on upstream versus downstream sampling locations during the summer sampling inverval.

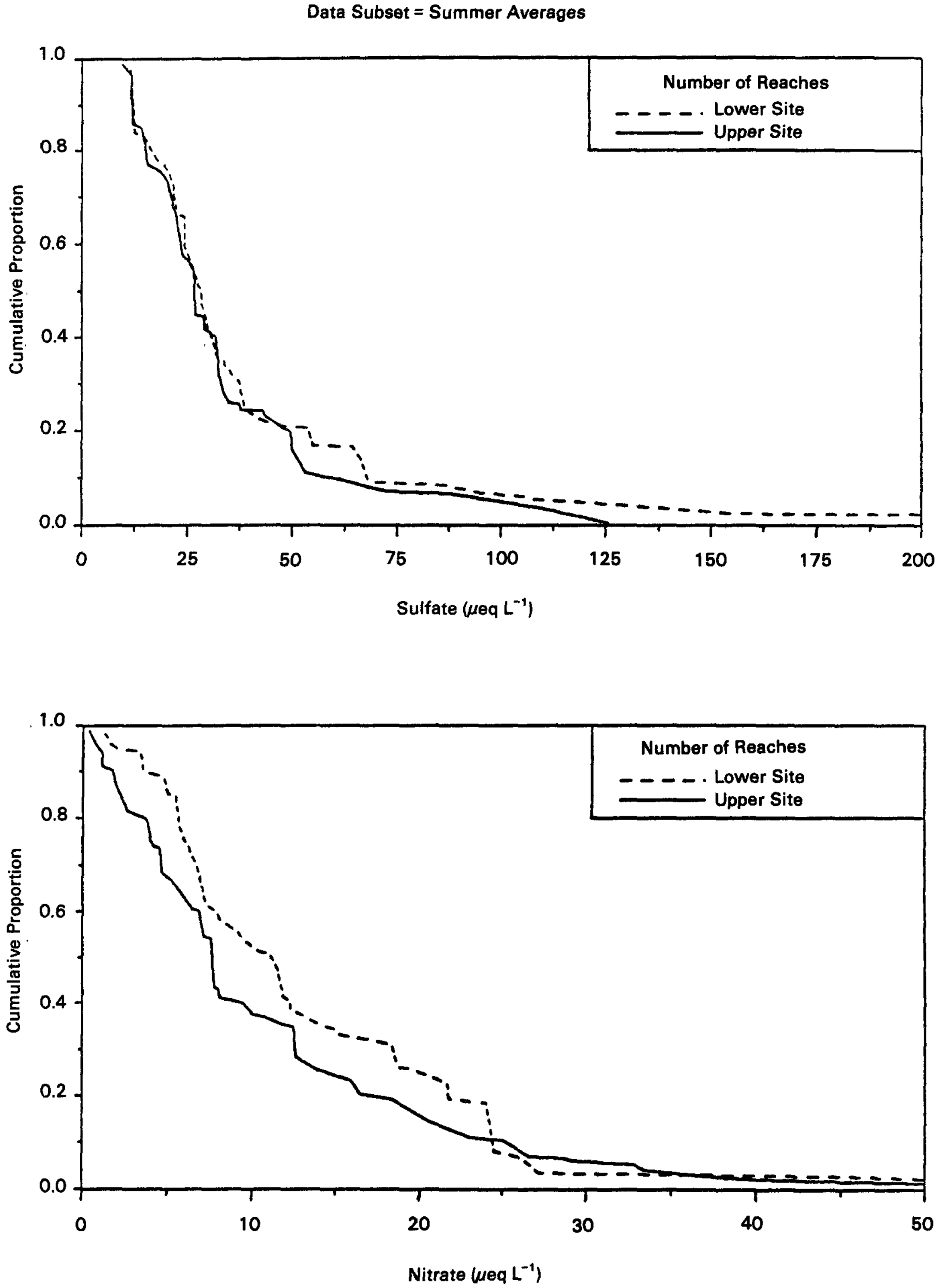


Figure 5-12. Comparisons of frequency distribution estimates for chloride and aluminum concentrations in Phase I-Pilot Survey streams based on upstream versus downstream sampling locations during the summer sampling interval.

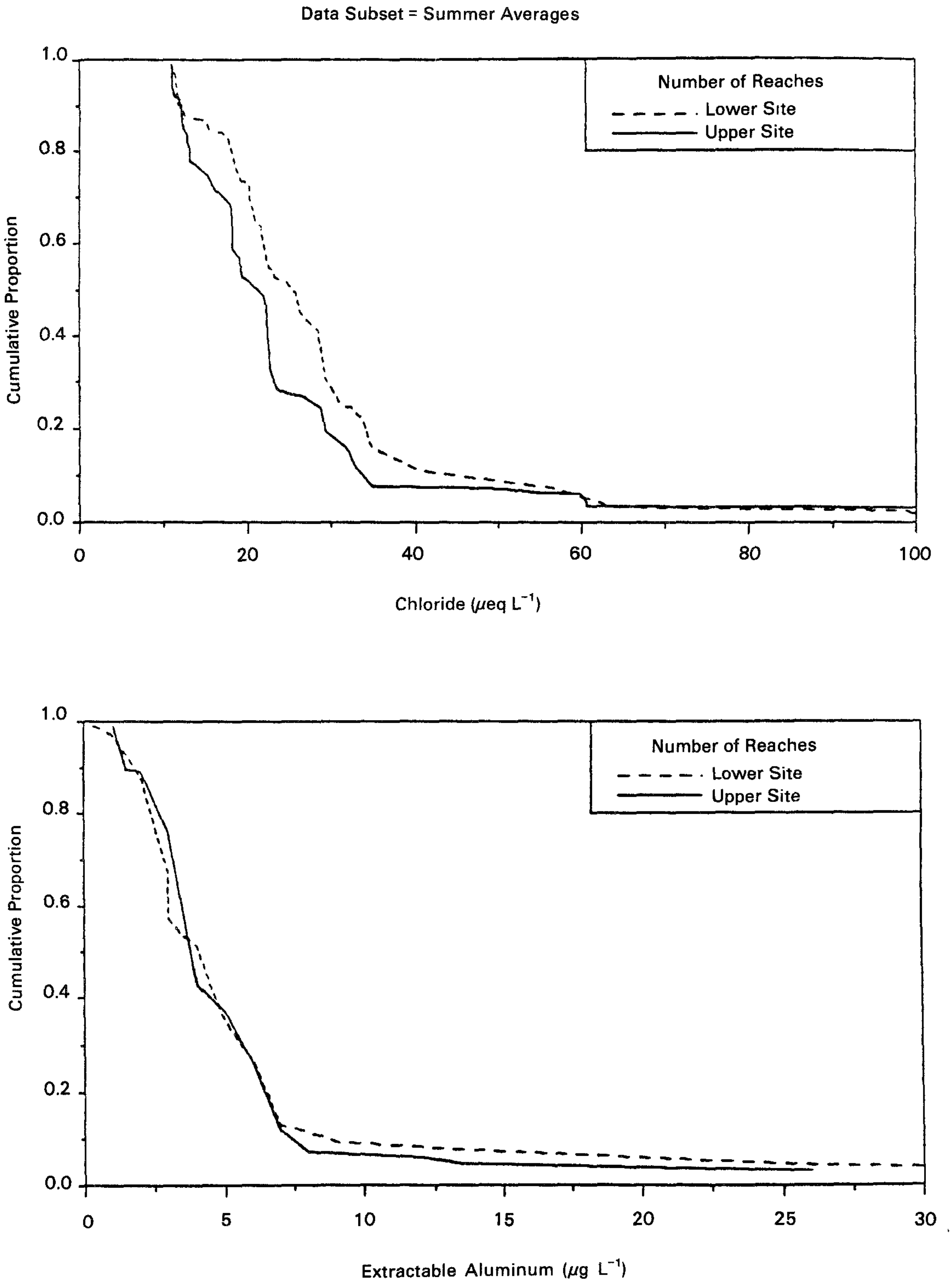


**Table 5-4.** **Comparison of Upstream/Downstream Chemistry During the Third Spring (SP3) and Summer (SU) Sampling Intervals, Based on a Paired t-Test with Differences Weighted to Reflect Inclusion Probabilities ($w_i$)***

| Chemical Variable | Sampling Interval<br>SP3<br>n = 14 | <br>SU<br>n = 31 |
|---|---|---|
| ANC | +14% | +26% |
| pH | +0.06 units | +0.13 units |
| Sulfate | +15% | +7% |
| Nitrate | +33% | +37% |
| Chloride | NS[a] | +23% |

[a] NS = not significant at p = 0.05.

*Only streams with mean spring ANC < 250 μeq/l are considered, and samples collected during hydrologic events have been excluded.

total reach length were estimated to contain water of less than 120 μeq $L^{-1}$ of ANC. Nearly 75% of the estimated length distribution was below the reference value of 200 μeq $L^{-1}$, a value often cited as separating potentially sensitive from relatively insensitive systems (Linthurst et al., 1986). However, only 6.3% of the target reach miles are expected to have ANC concentrations less than 50 μeq $L^{-1}$, a value that has been used to identify particularly acid-sensitive waters (Pfeiffer and Festa, 1980).

Despite the preponderance of low ANC in the target population, fewer than 8% of the reaches (upper 95% CI = 14%) exhibited non-episodic, average spring pH values below 6.7. Even when the episodes and the upstream node measurements were included in the data, no samples were collected during the Phase I-Pilot Survey that exhibited a pH value below 6.0. A "worst-case" estimate can be made for the spring index pH value in the target population streams by choosing a reference value at the low end of the range observed during the survey, and calculating the upper 95% confidence bound on the estimate. The exercise leads us to conclude that, with 95% confidence, less than 3.2% of the combined length of streams in the target population (based on the mean downstream spring average pH with episodes excluded) exhibited a pH below 6.4 during 1985. While it would be helpful to calculate the length of stream reach below some more meaningful value (e.g., 5.0), the method used to estimate confidence intervals cannot be applied below the minimum index value occurring in the sample (6.38). These observations and estimates are based on the closed-headspace pH measurements made at the mobile field laboratory, which were of consistently high quality throughout the project. All pH values were well above the range of 5.3 to 5.7 frequently cited as representing geochemical neutrality. Although this analysis does not address the question of whether pH values in these streams would be different in the absence of acid deposition nor what the lowest pH values were experienced during the spring, the "index values" are certainly not in a pH range that has been associated with deterioration of coldwater sport fisheries in the past (Howells, 1984; Magnuson et al., 1984). However, some estimate of transient chemical changes that may occur during hydrologic episodes is needed before a critical evaluation of chemical habitat quality can be complete.

Consistent with distributions for pH dominated by neutral conditions, the median extractable aluminum concentration (approximately 3 μg $L^{-1}$) was barely above the analytical detection limit, and the maximum concentration was only 23 μg $L^{-1}$. Inorganic monomeric aluminum concentrations, estimated as the difference between total extractable and non-exchangeable aluminum fractions, were below the decision limit in virtually all samples and are, therefore, not reported. Total extractable aluminum concentrations in the range 2-20 μg $L^{-1}$ are one to two orders of magnitude lower than the lowest concentrations at which short-term exposure of selected fish species have been observed to produce significant mortality (Schofield and Trojnar, 1980; Baker, 1981; Henriksen et al., 1984; Johnson et al., 1985).

The foregoing statements exemplify the kinds of univariate interpretations that represent one level of incremental information that can be used to satisfy the NSS primary objectives related to *description*. These statements characterize the Southern Blue Ridge as an area dominated by stream waters of moderately low acid-neutralizing capacity, but in which chronic acidic conditions are relatively rare. Although we believe this description to be fundamentally accurate, several caveats should be borne in mind.

First, the target population, represented by the sampled population, focuses on second to fourth order (Strahler order based on blue line representations on 1:24,000-scale topographic maps) reaches and thus does not include the first order, headwater reaches which might be expected to be "early warning" indicators of acidification. Furthermore, spring reach chemistry is characterized on the basis of the chemistry at the downstream node. Based on the limited spring data in Table 5-4, the upper nodes of the target reaches might be expected to be 14% lower in ANC than the corresponding lower nodes, and 0.06 units lower in pH. These data suggest that the target population estimates for ANC and pH based on reach length are somewhat high, although not markedly so. Almost half (44%) of the upper nodes of the target population reaches drain first order reaches (1:24,000 blue line), and thus the water draining from these headwater catchments is, as expected, lower in ANC and pH than that draining the larger catchments represented by the downstream nodes of the target population. Again, the differences are not large. This project did not measure the chemistry at the upper limits of flowing water, but such streams are likely to be extremely small, and many are likely to be ephemeral.

An alternative sampling design could have focused on these extremely small target reaches, with the objective of detecting early signs of acidification. However, the difficulty of access, together that the possibility that many of the second stage sample reaches may have been dry at their upper node or misrepresented on maps would have greatly increased the cost per site of field sampling. This translates to a smaller sample, or less areal coverage per research dollar, especially given the fixed cost component of a project. Add to this factor the highest degree of chemical variance in the smaller catchments resulting from increased heterogeneity and shorter hydraulic residence times, and the efficiency of the survey decreases accordingly. By including (or focusing on) first order streams, we might discover more acidic streams, but they would represent a very small percentage of the resource at risk, and the confidence bounds on the estimate might well overlap those obtained with the present design. If the chemistry of the smallest streams in a critical component of the assessment activity, an alternative, more efficient approach is to focus future headwater sampling on areas found to contain significant percentages of low ANC systems in Phase I.

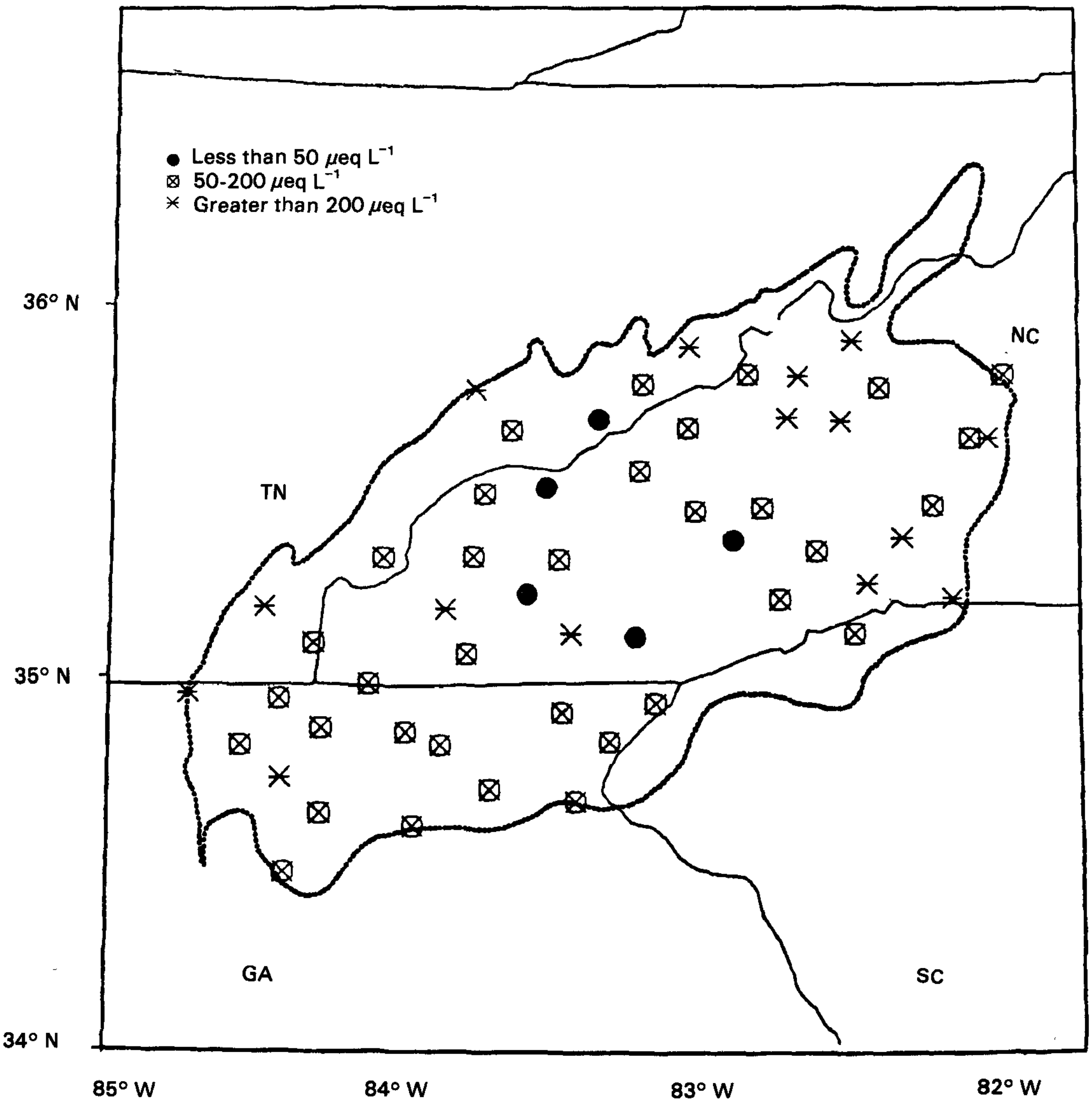
In a temporal setting, the population estimates here strictly refer to spring and summer of 1985. Precipitation was approximately half of normal during the spring, but 5% above normal during July. If the storm tracks were also unusual, 1985 may represent an unusual year. Some idea of the representativeness of any single year synoptic sample can be gained by comparing historical records for the special interest sites sampled in each NSS subregion. These data were not available for the Southern Blue Ridge sites as this report was being prepared.

Spring may not represent typical annual low pH or low ANC conditions in the study area. Discussions with local investigators indicated that (with the possible exception of late winter) spring did appear to represent typically low pH and ANC conditions in the region, however, and that the sensitive swim-up fry life stages of salmonids in the region were present at that time. Therefore, lower pH conditions in mid-winter (if they occur) may be of less ecological interest. The population estimates do not include the effects of episodes. Although episodes are likely to be critical determinants of fish survival, the duration of such events may be extremely short in the Southern Blue Ridge, and thus extremely difficult to measure in a synoptic survey. Even though several hydrologic events were sampled in the Survey (none of which produced pH depressions of greater than 0.4 units or pH values below the minimum reported above, Table 5-2), the study design does not provide an estimate of the minimum pH experienced by these streams during rainstorms, nor of the temporal or spatial extents of pH depression associated with rainstorms. Rather than attempting to quantify these transient effects in a synoptic survey, it is planned to target episodes monitoring at typical low ANC sites in future studies, and subsequently to expand the results via the Phase I population estimate to the target population in each subregion. This plan depends on classification of Phase I sites, and is discussed further in Section 5.3.

Interpretation of the population estimates also involves a philosophical viewpoint. For example, one person may view a hypothetical population estimate of 1% of combined stream length in acidic condition as acceptable, while another may view the same estimate expressed as 200 km as quite the opposite, especially if the 200 km coincides with the only blue-ribbon trout streams in an area. While the first consideration is beyond the scope of statistical estimation, additional data analyses employing maps and overlays may be useful. For example, the geographic distribution of ANC for the target population streams is depicted in Figure 5-13 with respect to the 50 and 200 $\mu$eq $L^{-1}$ reference values noted earlier. The map shows that the lowest ANC reaches are focused in the highlands in the north central part of the region (see Figure 2-2). The highest ANC reaches are located along the border with the calcareous Valley and Ridge Province to the west and in the agricultural valleys of the Broad and French Broad Rivers. This map is not directly comparable with the alkalinity map of Omernik and Powers (1983) for the region, as the latter also includes data from larger rivers and reservoirs, but both maps convey a similar image of the proportions of the region represented by the three ANC classes, if not their specifications. The utility of using"non-standard"reference values to delineate map isopleths will be discussed in Section 5.3 in the context of stream classification.

While the previous discussion has focused on statistical population estimates based on single variables, it should also be borne in mind that single

**Figure 5-13.** ANC distribution in the Southern Blue Ridge based on downstream spring average chemistry with effects from storm events removed.



variables seldom provide adequate answers to complex questions. For example, all other things being equal, low ANC waters are by definition more susceptible to acidification than are high ANC waters. Indeed, high ANC waters are unlikely to be susceptible to acid deposition in any near-term scenario (e.g., $< 100$ years). However, low ANC systems in catchments that never were exposed to glaciation may have a variable degree of buffering capacity in their soils to delay marked declines in pH over 10-100 years of exposure to acid deposition (Galloway et al., 1983; Rochelle et al., 1986). Therefore, the term "potentially susceptible," based on ANC alone, should best be thought of as being opposed to "unlikely to be susceptible."

Also, univariate population estimates address the question of whether the pH and ANC of streams in an area are different than they would have been in the absence of acid deposition. One of the strengths of the NSS approach, however, is that the distribution of any derived datum from manipulations involving ion ratios, models, or other transformations can be estimated for the target population using the Phase I sampling design. Also, estimates involving parts of the population (e.g., streams above 1000 m elevation or draining watersheds $< 10$ km$^2$) also can be made. Relationships among chemical, hydrologic, and land use variables can be explored. While such inferences cannot prove cause and effect, it can be extremely helpful in generating testable hypotheses. This level of analysis is already underway for the Phase I-Pilot Survey data, and will be the subject of future reports.

## 5.3 Stream Classification

In addition to providing population estimates that are useful for environmental assessment, classification of streams for future intensive studies is the other primary objective of the NSS. Future studies will focus on determining temporal variability, biotic conditions, and long-term trends on a relatively small number of streams, and thus will require extrapolation of the results to a larger target population. While classification could be based on arbitrary criteria (such as streams with index ANC greater than or less than 200 $\mu$eq L$^{-1}$), a preferable scheme would be based on evidence for two or more distinct natural chemical classes, with different expected responses to acid deposition. If such natural classes do exist, it should be possible to accurately classify streams on the basis of a minimum number of samples, with a low probability of misclassification. Finally, any classification system should not only be *qualitatively* consistent with current scientific understanding, but should also be *quantitatively* objective and repeatable.

In the following sections, we present results from two subjective classification schemes based on geochemistry and geography, and from cluster analysis, a method of objective multivariate analysis. Examples of ways in which such classification schemes could be used in future phases of the NSS are also provided.

### *5.3.1 Univariate Models*

A potentially useful subjective classification scheme appeared early in analysis of the Phase I-Pilot Survey data. Preliminary examination of the data indicated that many of the variables were highly correlated with ANC, and that streams could be divided into at least three ANC groups or classes separated by large ranges of ANC over which no reaches were observed: $< 250$ $\mu$eq L$^{-1}$, 250-600 $\mu$eq L$^{-1}$, and $> 600$ $\mu$eq L$^{-1}$. A smaller break was observed at 25 $\mu$eq L$^{-1}$ along with a noticeable thinning of data in the 100-125 $\mu$eq L$^{-1}$ range, prompting tentative classification breaks at 25 and 115 $\mu$eq L$^{-1}$. Various ion ratios [(Ca + Mg)/(Na + K), (Ca + Mg)/ANC, (Ca+Mg)/($SO_4^{=}$), (Na)/(Cl), ($SO_4^{=}$)/($NO_3^-$ ] were calculated for each group, which revealed similar values in all of the 25-600 $\mu$eq L$^{-1}$ ANC groups. However, the high ANC group demonstrated (Ca+Mg)/ANC and (Ca+Mg)/(Na+K) ratios typical of calcareous systems. The single low ANC ($< 25$ $\mu$eq L$^{-1}$) site showed an unusually high ratio of (Ca+Mg)/ANC and a low ($SO_4^{=}$)/($NO_3^-$) ratio. These sites thus appeared to be atypical of most streams in the target population. When plotted on a map, the major ANC groups exhibited considerable spatial continuity, as discussed below (Section 5.3.2). The initial univariate ANC classification scheme served as a "straw man" for many of the subsequent data analyses.

### *5.3.2 Geographic Distributions*

The geographic distributions of spring downstream average concentrations of the six primary NSS variables across the Phase I-Pilot Survey study area are shown in Figures 5-14 through 5-19. The classifications are based on natural univariate groupings of the data for each variable, as noted above, and do not represent any particular water quality criterion with respect to acid deposition. Special interest sites are not shown on the maps. The ANC map (Figure 5-15) demonstrates the approximately contiguous geographic distributions of the major ANC classes noted above. Three high ANC ($> 600$ $\mu$eq L$^{-1}$) sites are located along the northern and western edges of the study area, where limestone from the adjacent Ridge and Valley Province frequently is mixed with the felsic saprolites of the Southern Blue Ridge (e.g., Hunt, 1974). A second, intermediate ANC group (250-600 $\mu$eq L$^{-1}$) is located in the predominantly agricultural valleys.

**Figure 5-14.** Geographic distribution of average springtime downstream pH in the NSS Phase I-Pilot Survey streams.

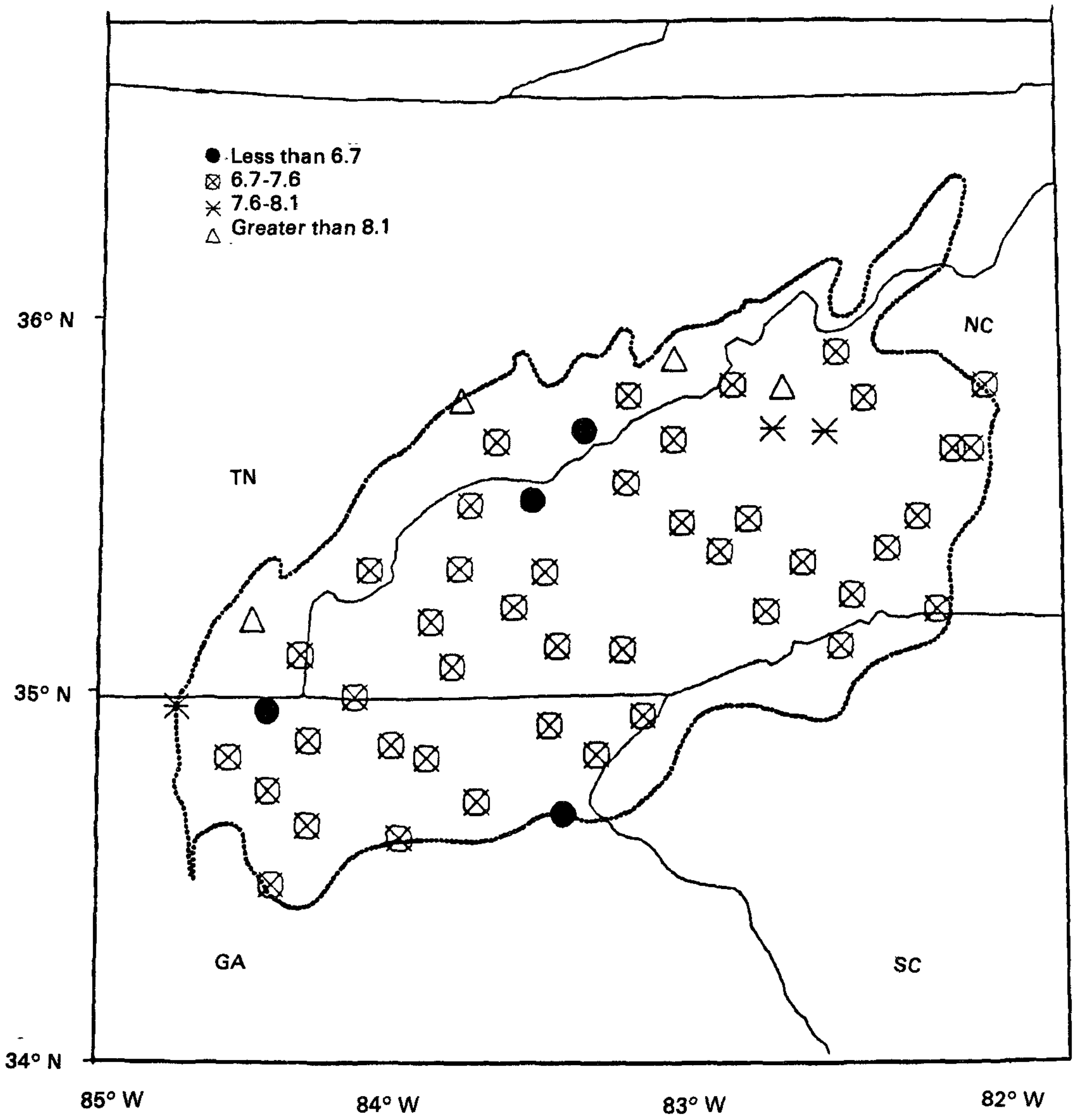


**Figure 5-15.** **Geographic distribution of average springtime downstream ANC in the NSS Phase I-Pilot Survey streams.**

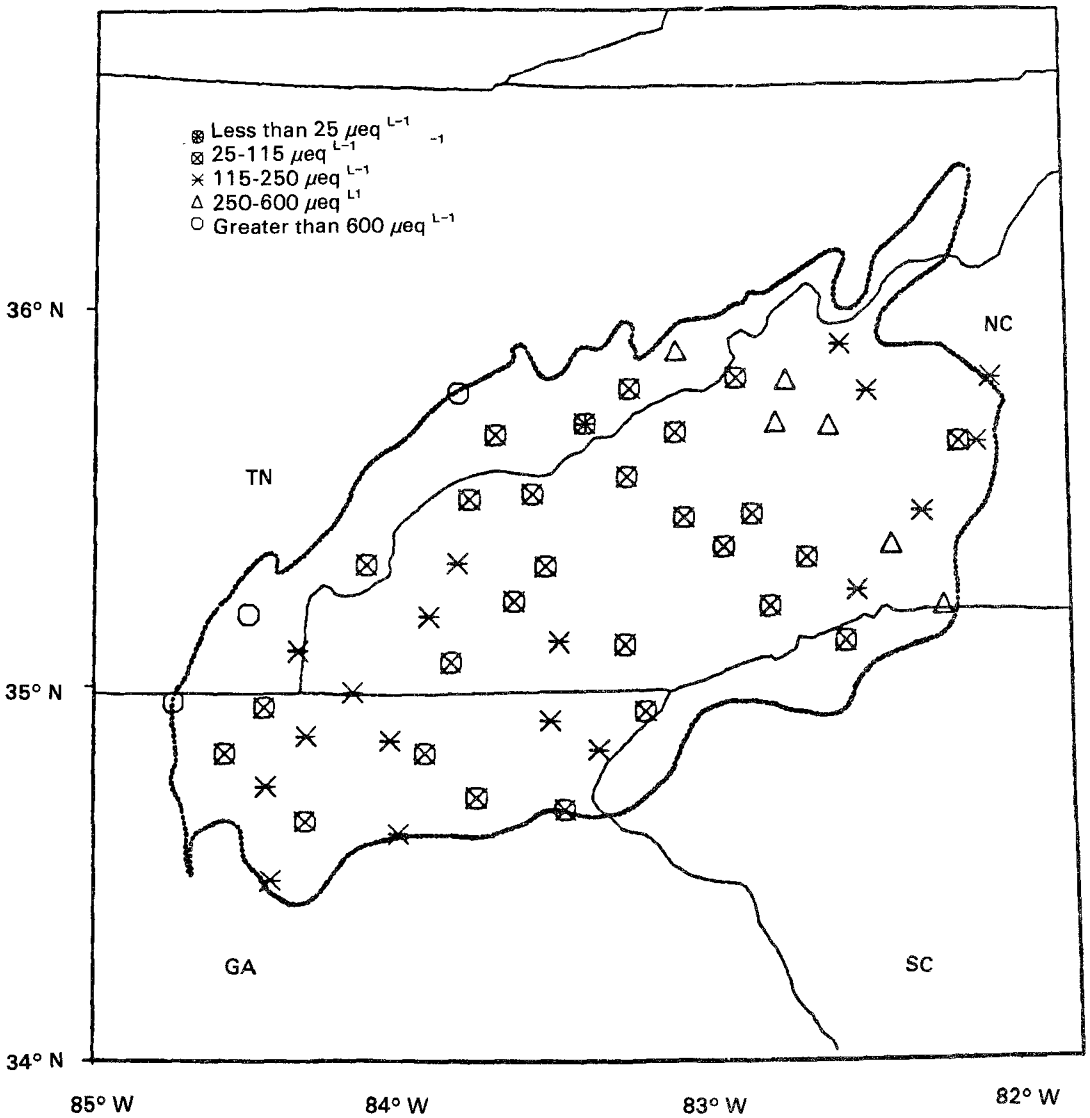


Figure 5-16. Geographic distribution of average springtime downstream sulfate concentrations in the NSS Phase I-Pilot Survey streams.

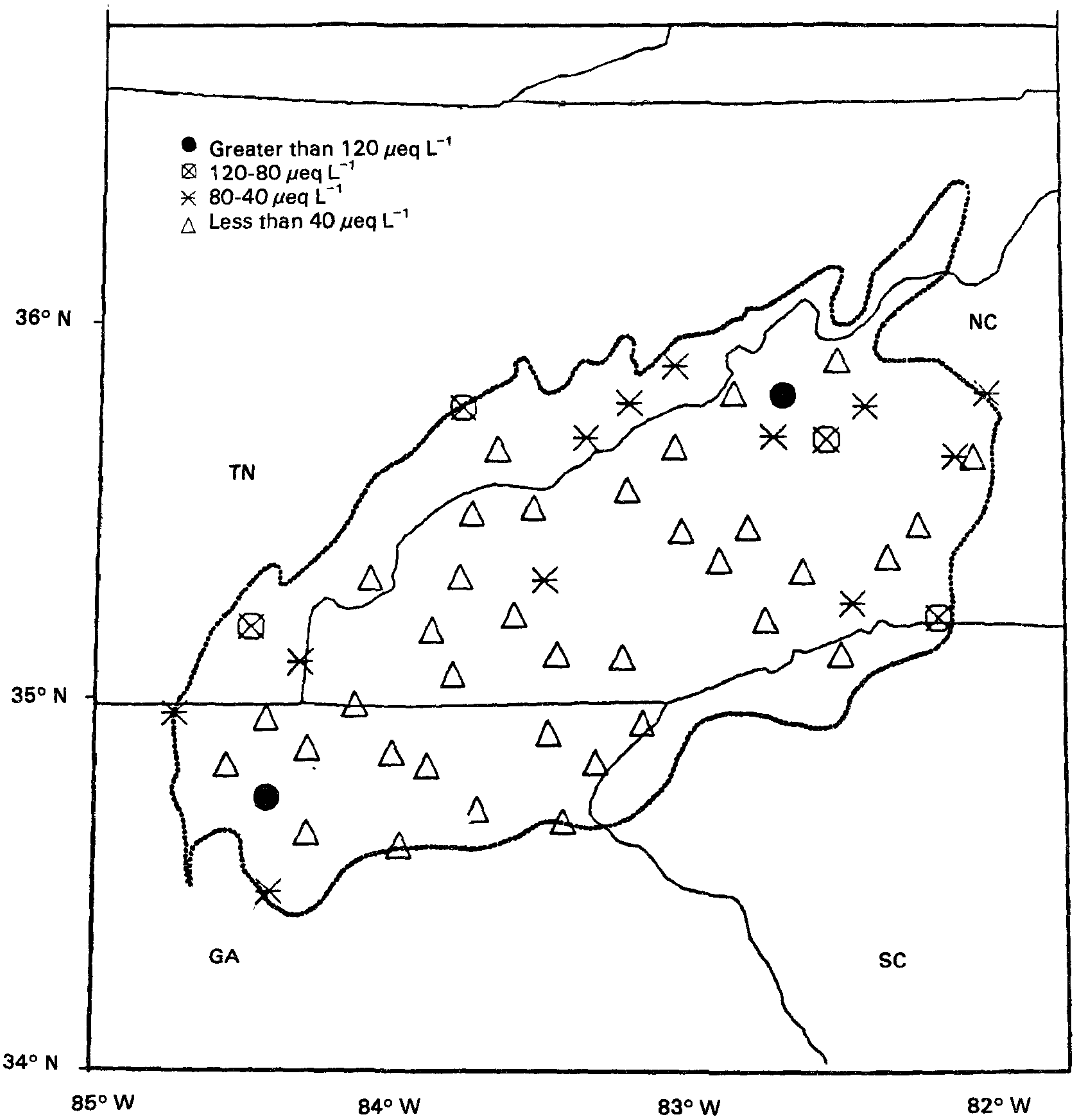


**Figure 5-17.** Geographic distribution of average springtime downstream nitrate concentrations in the NSS Phase I-Pilot Survey streams.

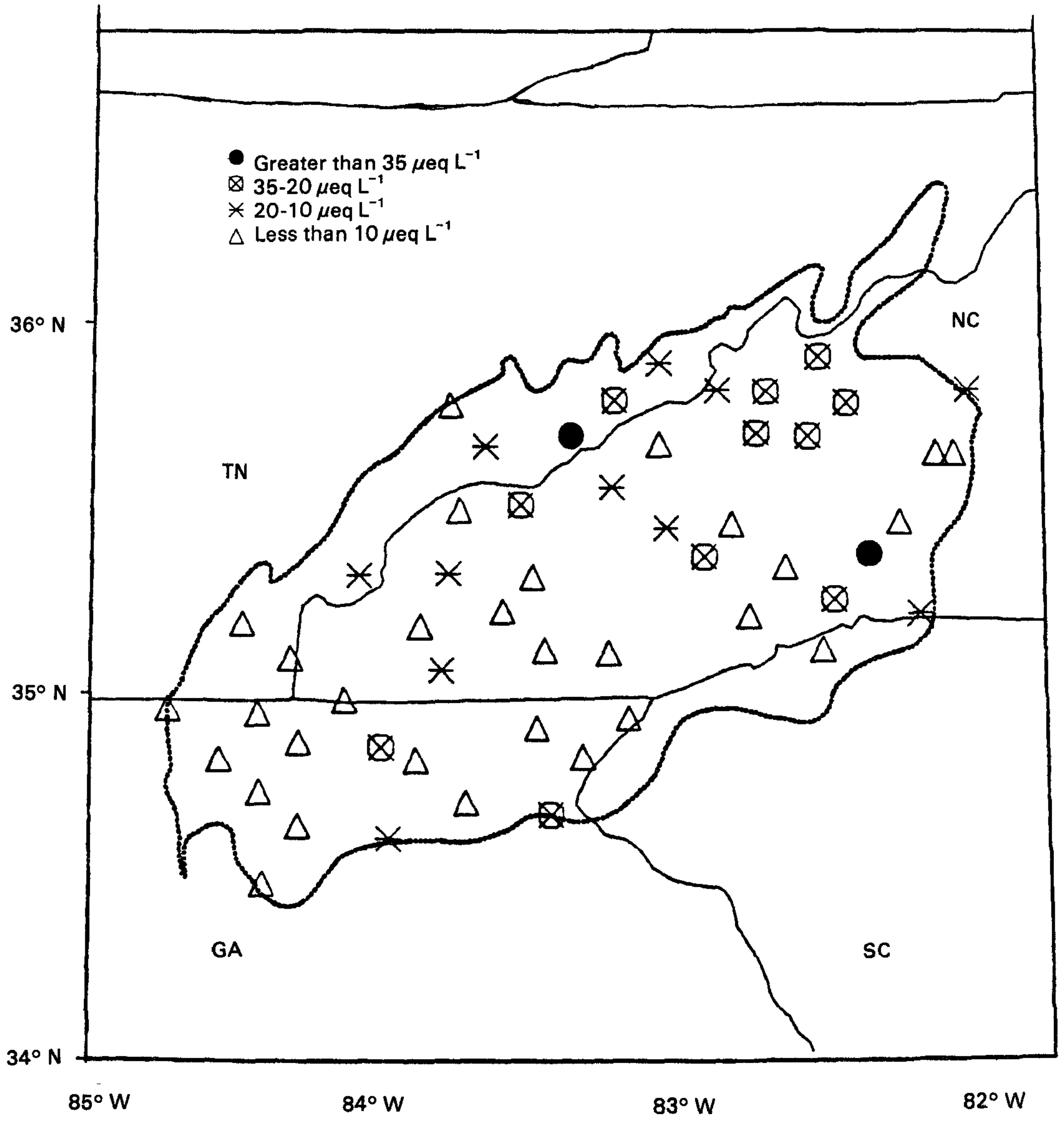


**Figure 5-18.** Geographic distribution of average springtime downstream chloride concentrations in the NSS Phase I-Pilot Survey streams.

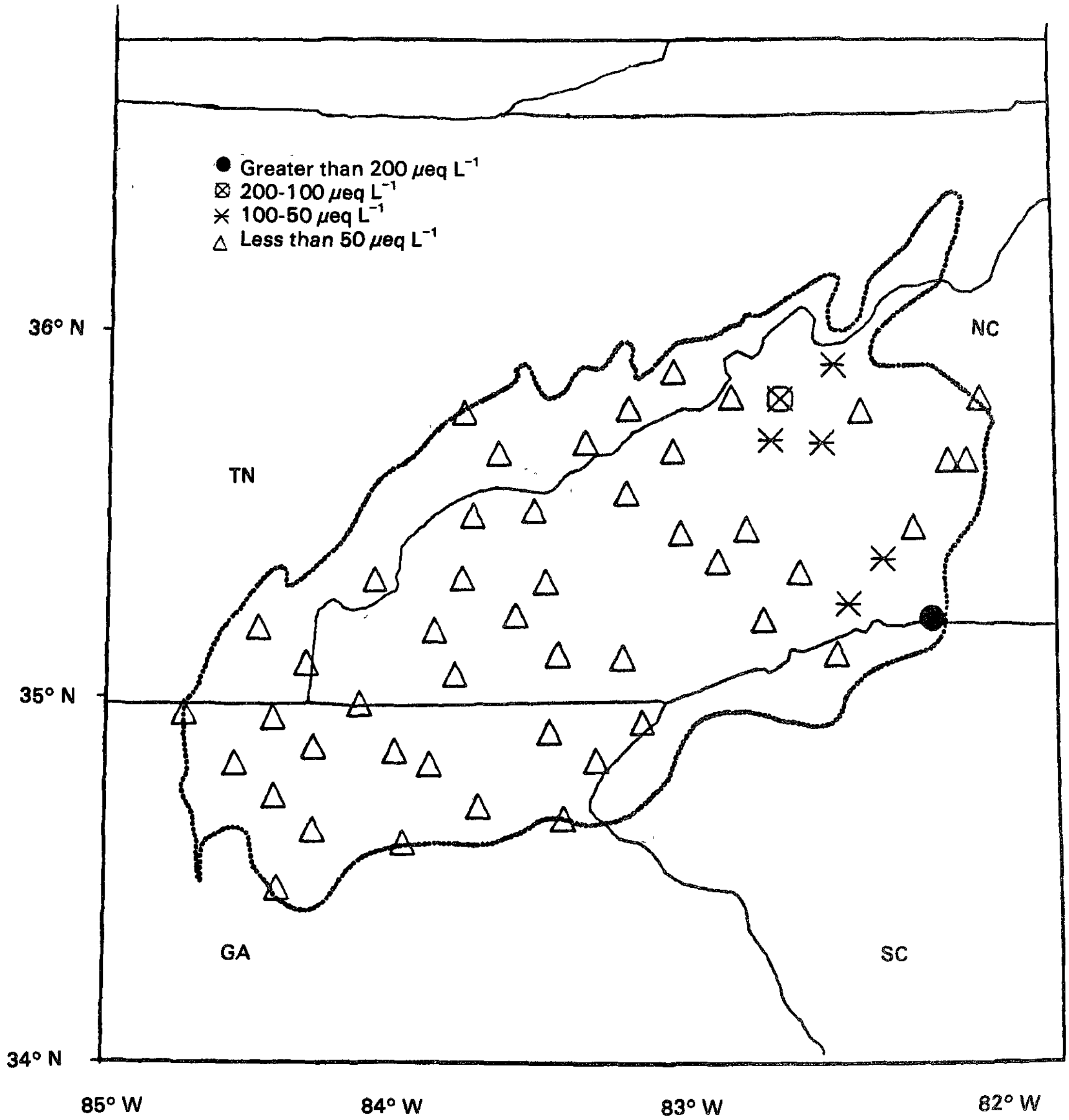
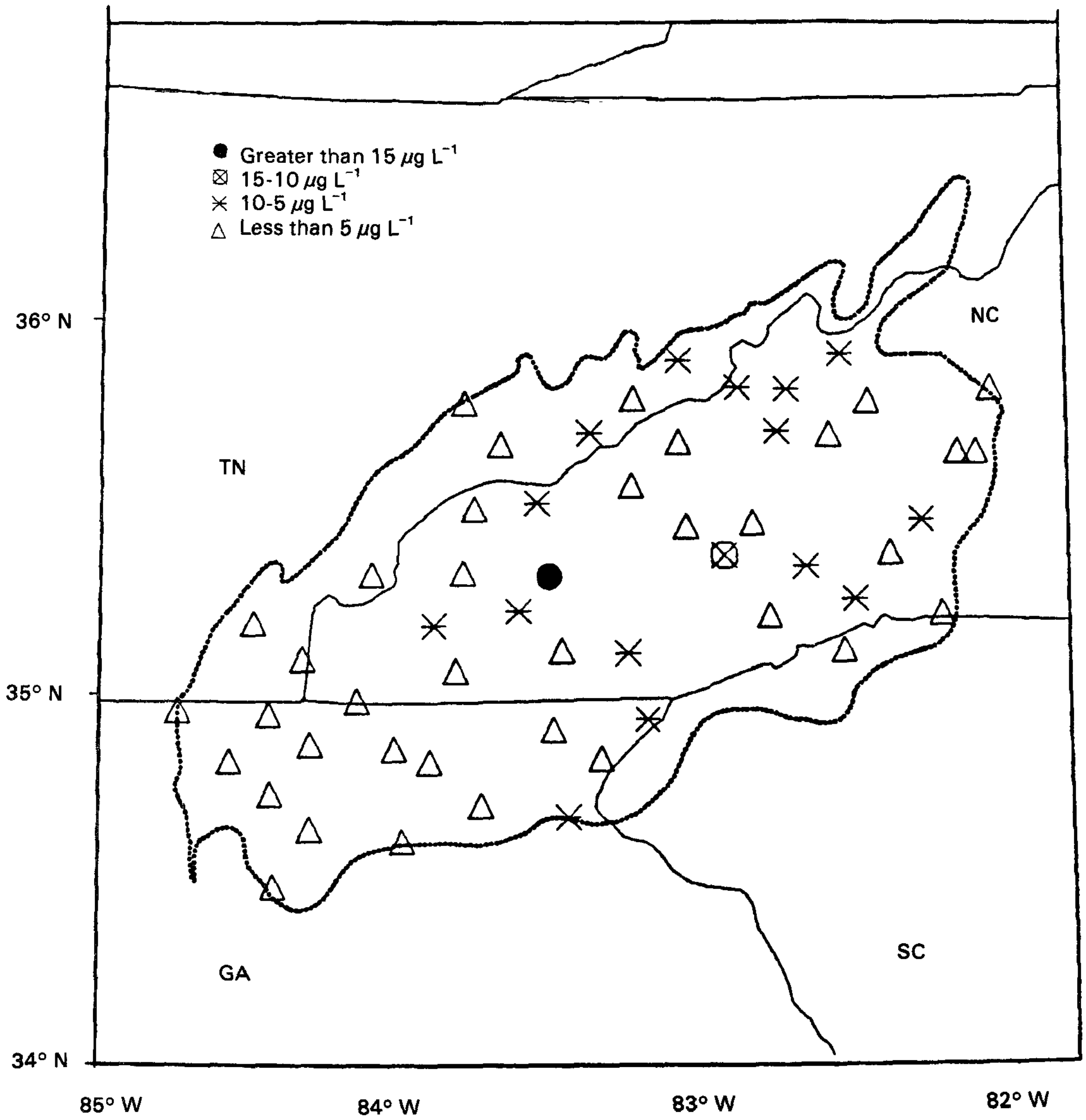


**Figure 5-19.** Geographic distribution of average springtime downstream extractable aluminum concentrations in the NSS Phase I-Pilot Survey streams.



These reaches also exhibit elevated chloride concentrations (Figure 5-18). It is not known at this time whether the high chloride concentrations are indicative of anthropogenic sources, or are simply correlated with the characteristics of valley soils suitable for farming. The consistently low ANC sites (including the only site with ANC $< 25$ $\mu$eq $L^{-1}$) form an inverted L-shaped area that includes the highlands just west of Asheville, NC and the high elevation ridge that defines the North Carolina-Tennessee border including Great Smoky Mountains National Park. The remaining areas appear to form a patchwork containing 25-115 $\mu$eq $L^{-1}$ and 115-250 $\mu$eq $L^{-1}$ sites.

Low pH sites (Figure 5-14) show general agreement with the low ANC patterns, although two relatively low pH sites stand out in the Georgia section of the Survey. A different anomalously high sulfate site (Figure 5-16) also stands out in Georgia, with the remainder of the high sulfate sites co-occurring with high ANC. The nitrate map (Figure 5-17) exhibits a cluster of relatively high nitrate (20-35 $\mu$eq $L^{-1}$) sites in the northeast part of the study area, and a very high nitrate value corresponding to the lowest ANC site located in Great Smoky Mountain National Park. It has been suggested that this site might be typical of old-growth forests in this part of the study area, which are at steady state with respect to nitrate inputs (*R. Turner and P. Mulholland, Oak Ridge National Laboratory, personal communication*). No pattern is evident in the extractable aluminum concentrations, although concentrations greater than 5 $\mu$g $L^{-1}$ are apparently rare in the western part of the study region. Possible geochemical or anthropogenic causes for the remaining "unusual" sites are being investigated as geology and land use data are acquired for the Phase I-Pilot Survey watersheds.

ANC maps (such as Figure 5-15) were plotted and compared for each spring and summer sampling interval. Although a few sites changed categories on each map, the overall geographic distribution of ANC within the study area remains identical throughout the spring. During summer, the area of higher ANC categories expanded, apparently due to changes in the relative volumes of source water detained in the soil mantle for short and long periods of time before entering the channel. While all spring samples during 1985 provided similar geographic ANC maps of the region, the summer sample provided a map with considerably wider areas of high-ANC stream water.

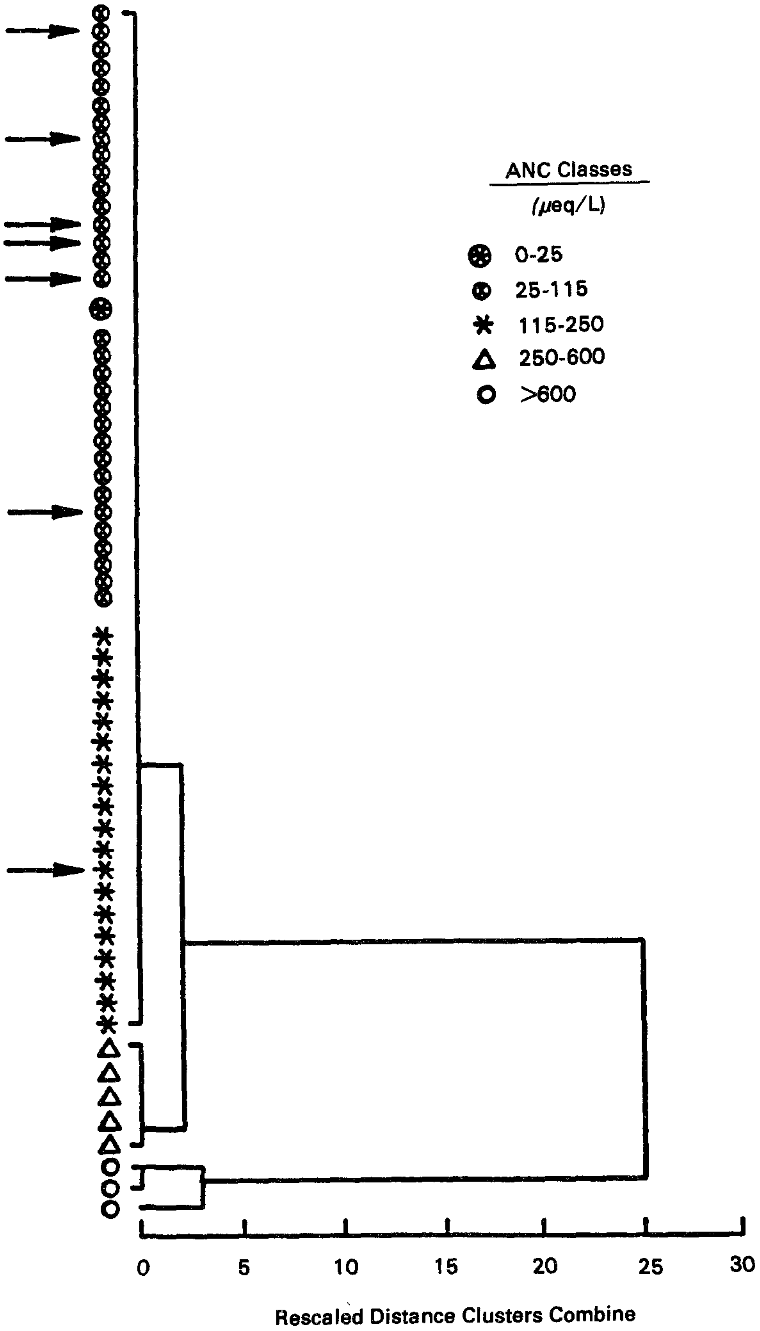
### 5.3.3 Cluster Analysis

Previous sections have dealt with subjective interpretation and classification of multivariate data. Cluster analysis (Romesburg, 1984) is a multivariate statistical technique that can be used to make such classifications more objective, but the results are sufficiently dependent on the particular algorithm used that such classifications should be used with caution. Phase I-Pilot Survey data were subjected to hierarchical cluster analysis using a number of different clustering methods and sets of chemical variables, both with and without episodes removed. A polythetic agglomerative technique (in contrast to a devisive technique) based upon Euclidean distance and the maximization of the average linkages within sample site clusters appeared to produce the most robust and useful classifications and was employed using a "full"set of 30 chemical variables to produce the dendrograms discussed below.The agglomerative clustering technique used is more efficient at identifying outlying groups than at minimizing within-group variance.

The dendrogram resulting from a clustering run based on the spring downstream averages with episodes removed is shown in Figure 5-20. This dendrogram is typical of all runs on individual spring sampling intervals, in that the three high-ANC sites cluster far from the remaining variables, the intermediate ANC (250-600 $\mu$eq $L^{-1}$) sites form a second cluster, and the lower ANC ($<$ 250 $\mu$eq $L^{-1}$) sites form a third cluster with similar ANC groups appearing near each other. Two episodes occurring during the third spring sampling interval changed the average spring chemistry sufficiently to cause the sites to appear as outliers on a similar dendrogram. Major episodes thus cause sufficient changes to confound reach classification based on agglomerative cluster analysis of stream chemistry. On the other hand, cluster analysis may be useful for identifying putative episodes in cases where stage changes are not available. The special interest sites are indicated by arrows in the diagram, and most can be seen to be typical of the 25-115 $\mu$eq $L^{-1}$ ANC class reaches.

During the course of analysis, it became evident that the presence of two small classes of high ANC sites with highly distinct chemistry dominated site classification in the Pilot Survey. Furthermore, these high ANC sites are not particularly interesting from an acidification standpoint. Cluster analysis of the same variables, after removing the three high ANC sites, caused one of the intermediate ANC sites consistently to appear as an outlier. Removal of this site resulted in a strong cluster containing the intermediate ANC sites, another cluster breaking at approximately 190 $\mu$eq $L^{-1}$, and a weaker cluster breaking at 115 $\mu$eq $L^{-1}$. These clusters were most pronounced during the first spring sample, and each $<$ 250 $\mu$eq $L^{-1}$ cluster expanded or contracted by

Figure 5-20. Hierarchical cluster diagram of all NSS Phase I—Pilot Survey sites based on downstream spring average values for 39 chemical variables. Episodes have been removed. Arrows indicate special interest sites.



fewer than five sites during the second and third spring sampling interval (occasionally the intermediate cluster split into two). Interestingly, the lowest ANC site did not appear as an outlier, despite its unusual ion ratios. The geochemical significance of the remaining clusters, and the effect of removing all $> 250$ $\mu eq\ L^{-1}$ sites from the clustering process, is presently under investigation. Use of devisive clustering techniques (which are less sensitive to sample outliers than are agglomerative techniques) may enable robust classification of sample streams without necessitating the removal of sites of unusual chemical composition.

### *5.3.4 Utility of Classification for Regional Assessment*

One of the two primary data quality objectives (DQOs) of the National Stream Survey is to classify streams for future intensive studies. The foregoing examples illustrated how univariate and multivariate analyses of water chemistry data could provide a useful framework for understanding the spatial distribution of chemical variables and the relationships among sites arranged according to single and multiple variables. All of the classification results were consistent with a relatively simple geochemical interpretation of the chemistry of streams in the Southern Blue Ridge.

Figure 5-21 shows the Phase I-Survey data plotted on a mineral stability diagram for potassium feldspar, an important component of the parent geologic material in the area. The position and slope of data plotted on such a diagram enable one to hypothesize the geochemical weathering processes controlling water chemistry in natural waters in contact with soil and rock. The data points are coded according to ANC classes described in the preceding section. As shown in the lower left region of the diagram, a paucity of potassium and silica is accompanied by low values for ANC, and is probably indicative of intense weathering due to high precipitation loadings (Velbel 1985a, 1985b). This relationship is not evident in the highest ANC stream group, whose numbers are characterized by considerably lower ratios of potassium (and higher ratios of calcium) to ANC than those in lower ANC groupings. The streams with ANC $> 600$ $\mu eq\ L^{-1}$ drain watersheds which contain underlying limestone inclusions (see below). One of the 250-600 $\mu eq\ L^{-1}$ ANC streams also appears as an outlier in this analysis. In the lower ANC range of watersheds in the Southern Blue Ridge, ANC thus appears to be correlated with feldspar weathering.

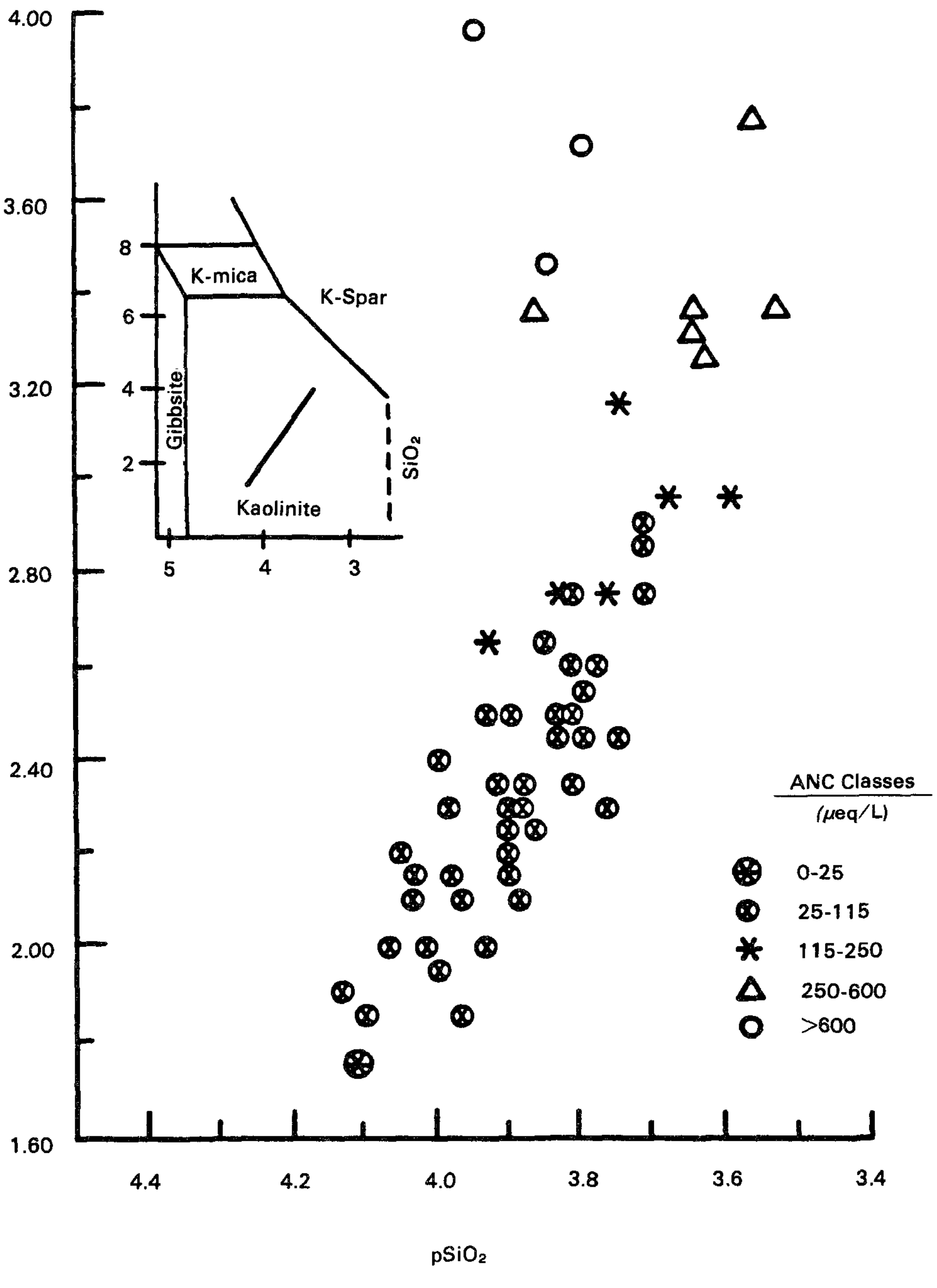
The geochemistry of streams in the Southern Blue Ridge has been hypothesized to be controlled primarily by weathering kinetics (Velbel, 1985a,b). To draw a simple analogy, water moves through the silacious saprolites (subsoils) in these watersheds, dissolving minerals that comprise the pseudomorphous parent materials, much as water acquires a pleasant flavor when in contact with a tea bag. As in the case of tea, the strength of the brew is controlled by the residence time of the water in the bag, and the number of times the bag was previously used. In the field, the former part of the analogy involves the hydrology of the watershed and the second part depends upon the age and degree of weathering of the predominant geologic formation in the area (Coweeta Group or Tallulah Falls Formation). It would be convenient for classification purposes if acid neutralizing capacity in the region could be predicted largely on the basis of the degree of weathering in a watershed, which could in turn be related to hydrology.

The chemical classification of stream reaches described above is a first step toward understanding the regional relationships between watershed characteristics, acid deposition, and water chemistry variables. In the future, such chemical classifications will be refined as additional data on Phase I streams and watersheds are obtained. Water chemistry data will be related to such watershed characteristics as topography, drainage area, bedrock geology, soil residence time, vegetation, and land use data. Subsequent reclassification on the basis of these variables will provide a framework which can be utilized for the following purposes:

1. Identification of scientifically-based groupings of sites according to water chemistry and presumed vulnerability to acidification.
2. Generation or refinement of hypotheses regarding the relationships among watershed, atmospheric, and water quality variables.
3. Identification and delineation of distinct classes of sites which can be considered separately with regard to a variety of NSWS objectives.

The identification of distinct classes of sites is a particularly important goal of classification, because it allows individual stream reaches and their watersheds to be identified for intensive research or long-term monitoring. The index chemistry of the special interest sites studied in the Phase I-Pilot Survey exemplifies the utility of classification. The estimated population distributions for the various chemical variables in the Southern Blue Ridge target population are particularly interesting when compared to the chemistry of the special interest sites.

**Figure 5-21.** Potassium-feldspar mineral stability diagram for streams in the NSS Phase I-Pilot Survey. Values represent spring downstream average with episodes removed. pH is based on 300 ppm $CO_2$ equilibrated values.



These sites have been chosen by previous investigators as being "typical" of the region, in addition to providing a reasonable degree of accessibility for field work. Six of the seven special interest sites had mean spring ANC values below 50 $\mu$eq $L^{-1}$ during the study, and thus represent less than 7% of the target population streams in the area. On the other hand, they did not appear as outliers in the multivariate chemical classification of streams in the region, and pH values were higher than at several of the probability sites. Results gained from geochemical research and monitoring programs at these sites can thus probably best be considered as typical of a small but significant group of target population streams in the area.

The identification of individual reaches or watersheds for intensive study of episodic acidification due to hydrologic events will require that these systems be suitably representative of appropriate classes described above. Current understanding of episodes suggests that deposition loading, watershed hydrology, baseflow chemistry, and land use may be the important components of a classification scheme for studying episodes. Developing indices for each of these components is a critical task prior to undertaking detailed, intensive studies of episodes in regions receiving acid deposition.

## 5.4 Future Analyses

While the findings of the Phase I-Pilot Survey were sufficient to allow Phase I to proceed with appropriate modifications, several additional analyses of the Phase I-Pilot Survey are presently underway. These include:

1. Applying empirical models to search for evidence (if any) of acidification by atmospheric deposition.
2. Investigating effects of runoff and subsurface geology on ANC and chemical variables associated with weathering.
3. Linking chemistry to geography and land use, including nonpoint sources of pollution.
4. Creating or revising ANC maps.
5. Calibrating target population data obtained from 1:250,000-scale maps with smaller scale maps and remote imagery.
6. Devising population estimates based on areal export coefficients (using Equation [5.1]).
7. Comparing the Phase I-Pilot Survey data with other intensive and synoptic stream and lake data available for the Southern Blue Ridge.
8. Developing robust classification schemes for selecting sites for intensive process-oriented research, ecological effects studies, and long-term monitoring.

The results of these studies will be published as open-file reports or in the professional scientific literature as they become available.

# *6. Conclusions and Recommendations*

## 6.1 Conclusions

The primary objectives of the Phase I-Pilot Survey were to (1) test the ability of the proposed sampling design to meet the Phase I objectives and (2) evaluate the logistics plan and data analysis plan for Phase I. The Phase I-Pilot Survey demonstrated that a regional-scale synoptic survey of streams of the size targeted in the data quality objectives can be accomplished logistically, will produce robust population estimates for important chemical variables based on a single spring sampling, and has the potential of producing a relatively simple geochemical grouping of streams with reasonable support in the scientific literature. The results of the study were deemed to be adequate to meet the Phase I objectives, so no further Phase I field work is planned for the Southern Blue Ridge Province. It is important to avoid sampling during major hydrologic events or post-stratify the data, so that the distributions are not affected by episodes, during which pH and ANC are temporarily depressed. For population estimation alone, there is apparently little value in replication, if sampling is confined to the spring of the year. In the Southern Blue Ridge, pH showed virtually identical population distributions in spring and summer. However, ANC increased substantially between the two periods. Summer sampling did not affect the interpretation of sulfate and nitrate distribution estimates generated from spring data.

The Phase I-Pilot Survey used a sample size of 54 to generate distribution estimates for chemical variables, but subsequent analyses could be performed to determine the effects of sample size on the distributions. Such experiments would also be useful in evaluating the absolute minimum sample size that is likely to be useful for assessment purposes.

There were significant differences in the concentrations of most important NSWS variables between the upstream and downstream nodes of the reaches in the target population. The changes varied sufficiently in both magnitude and direction that calibration of one value on another does not appear to bepossible. Univariate and multivariate regressions indicated that of all of the geographic variables tested, only elevation showed any significant relationship to pH or ANC concentration on a region-wide basis. Even this relationship proved to be too weak for predictive or descriptive purposes.

Classification of streams for further study also appears to be possible on the basis of a single synoptic sampling of the Southern Blue Ridge streams. However, it is desirable to have two samples to make chemical changes associated with hydrologic or pollution events easier to identify, and to provide an estimate of the degree of robustness of the classification. The latter factor is particularly important if the Phase I streams themselves are to be the primary candidates for study in future phases of field work. However, it would be valuable even if they serve only to identify the desired characteristics of other sites chosen for their greater accessibility.

The Phase I-Pilot Survey was useful in greatly increasing the probability of success and decreasing the cost of a full Phase I Survey. Evaluation of the logistics plan indicated that a ground-based synoptic survey of randomly chosen streams over a large geographic region could be carried out safely and successfully. Field experiments and evaluations identified the most promising techniques and protocols, as well as potential problems ranging from instrument malfunctions to disbursing pay envelopes to field crews. The data management and QA/QC programs proved largely successful, and experience gained in these programs will undoubtedly reduce unnecessary sample processing costs and eliminate many troublesome communication bottlenecks. The successful completion of the pilot study and the timely analysis of the data were critical in producing a scientifically acceptable and cost-effective Phase I research plan.

Finally, the Phase I-Pilot Survey data set can and will certainly be used in an assessment context, as regulators, resource managers, and others charged with environmental assessment seek to quantify the extent of acidic and low ANC waters of the United States that are potentially susceptible to acidification by atmospheric deposition. While the target population of reaches was characterized by a high proportion of low ANC reaches, less than 3.2% of the stream length in the target population was estimated to have an index pH below 6.4. Thus, the

Phase I-Pilot Survey data base provides a snapshot in time of the resource at risk as represented by the target population. This information will become increasingly meaningful as our overall understanding of the relationships between acid deposition, water quality, and aquatic biota improves.

## 6.2 Recommendations for Phase I

Analysis of the Phase I-Pilot Survey results were used in formulating recommendations for changes in the proposed Phase I sampling design, logistics plan, QA and methods plan, and in the data management system. It is not known to what extent the recommendations made are based on conclusions drawn about a unique geographic region, the Southern Blue Ridge Province. Therefore, scientific judgment exercised by EPA, contractor, and external scientists was in many cases used to extrapolate the Pilot Survey results to other regions of study. In particular, the input of scientists who work extensively or exclusively on ecosystems in these new regions of study were crucial in altering the proposed Phase I design in a responsible and timely way. The modified Phase I Research Plan was deemed sufficient to proceed with a full scale Phase I Survey in the Mid-Atlantic region during the spring of 1986 (U.S. EPA, 1985b). The following list summarizes the modifications in the proposed Phase I design which were recommended and enacted.

1. Population estimates based on data collected during the spring sampling season provide a good "index" for characterizing the chemical status of mid-sized streams. Because ANC and pH are not lower during the summer and the most sensitive life stages of fish are typically present during the spring, summer sampling is unnecessary for population description purposes.

2. Whereas one spring sampling appears adequate for population description, replication is desirable for classifying streams. This is particularly true if the goal of classification is to identify Phase I streams for further intensive studies. Therefore, two samplings are recommended for meeting both primary Phase I objectives.

3. Because the goal of Phase I is to describe the population of target reaches using the "index" concept, it is important to avoid sampling under transient hydrologic conditions such as major rain storms or snowmelt events, during which relatively large changes in many chemical variables may occur. Regional studies of episodic acidification, like long term monitoring and studies of biological resources, will almost certainly be performed on a limited number of aquatic systems that can be considered as "regionally representative"based on Phase I classification, acid deposition inputs, land use, physiography, and other characteristics. Therefore, it is recommended that Phase I sampling be conducted so that field sampling does not occur during or immediately after major rainfall or snowmelt events.

4. Observed differences in chemical concentrations measured at upstream and downstream nodes were statistically significant for five of the six major variables. In Phase I, it will be desirable to estimate the chemistry of the entire reach, so it is recommended that both nodes of each reach be sampled. The chemistry of the intervening water will then be estimated by interpolation. Although not totally satisfactory, this practice should improve the population estimates to some extent. As an added benefit, chemistry from the upstream node can be used to make estimates for the smaller watersheds draining into the NSS target population reaches, as well as to estimate an areal contribution index for the watersheds contained in the target population itself.

5. In subsequent Phase I surveys, it is recommended that revised site inclusion criteria be used to identify the target population. The following criteria are suggested, and these are summarized in the 1986 Draft Research Plan (U.S. EPA, 1985b).

   a. The boundary reach criteria should be consolidated into one rule: reaches should be considered non-reaches to a given subregion if greater than 50% of the blue line length lies outside the region boundary.

   b. It is now assumed that reservoirs in watersheds of $< 60$ mi$^2$ are unlikely to significantly affect reach chemistry, and that downstream nodes of influent reaches can be identified adequately during field reconnaissance. Reservoir tailwater reaches are included as a special class of interest reaches (N2R) in Phase I.

   c. New categories were subsequently added to the Phase I site rules as problems with the original rules were encountered in new regions. Urban reaches (based on areas indicated in yellow on USGS 1:24,000-scale topographic maps) are defined as non-interest reaches in Phase I. This decision was made because of the operational difficulty of determining drainage boundaries when no contours are shown within the mapped urban areas, and also because of the perception that these reaches are not at risk. Inappropriate physical habitat or gross point-source pollution reduce the importance of possible impacts due to acidification. Special categories of interest reaches have been added to the Phase I site rules to include wetland reaches with indistinct topographic drainage boundaries and large "headwater" reaches with drainage areas $> 60$ mi$^2$.

An addition to these changes in sampling design, the following changes in the logistics and QA plans were recommended for Phase I:

1. As a result of the comparability of the two field pH methods, it is recommended that the closed-system measurement be dropped in Phase I. $CO_2$ degassing is apparently slow enough in quiescently stirred solutions, so that electrode instability is not a problem in the open-system measurement. The open-system measurement is much easier to perform in the field, and requires less equipment.
2. An automated aluminum speciation and measurement technique using pyrocatechol violet (Dougan and Wilson, 1974; Rogeberg and Henriksen, 1985) will be instituted in Phase I to avoid problems associated with the manual technique used in the Phase I-Pilot Survey.
3. Sample holding times for syringe and Cubitainers will be increased from 12 to 24 hours based on results from several holding time experiments that we performed during the Phase I-Pilot Survey. Given this decision, it is recommended that the mobile field laboratory be deployed in Las Vegas during Phase I, rather than at base sites in the field. Samples will be transported by overnight air courier in coolers kept at 4°C to Las Vegas, and preservation at the laboratory will occur within 24 hours of sample collection.
4. Because the contract laboratory met the limits for matrix spike recovery for every batch of samples analyzed in the Phase I-Pilot Survey and no matrix interferences were observed, matrix spike QC samples will not be used during the Phase I Survey.

## 6.3 Related Documents

In addition to this report, supplemental information on the National Stream Survey Phase I-Pilot Survey can be found in the series of ancillary manuals and reports. Many of the technical manuals used were in draft form at the time the Phase I-Pilot Survey was conducted. If substantive changes were not anticipated to technical manuals to be used for the full-scale Phase I Survey, then separate Pilot Survey manuals will not be published. Major changes in Pilot Survey methods and procedures planned for Phase I were summarized in this report. The related documents include:

1. Field Operations Report, National Surface Water Survey, National Stream Survey, Pilot Survey. 1986. Knapp, C. H., C. L. Mayer, D. V. Peck, J. R. Baker, and G. J. Filbin. Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada 89109 (draft).
2. Quality Assurance Plan for the National Surface Water Survey. Stream Survey (Middle Atlantic Phase I, Southeast Screening and Middle Atlantic Episodes Pilot). 1986. Drousé, S. K., D. C. Hillman, L. W. Creelman, and S. J. Simon. Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada 89109 (draft).
3. Evaluation of Quality Assurance and Quality Control Sample Data for the National Stream Survey (Phase I-Pilot Survey). 1986. Drousé, S. K. Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada 89109 (draft).
4. Analytical Methods Manual: National Surface Water Survey, Stream Survey (Middle Atlantic Phase I, Southeast Screening, and Middle Atlantic Episodes Pilot). 1986a. Hillman, D. C., S. H. Pia, and S. J. Simon. Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada 89109 (draft).
5. Data Management and Analysis Procedures for the National Stream Survey. 1987. Sale, M. J. (editor). ORNL/TM. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831 (draft).
6. Draft Research Plan, National Surface Water Survey: National Stream Survey, Mid-Atlantic Phase I and Southeast Screening. 1985. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C. 20460.
7. Draft Sampling Plan for Streams in the National Surface Water Survey. Technical Report 114 (July 1986) Overton, W. S. Department of Statistics, Oregon State University, Corvallis, Oregon 97331.

# 7. References

Baker, J. 1981. Aluminum Toxicity to Fish as Related to Acid Precipitation and Adirondack Surface Water Quality. Ph.D. Thesis, Cornell University, Ithaca, NY.

Beamish, R. J., and H. H. Harvey. 1972. Acidification of the LaCloche Mountain Lakes, Ontario, and Resulting Fish Mortalities. J. Fish. Res. Board Can. 29:1131-1143.

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

Bovee, K. D., and D. Cochnauer. 1977. Development and evaluation of weighted criteria probability-of-use curves for instream flow assessments. Fisheries Instream Flow Information Paper No. 3. FWS/OBS-77/63. Cooperative Instream Flow Service Group, Ft. Collins, Colorado 38 pp.

Burke, E. M., and D. C. Hillman. 1987. Syringe Holding Time Study. pp. 59-75. *In* Knapp et al. NSWS: NSS-Pilot Survey. Field Operations Report. EPA/600/8-87/019.

Chorley, R. J., and P. F. Dale. 1972. Cartographic problems in stream channel delineation. Cartography 7:150-162.

Cochran, W. G. 1977. Sampling Techniques, 3rd Ed. Wiley: New York.

Cogbill, C. V., G. E. Likens, and T. A. Butler. 1984. Uncertainties in historial aspects of acid precipitation: getting it straight (including comments by Hansen and Hidy). Atmos. Environ. 18:2261-2270.

Cosby, B. J., G. M. Hornberger, and J. N. Galloway. 1985. Time scales of catchment acidification. Environ. Sci. and Technol. 19:1144-1149.

Dougan, W. K., and A. L. Wilson. 1974. The absorptiometric determination of aluminum in water: A comparison of some chromogenic reagents and the development of an improved method. Analyst 99:413-430.

Drablos, D., and A. Tollan, editors. 1980. Ecological impact of acid precipitation. Proceedings of an international conference, Sandefjord, Norway. March 11-14, 1980.

Driscoll, C. T. 1984. A procedure for the fractionation of aqueous aluminum in dilute acidic waters. Internat. J. Environ. Anal. Chem. 16:267-283.

Drousé, S. K., D. C. Hillman, J. L. Engels, L. W. Creelman, and S. J. Simon. 1986. National Surface Water Survey, National Stream Survey (Phase I-Pilot, Mid-Atlantic Phase I, Southeast Screening, and Episodes Pilot). Quality Assurance Plan. EPA/600/4-86/044. U.S. EPA, Las Vegas, Nevada.

Drousé, S. K. 1987. National Surface Water Survey, National Stream Survey (Phase I-Pilot Survey) Summary of Quality Assurance Results. U.S. EPA, Las Vegas, Nevada. In Press.

Fenneman, N. M. 1946. Physical divisions of the United States. U.S. Department of Interior, Geological Survey. Reston, Virginia.

Fountain, J., and D. T. Hoff. 1985. AQUARIUS User's Guide. Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada (unpublished MS).

Galloway, J. N., S. A. Norton, and M. R. Church. 1983. Freshwater acidification from atmospheric deposition of sulfuric acid: a conceptual model. Environ. Sci. and Technology 17(11):541-545.

Gunn, J. M., and W. Keller. 1984. Spawning site water chemistry and lake trout (*Salvelinus namaycush*) sac fry survival during spring snowmelt. Can. J. Fish. Aquat. Sci. 41:319-329.

Hagley, C. A., C. M. Knapp, C. L. Mayer, and F. A. Morris. 1986. National Surface Water Survey, Stream Survey (Middle Atlantic Phase I, Southeast Screening, and Middle Atlantic Episode Pilot). Field Training and Operations Manual. Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada.

Haines, T. A. 1981. Acidic precipitation and its consequences for aquatic ecosystems: a review. Trans. Am. Fish. Soc. 110:669-707.

Haines, T. A. 1982. Interpretation of aquatic pH trends. Trans. Am. Fish. Soc. 111:779-786.

Haines, T. A., and J. J. Akielaszek. 1983. A regional survey of the chemistry of headwater lakes and streams in New England: Vulnerability to acidification. *In* Air Pollution and Acid Rain. Report No. 15, U.S. Dept. Interior, Fish and Wildlife Service, FWS/OBS-80/40/15. 141 p.

Havas, M., T. C. Hutchinson, and G. E. Likens. 1984. Red herrings in acid rain research. Environ. Sci. Technol. 18:176A-186A.

Henriksen, A., O. Skogheim, and B. Rosseland. 1984. Episodic changes in pH and aluminum-speciation kill fish in a Norwegian salmon river. Vatten 40:255-260.

Hillman, D. C., D. V. Peck, J. R. Baker, F. A. Morris, K. J. Cabble, and S. L. Pierett. 1985. National

Stream Survey Field Training and Operations Manual. Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada.

Hillman, D. C., S. H. Pia, and S. J. Simon. 1986a. National Surface Water Survey, National Stream Survey (Phase I-Pilot, Mid-Atlantic Phase I, Southeast Screening, and Episodes Pilot). Analytical Methods Manual. EPA/600/8-87/005. U.S. EPA, Las Vegas, Nevada.

Hillman, D. C., J. F. Potter, and S. J. Simon. 1986b. National Surface Water Survey, Eastern Lake Survey (Phase I-Synoptic Chemistry), Analytical Methods Manual. EPA-600/4-86-009, U.S. Environmental Protection Agency, Las Vegas, Nevada.

Howells, G. D. 1984. Fishery decline: mechanisms and predictions. Phil. Trans. R. Soc. Lond. B*305*, 529-547. Lockheed-EMSCO, Las Vegas, Nevada.

Hughes, R. M., and J. M. Omernik. 1981. Use and misuse of the terms watershed and stream order. Am. Fish. Soc. Warmwater Streams Symposium, pp.320-326.

Hughes, R. M., and J. M. Omernik. 1983. An alternative for characterizing stream size. pp. 87-101. In: T. D. Fontaine III and S. M. Bartell (eds.). Dynamics of Lotic Ecosystems, Ann Arbor Science, Ann Arbor, Michigan.

Hunt, C. B. 1974. Natural Regions of the United States and Canada. W. H. Freeman and Company, San Francisco.

Jeffries, D. S., B. LaZerte, and R. A. Linthurst. 1985. Effects of acid deposition on the chemistry of aquatic ecosystems in eastern North America. International Symposium on Acidic Precipitation, Muskoka Conference, September 1985 (Abstract).

Johnson, D., J. Colquhoun, F. Flack, and H. Simonin. 1985. In situ Bioassays of Fish in Acid Waters. Final Report to EPA/NS4CSU Acid Deposition Program, Raleigh, NC.

Kanciruk, P., R. J. Olson, and R. A. McCord. 1986. Quality Control in Research Data Bases: The U.S. Environmental Protection Agency National Surface Water Survey Experience. In: W. K. Michener (ed.). Research Data Management in the Ecological Sciences, University of South Carolina Press, Columbia, South Carolina. pp. 193-207.

Kelso, J. R. M., and J. M. Gunn. 1982. Responses of fish communities to acid waters in Ontario. In G. R. Hendrey (ed.). Chronic stress of acidification on aquatic biota: pH 5 to 6. Am. Chem. Soc. Symp. Ser., Ann Arbor Science Publishers, Ann Arbor, Michigan.

Knapp C. M., C. L. Mayer, D. V. Peck, J. R. Baker, and G. J. Filbin. 1987. NSWS: NSS-Pilot Survey; Field Operations Report. EPA/600/8-87/019. U.S. EPA, Las Vegas, Nevada. 94 pp.

Krug, E. C., P. J. Isaacson, and C. R. Frink. 1985. Appraisal of some current hypotheses describing acidification of watersheds. JAPCA 35:109-114.

Lefohn, A. S., and R. W. Brocksen. 1984. Acid rain effects research—a status report. JAPCA 34:1005-1013.

Linthurst, R. A., D. H. Landers, J. M. Eilers, D. F. Brakke, W. S. Overton, E. P. Meier, and R. E. Crowe. 1986. Characteristics of Lakes in the Eastern United States Volume I: Population Descriptions and Physico-Chemical Relationships. U.S. Environmental Protection Agency (EPA-600/4-86-007A).

Magnuson, J. J., J. P. Baker, and E. J. Rahel. 1984. A critical assessment of acidification on fisheries in North America. Phil. Trans. R. Soc. Lond. B*305*, 501-516.

Minshall, G. W., R. C. Petersen, K. W. Cummins, T. L. Bott, J. R Sedell, C. E. Cushing, and R. L. Vannote. 1983. Interbiome comparison of stream ecosystem dynamics. Ecol. Monogr. 53:1-25.

Morris, F. A., D. V. Peck, M. B. Bonoff, K. J. Cabble, and S. L. Pierett. 1986. National Surface Water Survey, Eastern Lake Survey-Phase I-Synoptic Chemistry, Field Operations Report. EPA-600/4-86-010. U.S. Environmental Protection Agency, Las Vegas, Nevada.

Muniz, I. P., and H. Leivestad. 1980. Toxic effects of aluminum on the brown trout, *Salmo trutta* L. In: D. Drablos and A. Tollan (eds.). Ecological Impacts of Acid Precipitation, Proc. Int. Conf., Sandefjord, Norway, SNSF Project 1432 AS-NLW, pp. 320-321.

National Research Council. 1981. Atmosphere-Biosphere Interactions: Toward a Better Understanding of the Ecological Consequences of Fossil Fuel Combustion. National Academy Press.

National Research Council. 1983. Acid Deposition: Atmospheric Processes in Eastern North America—a Review of Current Scientific Understanding. National Academy Press: Washington, D.C. 375 pp.

National Research Council. 1984. Acid Deposition: Processes of Lake Acidification, National Academy Press.

Oden, S. 1976. The acidity problem -- an outline of concepts, pp. 1-36. *In* Proc. of the First Intern. Symp. on Acid Precip. and the Forest Ecosystem. Dochinger, L. S. and T. A. Seliga, eds. U.S. Dept. Agric. For. Serv. Gen. Tech. Rep. NE-23.

Office of Science and Technology Policy. 1984. Report of the Acid Rain Peer Review Panel; July 1984.

Office of Technology Assessment. 1984. Acid Rain and Transported Air Pollutants: Implications for Public Policy, Report OTS-0-204; U.S. Congress, Washington, D.C. June 1984.

Olem, H. 1984. Stream acidification during storm events in southern Appalachian watersheds. Aquatic Effects Task Group (E) and Terrestrial Effects Task Group (F) Peer Review Research Summaries. NAPAP. ADP. North Carolina State Univ. pp. 61-66.

Olsen, J. E., E. A. Whippo, and G. C. Horak. 1981. REACH file Phase II report: A standardized method for classifying status and type of fisheries. U.S. Fish Wildl. Serv. FWS/OBS-81/31. 56 pp.

Omernik, J. M., and C. F. Powers. 1983. Total alkalinity of surface waters—a national map. Ann. Assoc. Amer. Geographers 73(1):133-136.

Overton, W. S. 1985. (Draft) Sampling Plan for Streams in the National Surface Water Survey. Technical Report 114 (July 1986). Department of Statistics, Oregon State University, Corvallis, Oregon.

Overton, W. S. 1987. A Sampling and Analysis Plan for Streams in the National Surface Water Survey. Technical Report 117. Department of Statistics, Oregon State University, Corvallis, Oregon.

Pfeiffer, M. H., and P. J. Festa. 1980. Acidity status of lakes in the Adirondack region of New York in relation to fish resources. New York State Department of Environmental Conservation, FW-PI68 (10/80).

Pierson, W. R., and T. Y. Chang. 1986. Acid rain in western Europe and northeastern United States—a technical appraisal. CRC Critical Reviews in Environmental Control 16:167-192.

Platts, W. S. 1979. Relationships among stream order, fish populations, and aquatic geomorphology in an Idaho river drainage. Fisheries 4:5-9.

Rochelle, B. P., M. R. Church, and M. B. David. 1986. Sulfur retention at intensively studied watersheds in the U.S. and Canada. Water, Air, and Soil Pollution (in press).

Rogeberg, E. J. S., and A. Henriksen. 1985. An automatic method for fractionation and determination of aluminum species in fresh-waters. Vatten 41:48-53.

Romesburg, F. 1984. Cluster Analysis for Researchers. Lifetime Learning, Belmont, Massachusetts.

Rosen, A. E., and P. Kanciruk. 1985. A Generic Data Entry Quality Assurance Tool. In: SAS User's Group International, Proceedings of the Tenth Annual Conference, SAS Institute, Cary, North Carolina. 1985. pp. 434-436.

Sale, M. J. (editor). 1987. Data Management and Analysis Procedures for the National Stream Survey. ORNL/TM. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37821 (draft).

Sale, M. J. 1986. Data Dictionary for the National Stream Survey. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831 (draft).

SAS Institute, Inc. 1983. SAS User's Guide: Basics, Version 5 Edition. SAS Institute, Inc., Cary, North Carolina. 1290 p.

SAS Institute, Inc. 1985. SAS User's Guide: Statistics, Version 5 Edition. SAS Institute, Inc., Cary, North Carolina. 956 p.

Schofield, C. L. 1976. Acid precipitation: effects on fish. Ambio 5:338-230.

Schofield, C. L., and J. R. Trojnar. 1980. Aluminum toxicity to brook trout (salvelinus fontinalis) in acidified waters, pp. 347-366. *In* Polluted Rain. Toribarn, T. Y., M. W. Miller and P. E. Morrow, Eds. Plenum Press, New York, NY.

Sharpe, W. E., D. R. DeWalle, R. T. Leibfried, R. S. Dinocola, W. G. Kimmel, and L. S. Sherwin. 1984. Causes of acidification of four streams on Laurel Hill, southwestern Pennsylvania. J. Environ. Qual. 13(4):619-631.

Shreve, R. L. 1966. Statistical law of stream numbers. Journal of Geology 74:17-37.

Silsbee, D. G. and G. L. Larson, 1982. Water quality of streams in the Great Smoky Mountains National Park. Hydrobiologia 89, 97-115.

Smith, R. A., and R. B. Alexander. 1983. Evidence for acid-precipitation—induced trends in stream chemistry at hydrologic benchmark stations. U.S. Geological Survey Circular 910. US DOI. 12 p.

Sports Fishing Institute Bulletin. 1984. Nov./Dec. No. 360.

Stapanian, M. A., A. K. Pollack, and B. C. Hess. 1986. Holding Time for Lake and Stream Samples: Effects on Twenty-Five (25) Analytes. Lockheed Engineering and Management Services, Inc., Las Vegas, Nevada (unpublished MS). 12 pp.

Storet User's Handbook. 1985. Computer Sciences Corporation, 6521 Arlington Boulevard, Falls Church, Virginia 22024.

Talbot, R. W. and A. W. Elzerman. 1985. Acidification of Southern Appalachian lakes. Environ. Sci. Technol. 19:552-557.

TIE Staff. 1981. Regional assessment of aquatic resources at risk from acid deposition (Inst. of Ecology, Indianapolis, Ind.).

Toth, J. 1963. A theoretical analysis of groundwater flow in small drainage basins. J. Geophys. Res. 67:4795-4812.

U.S. Environmental Protection Agency. 1983 (revised). Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

U.S. Environmental Protection Agency. 1984a. The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers. Volume 1. Atmospheric Sciences; Volume 2. Effects Sciences. ORD: Washington, D.C. EPA-600/8-83-016AF and -016BF.

U.S. Environmental Protection Agency. 1984b. National Surface Water Survey: National Stream Survey Draft 1985 Research Plan (EPA-ERL/C).

U.S. Environmental Protection Agency. 1985a. National Surface Water Survey: National Stream Survey; Draft 1985 Research Plan (March, 1985). ORD. Washington, D.C.

U.S. Environmental Protection Agency. 1985b. National Surface Water Survey; National Stream Survey; Mid-Atlantic Phase I and Southern

Screening Draft Research Plan. ORD, Washington, D.C.

U.S. Environmental Protection Agency. 1985c. National Surface Water Survey; Eastern Lake Survey Phase II Research Plan. EPA-ERL/C.

U.S. Environmental Protection Agency. 1985d. Direct/Delayed Response Project; Vol. I-V, August 30, 1985 (EPA-ERL/C).

Vannote, R. L., G. W. Minshall, K. W. Cummins, J. R. Sedell, and C. E. Cushing. 1980. A river continuum concept. Can. J. Fish. Aquat. Sci. 37:130-137.

Velbel, M. A. 1985a. Hydrogeochemical constraints on mass balances in forested watersheds of the southern Appalachians. *The Chemistry of Weathering*, J. I. Drever (ed.). D. Reidel Publishing Company. p. 231-247.

Velbel, M. A. 1985b. Geochemical mass balances and weathering rates in forested watersheds of the Southern Blue Ridge. Am. Jour. of Science, 285:904-930.

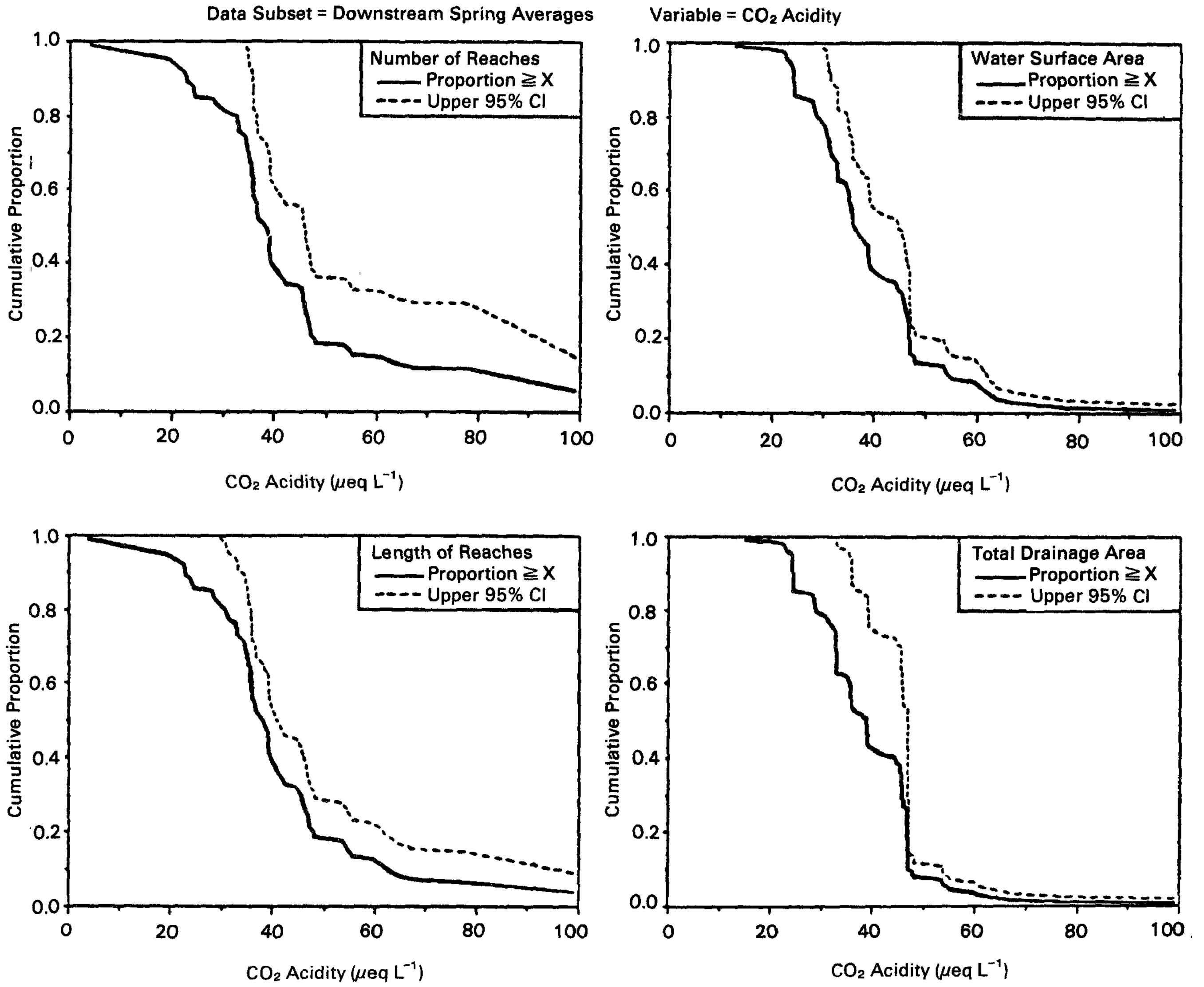
Velleman, P. F., and D. C. Hoaglin. 1981. Applications, Basics, and Computing of Exploratory Data Analysis. Duxbury Press, Boston, Massachusetts. pp. 354.

Watt, W. D., D. Scott, and S. Ray. 1979. Acidification and other chemical changes in Halifax County lakes after 21 years. Limnol. Oceanogr. 24:1154-1161.

Wright, R. F., and E. T. Gjessing. 1976. Acid precipitation: changes in the chemical composition of lakes. Ambio 5:219-223.

# Appendix A
# Cumulative Distributions for Chemical Variables

**Figure A.1. Population distribution estimate for $CO_2$ acidity, based on spring downstream averages.**

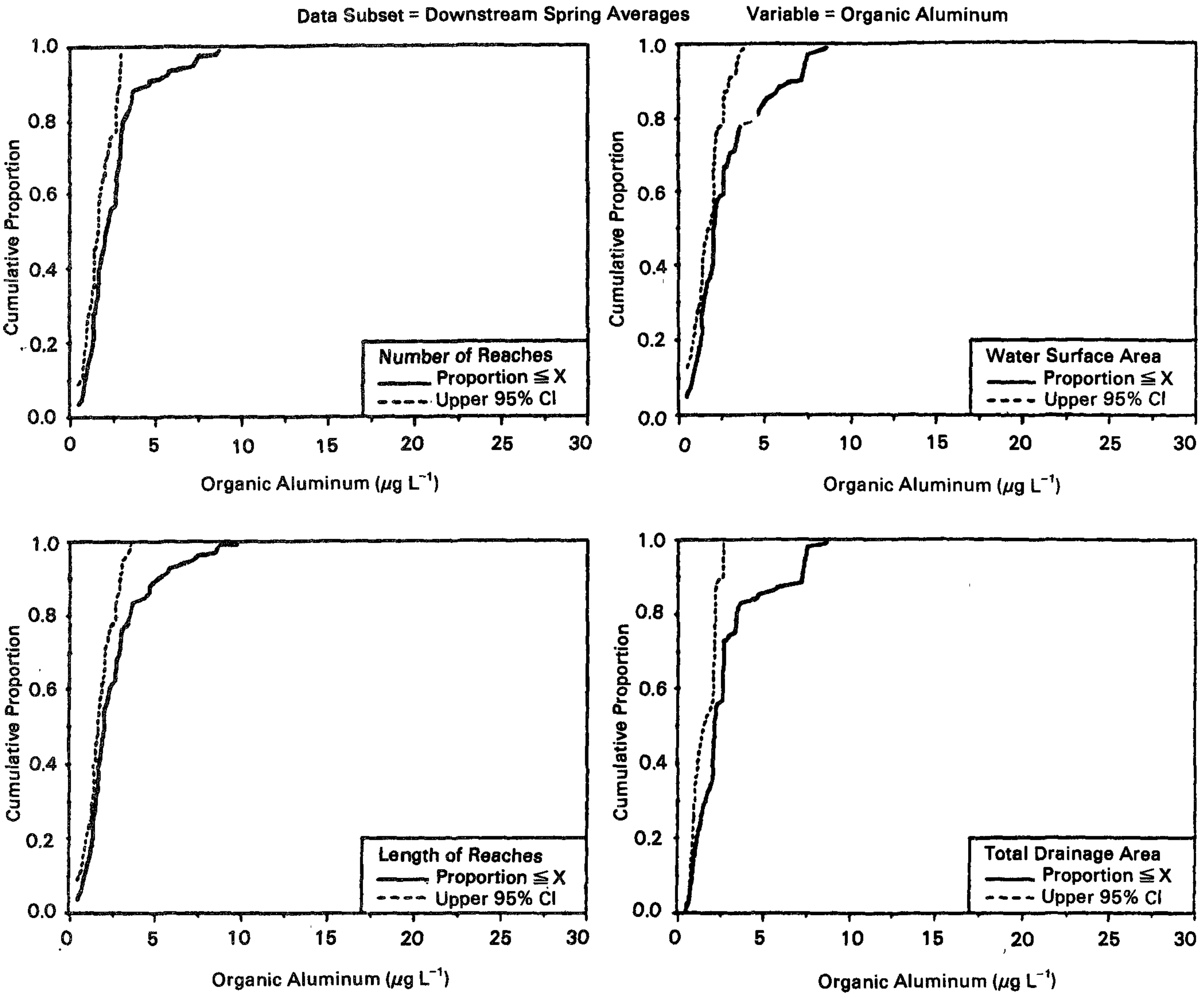


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (μeq $L^{-1}$) | 31.38 | 28.22 | 28.96 | 28.20 |
| 40 %ILE (μeq $L^{-1}$) | 35.62 | 33.90 | 35.50 | 35.32 |
| Median (μeq $L^{-1}$) | 37.33 | 35.74 | 36.64 | 38.76 |
| 60 %ILE (μeq $L^{-1}$) | 39.18 | 39.00 | 39.22 | 42.81 |
| 80 %ILE (μeq $L^{-1}$) | 46.98 | 46.49 | 47.21 | 46.39 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 52 | 84 |

| Sample Weighted Statistics (μeq $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 0.03 | 116.42 | 41.16 | 19.34 |

**Figure A.2.** Population distribution estimate for organic aluminum, based on spring downstream averages.

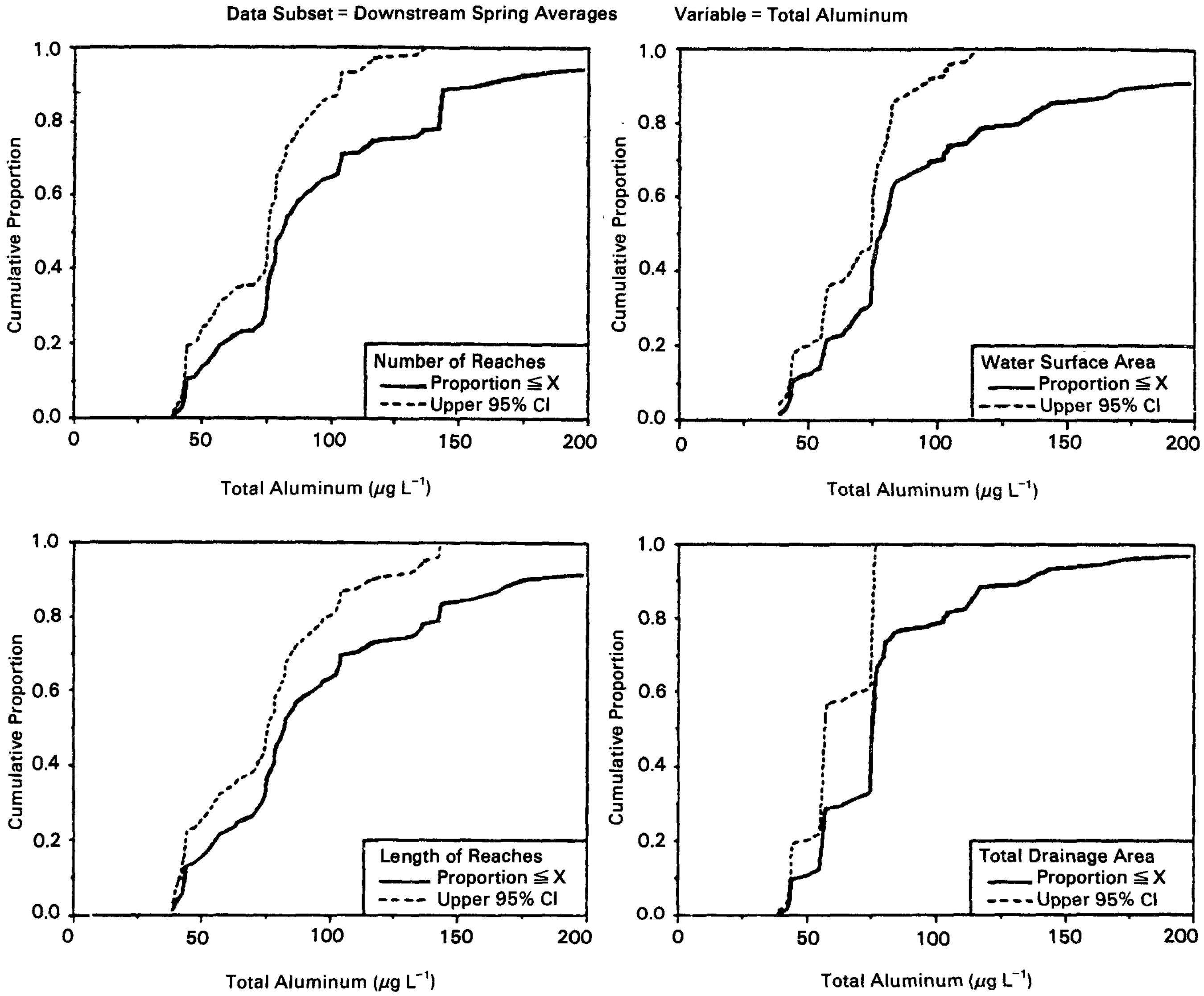


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (µg L$^{-1}$) | 1.27 | 1.26 | 1.32 | 1.14 |
| 40 %ILE (µg L$^{-1}$) | 1.68 | 1.97 | 1.71 | 2.02 |
| Median (µg L$^{-1}$) | 2.08 | 2.03 | 2.00 | 2.12 |
| 60 %ILE (µg L$^{-1}$) | 2.65 | 2.64 | 2.31 | 2.64 |
| 80 %ILE (µg L$^{-1}$) | 3.03 | 4.49 | 3.51 | 3.46 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 36 | 84 |

| Sample Weighted Statistics (µg L$^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 0.47 | 15.22 | 2.65 | 2.04 |

**Figure A.3.** Population distribution estimate for total aluminum, based on spring downstream averages.

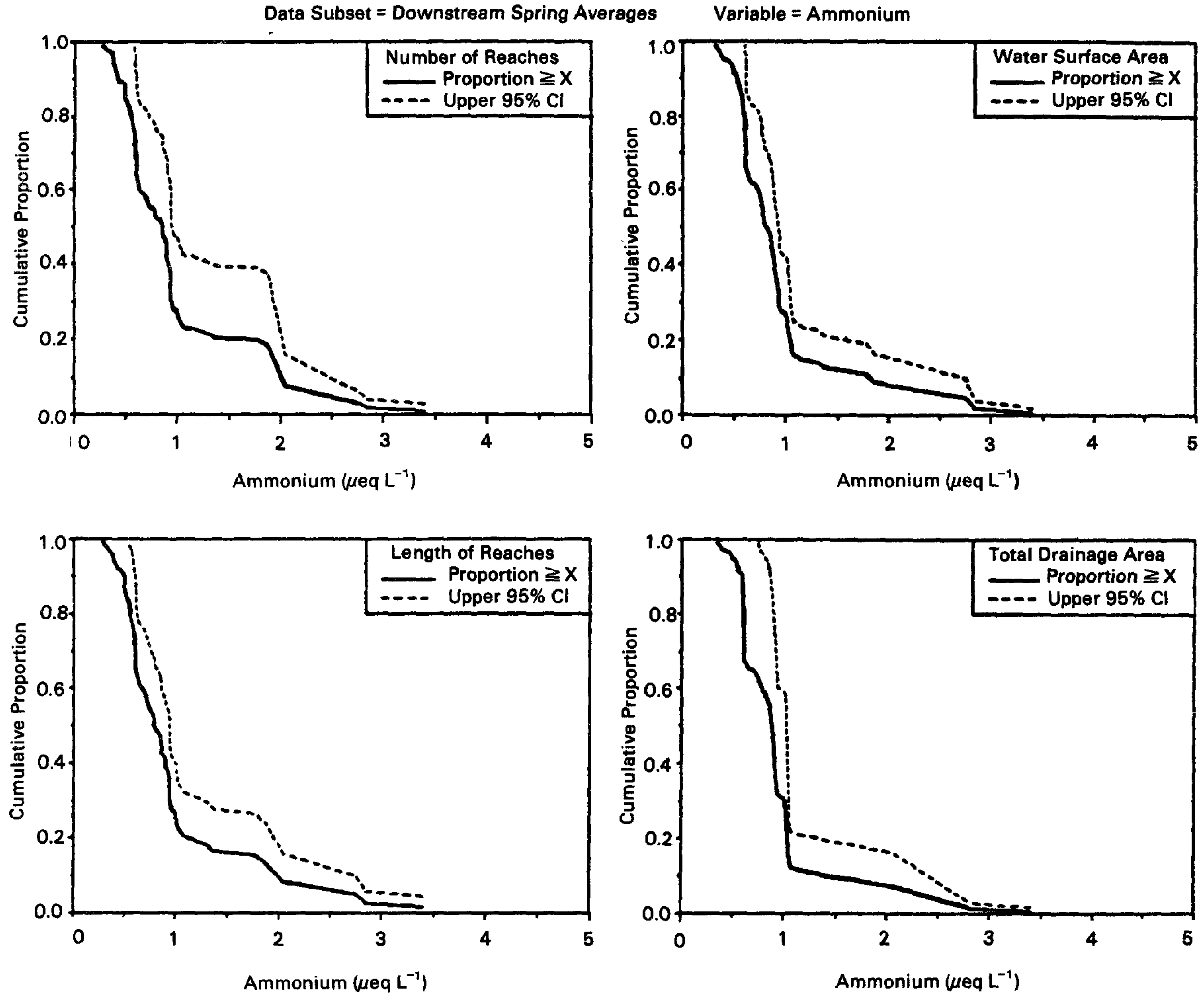


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu g$ $L^{-1}$) | 58.30 | 56.66 | 55.70 | 55.87 |
| 40 %ILE ($\mu g$ $L^{-1}$) | 76.98 | 75.04 | 77.84 | 74.87 |
| Median ($\mu g$ $L^{-1}$) | 81.08 | 78.34 | 82.35 | 75.38 |
| 60 %ILE ($\mu g$ $L^{-1}$) | 90.12 | 82.23 | 93.62 | 76.24 |
| 80 %ILE ($\mu g$ $L^{-1}$) | 142.59 | 131.22 | 142.63 | 102.61 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics ($\mu g$ $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 38.67 | 355.33 | 101.09 | 54.06 |

**Figure A.4. Population distribution estimate for ammonium, based on spring downstream averages.**

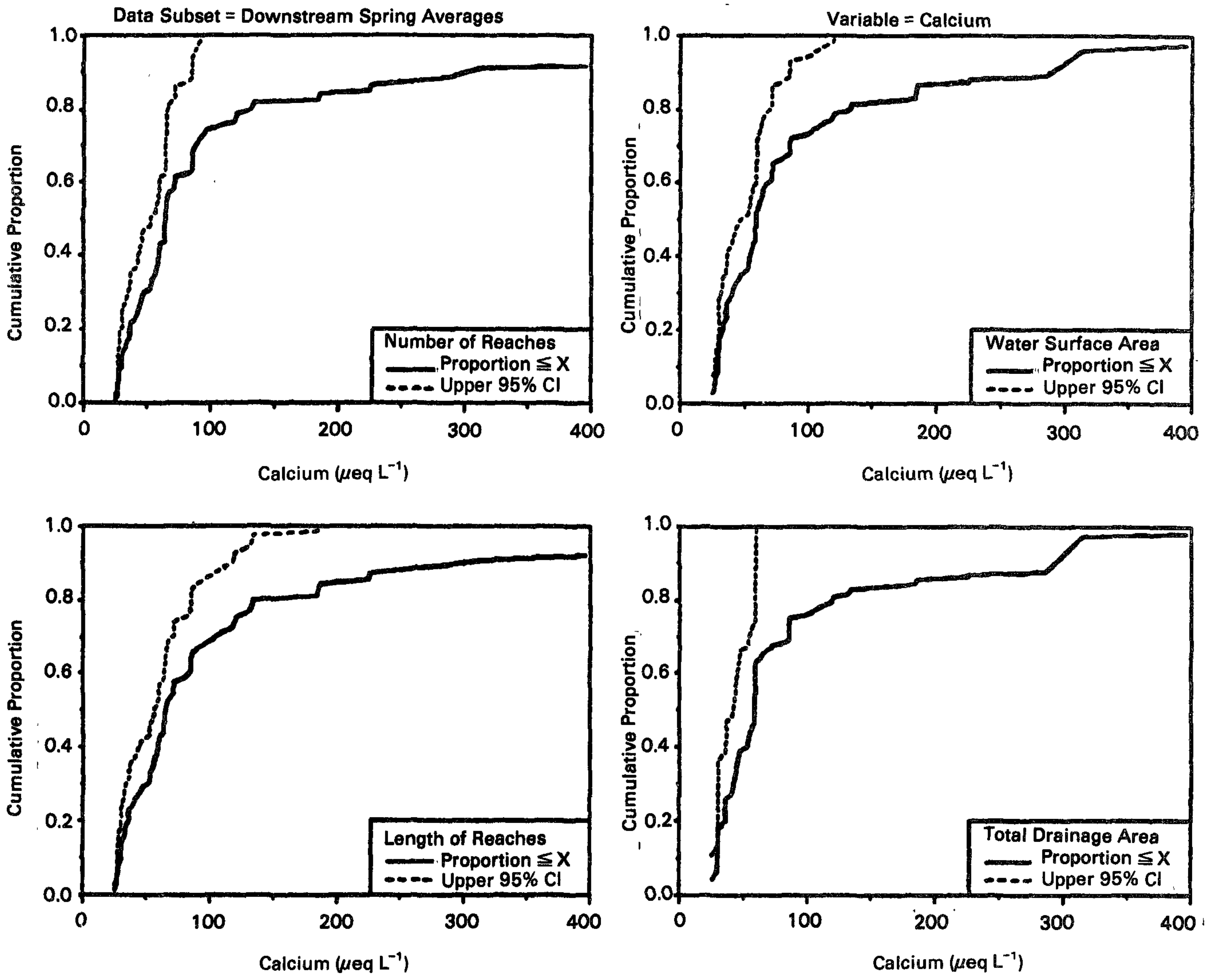


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu$eq $L^{-1}$) | 0.54 | 0.58 | 0.54 | 0.59 |
| 40 %ILE ($\mu$eq $L^{-1}$) | 0.61 | 0.72 | 0.64 | 0.78 |
| Median ($\mu$eq $L^{-1}$) | 0.86 | 0.79 | 0.79 | 0.86 |
| 60 %ILE ($\mu$eq $L^{-1}$) | 0.90 | 0.86 | 0.89 | 0.90 |
| 80 %ILE ($\mu$eq $L^{-1}$) | 1.36 | 1.01 | 1.07 | 1.01 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 52 | 84 |

| Sample Weighted Statistics ($\mu$eq $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 0.25 | 3.40 | 0.98 | 0.62 |

**Figure A.5.** Population distribution estimate for calcium, based on spring downstream averages.

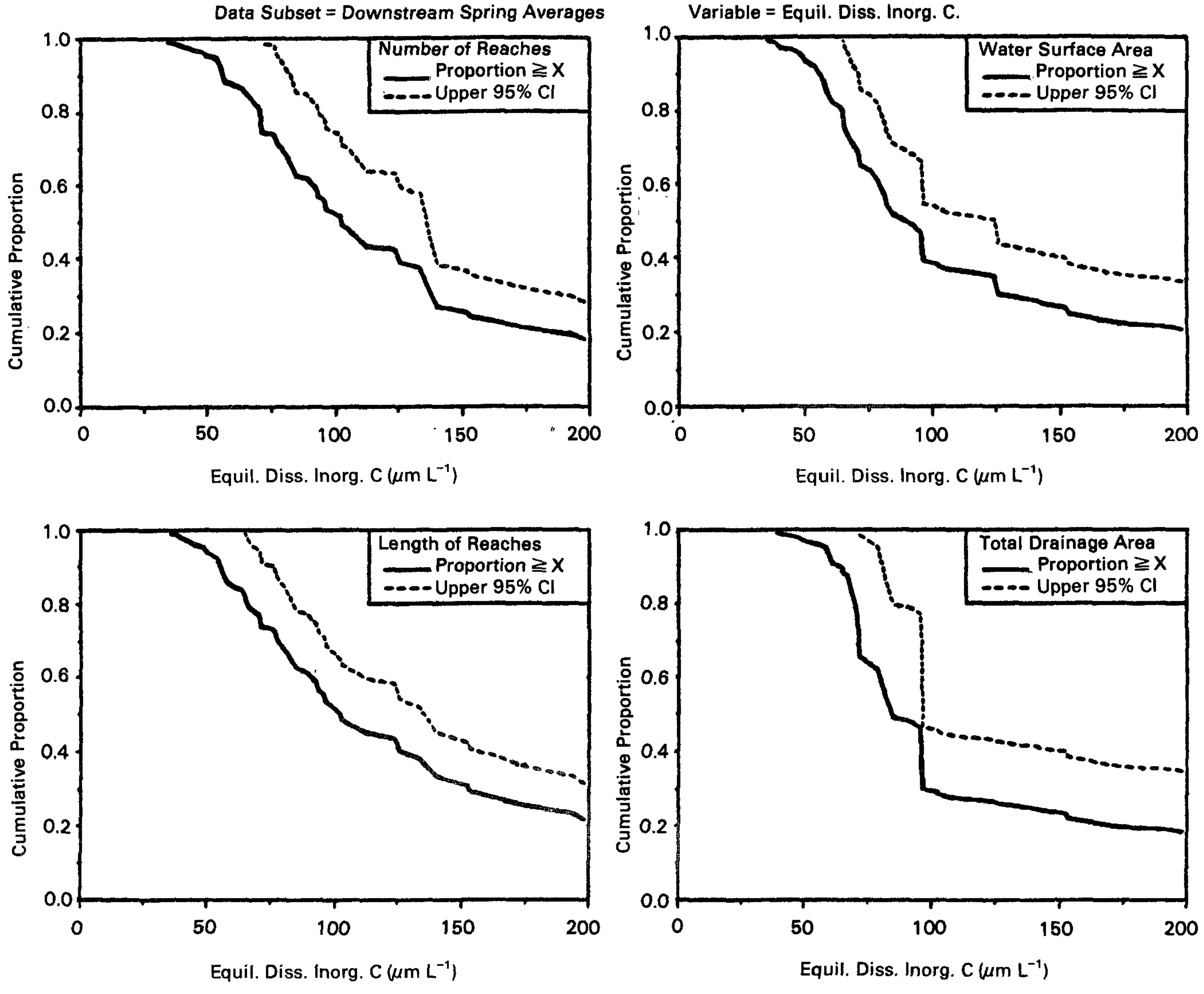


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu$eq $L^{-1}$) | 36.79 | 33.55 | 35.82 | 36.45 |
| 40 %ILE ($\mu$eq $L^{-1}$) | 59.74 | 55.10 | 59.80 | 53.14 |
| Median ($\mu$eq $L^{-1}$) | 64.69 | 59.71 | 65.86 | 59.24 |
| 60 %ILE ($\mu$eq $L^{-1}$) | 71.89 | 69.55 | 84.67 | 59.75 |
| 80 %ILE ($\mu$eq $L^{-1}$) | 131.81 | 132.82 | 136.73 | 119.50 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics ($\mu$eq $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 25.45 | 1588.5 | 190.79 | 362.59 |

**Figure A.6.** **Population distribution estimate for equilibrated dissolved inorganic carbon, based on spring downstream averages.**

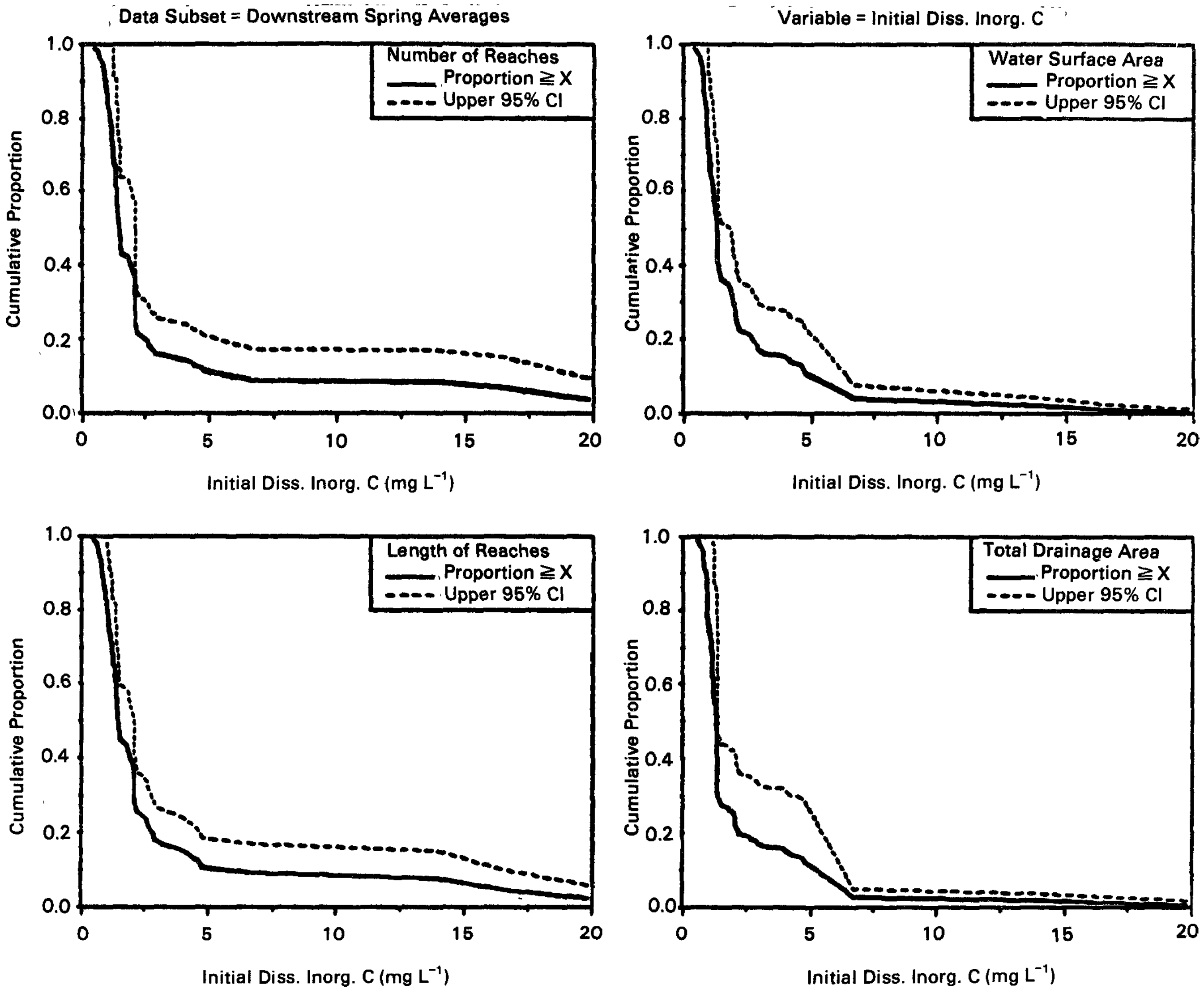


| | | Population Estimates | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu m\ L^{-1}$) | 67.34 | 62.91 | 64.81 | 66.33 |
| 40 %ILE ($\mu m\ L^{-1}$) | 87.55 | 77.85 | 87.03 | 78.02 |
| Median ($\mu m\ L^{-1}$) | 99.56 | 84.44 | 96.64 | 81.84 |
| 60 %ILE ($\mu m\ L^{-1}$) | 120.37 | 95.42 | 124.26 | 94.33 |
| 80 %ILE ($\mu m\ L^{-1}$) | 167.23 | 197.02 | 198.44 | 152.92 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 53 | 84 |

| Sample Weighted Statistics ($\mu m\ L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 26.39 | 1650 | 226.73 | 371.99 |

**Figure A.7.** Population distribution estimate for initial dissolved inorganic carbon, based on spring downstream averages.

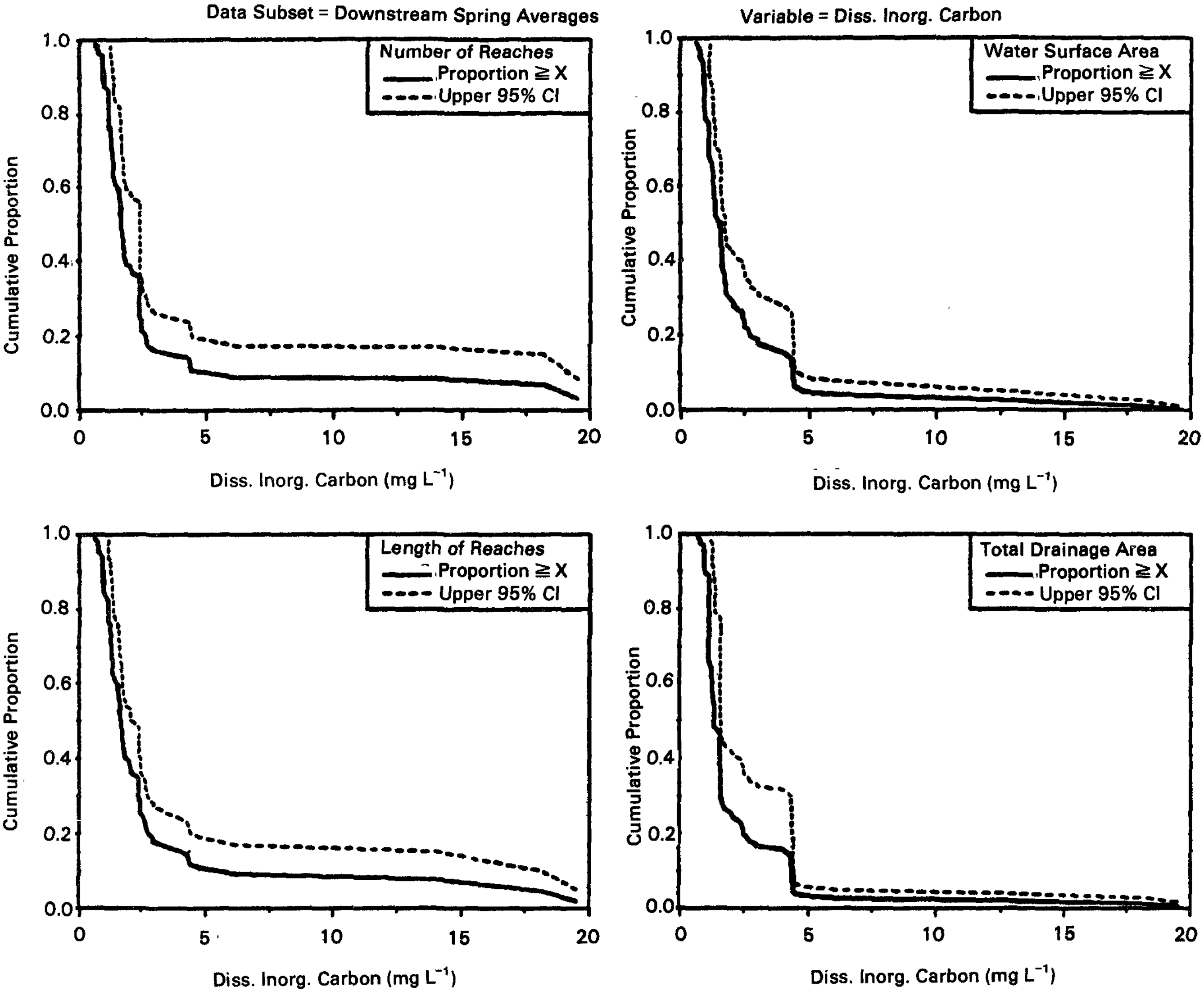


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (mg L$^{-1}$) | 1.06 | 0.87 | 0.97 | 0.96 |
| 40 %ILE (mg L$^{-1}$) | 1.31 | 1.11 | 1.31 | 1.14 |
| Median (mg L$^{-1}$) | 1.43 | 1.29 | 1.41 | 1.28 |
| 60 %ILE (mg L$^{-1}$) | 1.80 | 1.35 | 1.81 | 1.33 |
| 80 %ILE (mg L$^{-1}$) | 2.21 | 2.64 | 2.67 | 2.14 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics (mg L$^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 0.34 | 20.52 | 3.03 | 4.59 |

Figure A.8. **Population distribution estimate for dissolved inorganic carbon, based on spring downstream averages.**

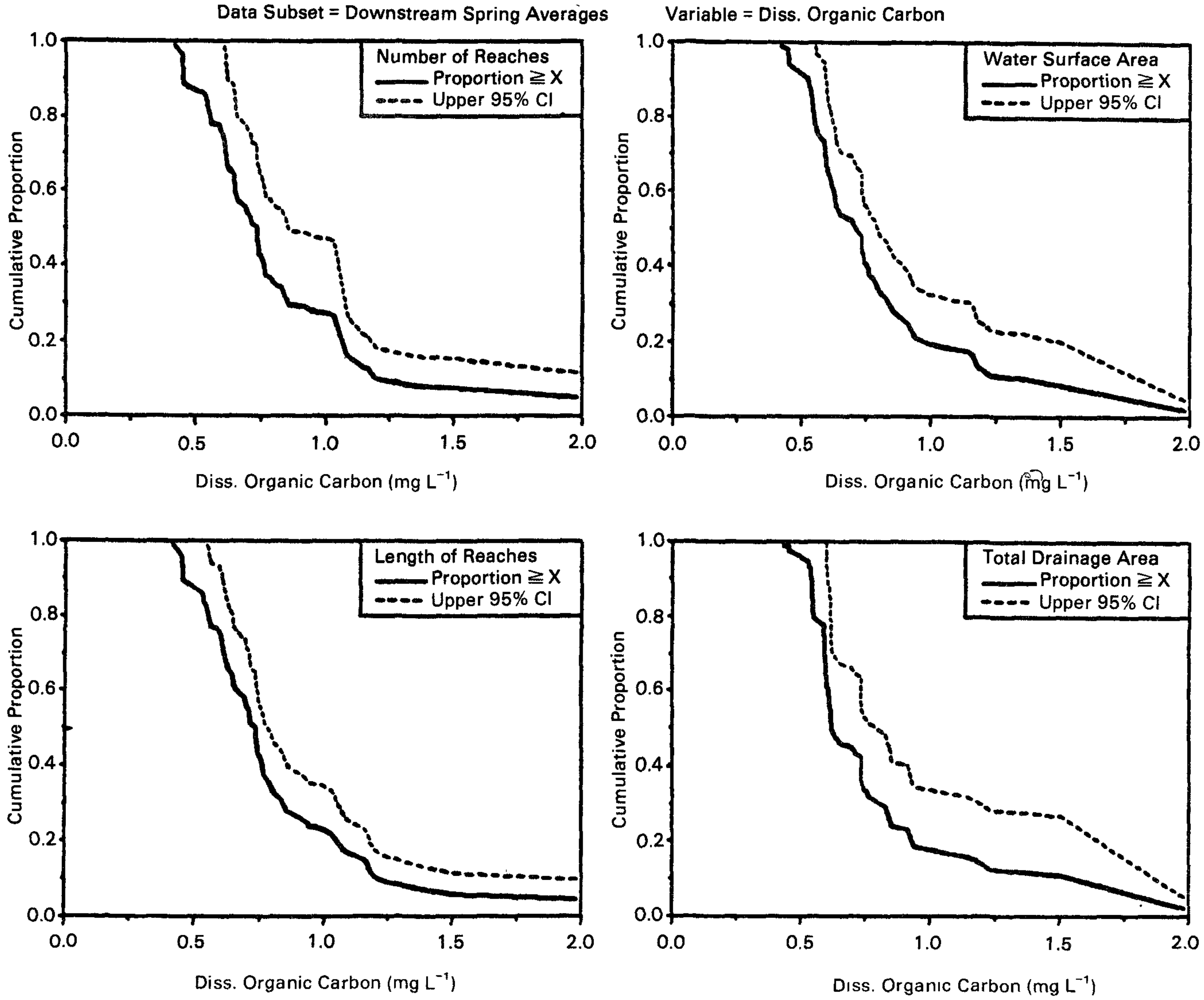


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (mg $L^{-1}$) | 1.12 | 0.92 | 1.12 | 1.12 |
| 40 %ILE (mg $L^{-1}$) | 1.36 | 1.26 | 1.39 | 1.20 |
| Median (mg $L^{-1}$) | 1.61 | 1.41 | 1.63 | 1.33 |
| 60 %ILE (mg $L^{-1}$) | 1.74 | 1.56 | 1.76 | 1.55 |
| 80 %ILE (mg $L^{-1}$) | 2.54 | 2.66 | 2.70 | 2.47 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics (mg $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 0.41 | 19.52 | 3.17 | 4.62 |

**Figure A.9.** Population distribution estimate for dissolved organic carbon, based on spring downstream averages.

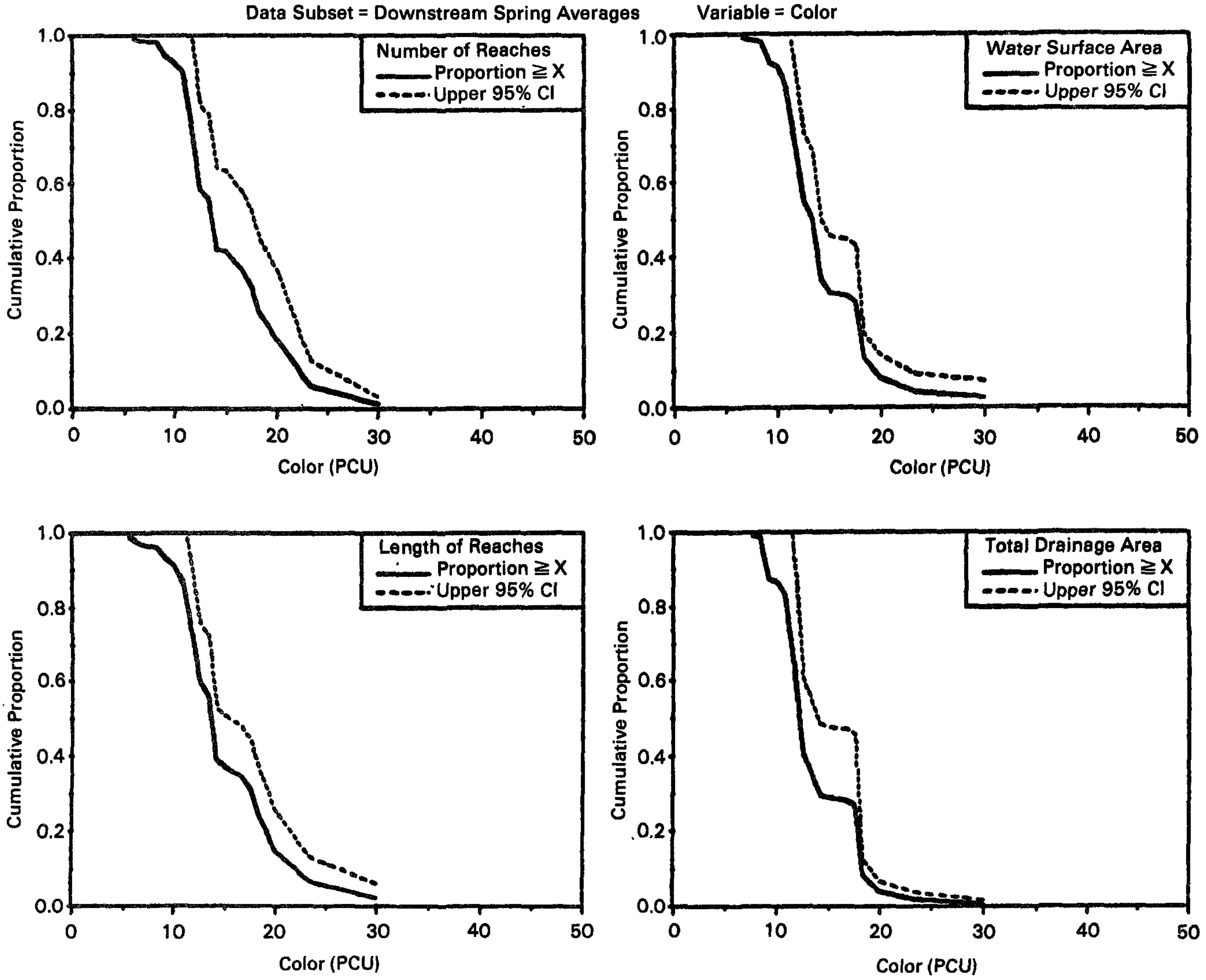


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (mg $L^{-1}$) | 0.55 | 0.55 | 0.55 | 0.55 |
| 40 %ILE (mg $L^{-1}$) | 0.64 | 0.62 | 0.65 | 0.60 |
| Median (mg $L^{-1}$) | 0.71 | 0.71 | 0.71 | 0.61 |
| 60 %ILE (mg $L^{-1}$) | 0.75 | 0.75 | 0.75 | 0.72 |
| 80 %ILE (mg $L^{-1}$) | 1.02 | 0.94 | 1.01 | 0.90 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 53 | 84 |

| Sample Weighted Statistics (mg $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 0.41 | 2.04 | 0.82 | 0.37 |

Figure A.10. Population distribution estimate for color, based on spring downstream averages.

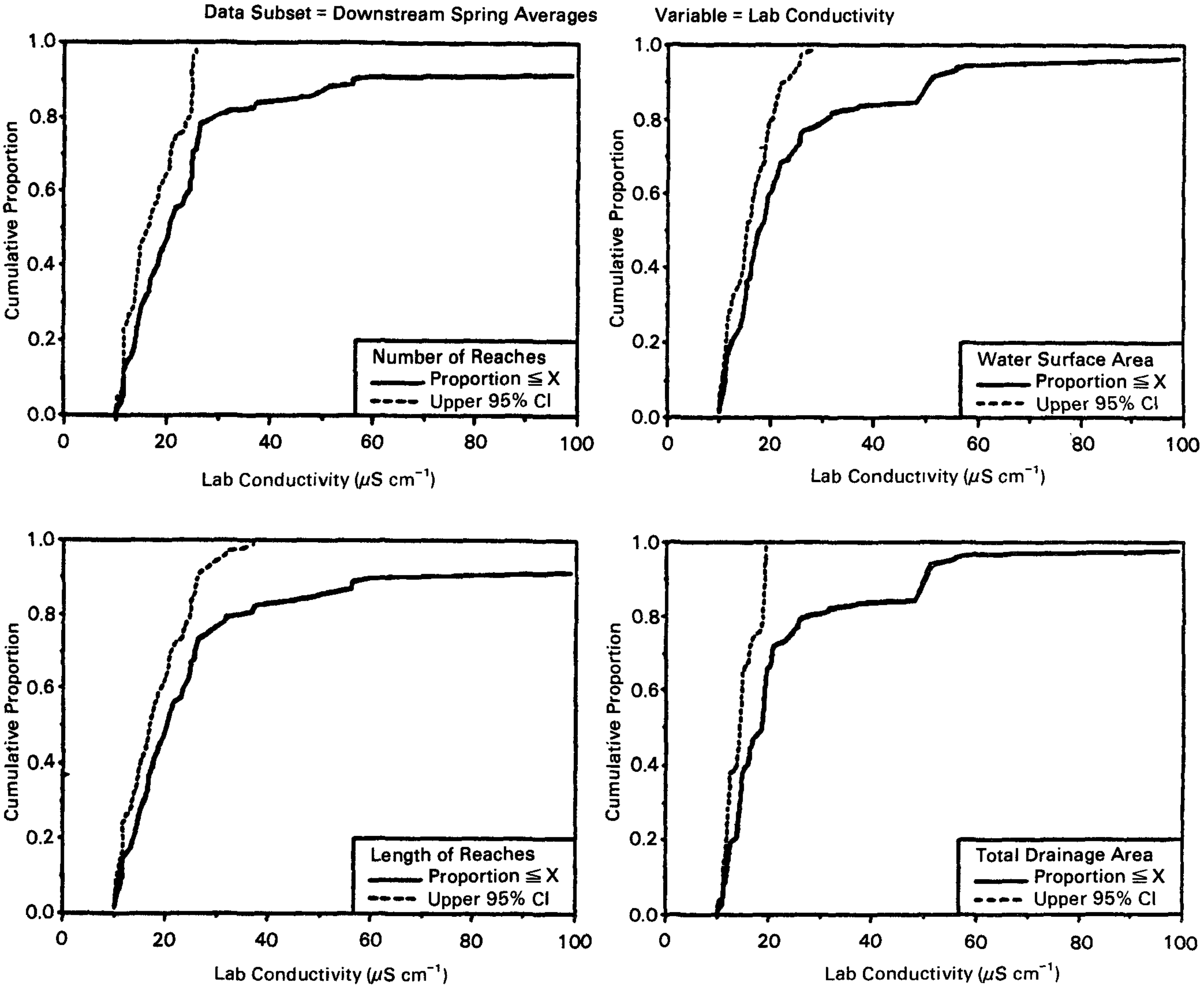


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (PCU) | 10.63 | 10.30 | 10.49 | 10.14 |
| 40 %ILE (PCU) | 11.60 | 11.39 | 11.67 | 10.97 |
| Median (PCU) | 12.86 | 12.50 | 12.81 | 11.33 |
| 60 %ILE (PCU) | 14.50 | 13.02 | 13.29 | 11.79 |
| 80 %ILE (PCU) | 18.18 | 17.12 | 17.85 | 16.98 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 17 | 84 |

| Sample Weighted Statistics (PCU) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 5.00 | 30.00 | 14.59 | 4.48 |

**Figure A.11.** **Population distribution estimate for lab conductivity, based on spring downstream averages.**

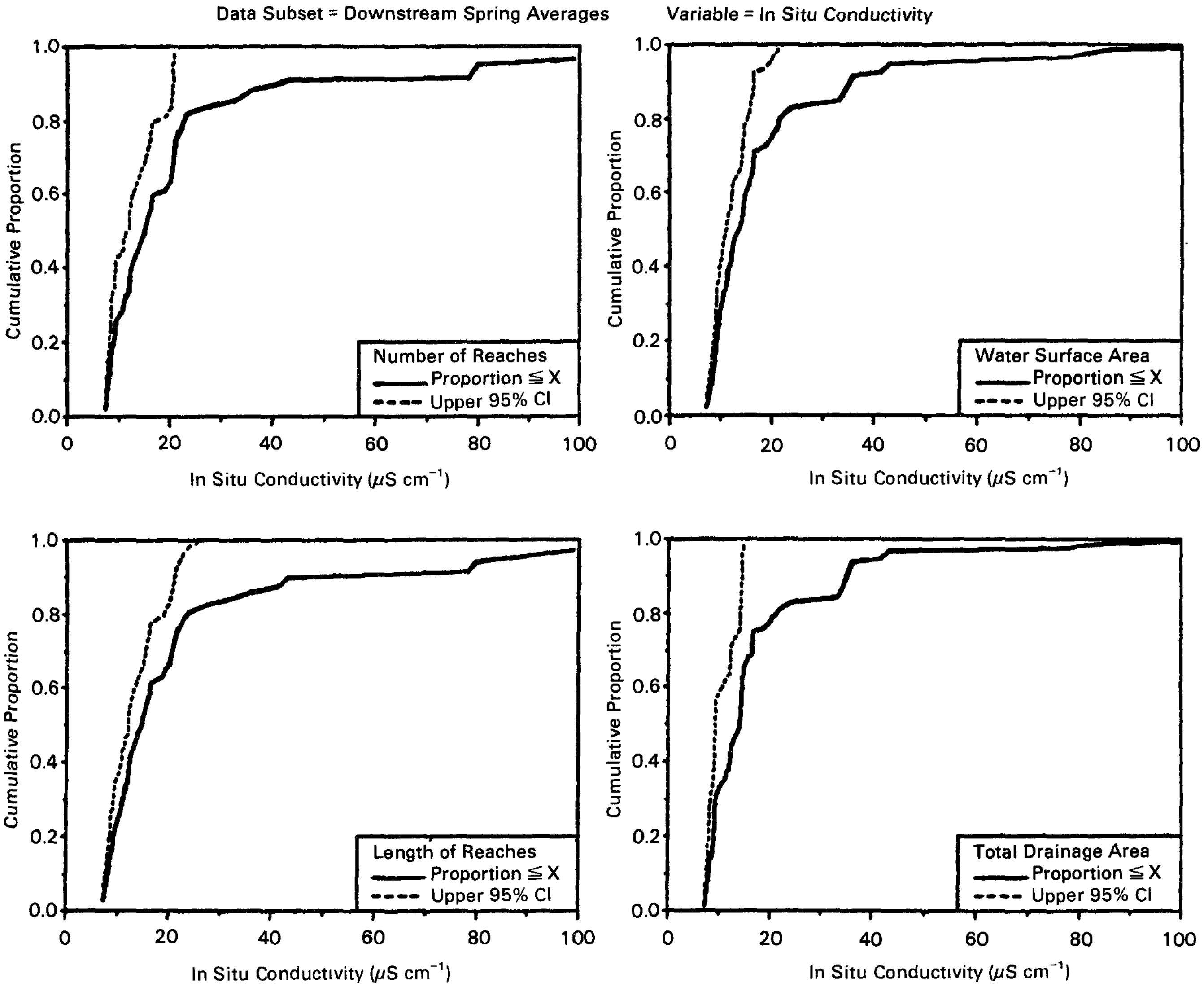


|  | Population Estimates |  |  |  |
|---|---|---|---|---|
|  | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu$S cm$^{-1}$) | 13.98 | 12.53 | 13.75 | 13.24 |
| 40 %ILE ($\mu$S cm$^{-1}$) | 18.30 | 16.22 | 17.62 | 15.60 |
| Median ($\mu$S cm$^{-1}$) | 20.62 | 17.82 | 20.43 | 18.57 |
| 60 %ILE ($\mu$S cm$^{-1}$) | 24.42 | 19.96 | 23.64 | 19.14 |
| 80 %ILE ($\mu$S cm$^{-1}$) | 29.30 | 30.72 | 34.54 | 27.41 |

| Sample Sizes |  |  |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics ($\mu$S cm$^{-1}$) |  |  |  |
|---|---|---|---|
| Min | Max | Mean | SD |
| 10.20 | 181.00 | 34.39 | 40.65 |

**Figure A.12.** **Population distribution estimate for in situ conductivity, based on spring downstream averages.**

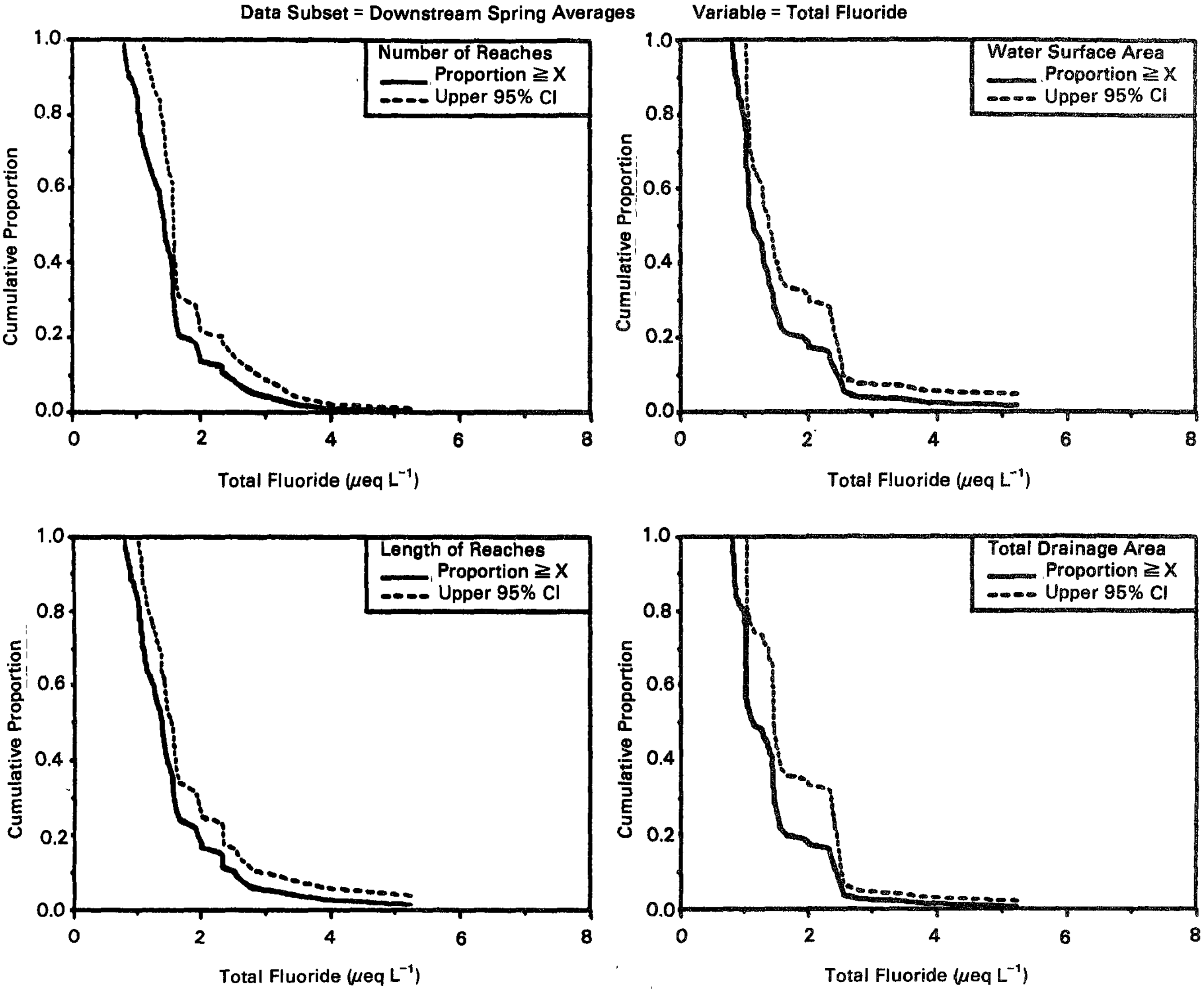

Data Subset = Downstream Spring Averages Variable = In Situ Conductivity

| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu$S cm$^{-1}$) | 9.04 | 9.24 | 9.22 | 9.04 |
| 40 %ILE ($\mu$S cm$^{-1}$) | 12.56 | 11.95 | 12.45 | 12.12 |
| Median ($\mu$S cm$^{-1}$) | 15.20 | 13.73 | 14.85 | 14.05 |
| 60 %ILE ($\mu$S cm$^{-1}$) | 17.47 | 15.14 | 16.42 | 14.46 |
| 80 %ILE ($\mu$S cm$^{-1}$) | 22.61 | 21.66 | 23.57 | 21.19 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 40 | 84 |

| Sample Weighted Statistics ($\mu$S cm$^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 7.33 | 136.00 | 24.27 | 27.49 |

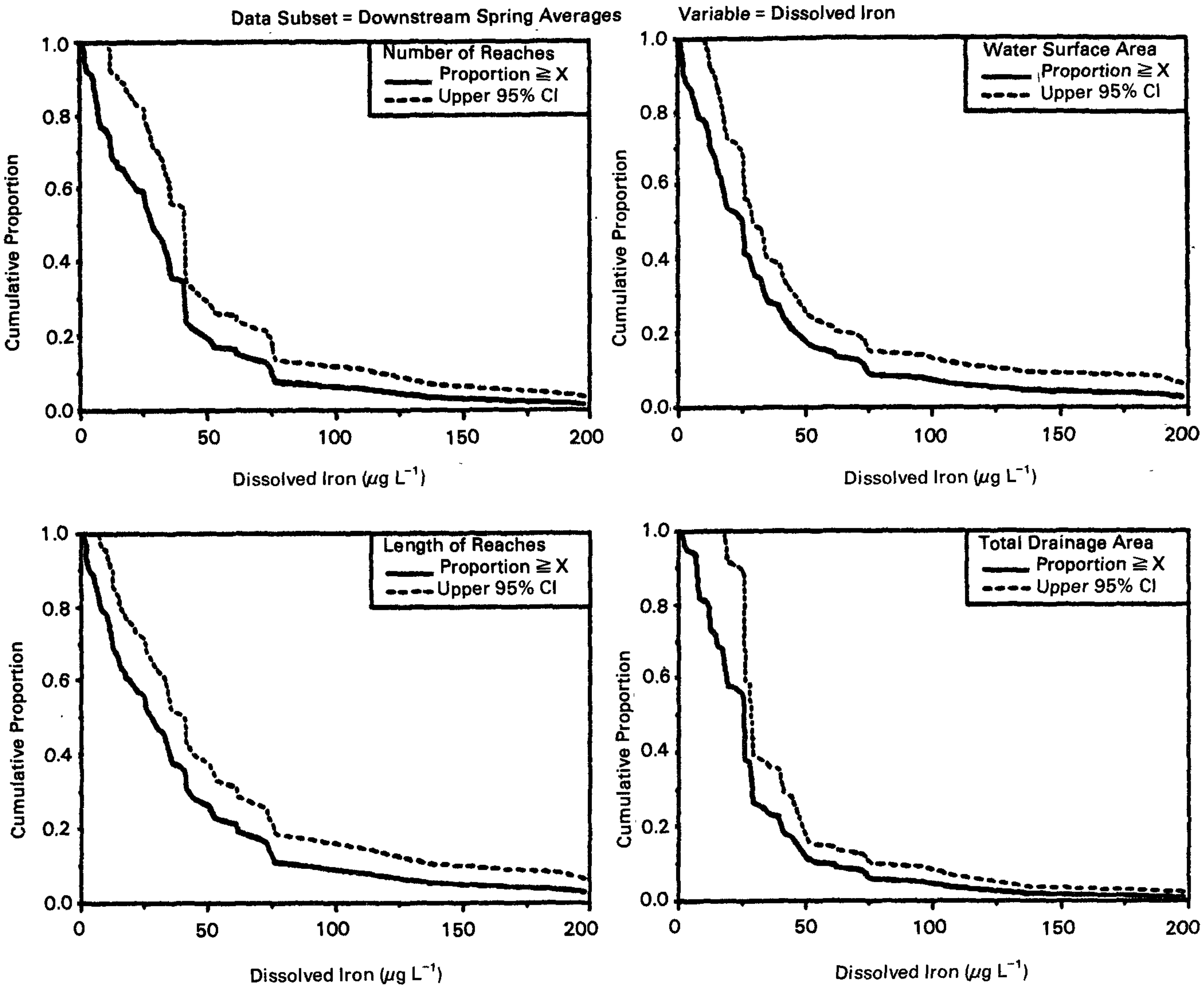
**Figure A.13.** **Population distribution estimate for total fluoride, based on spring downstream averages.**



| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu$eq L$^{-1}$) | 1.03 | 0.97 | 1.02 | 0.97 |
| 40 %ILE ($\mu$eq L$^{-1}$) | 1.31 | 1.06 | 1.15 | 1.02 |
| Median ($\mu$eq L$^{-1}$) | 1.42 | 1.13 | 1.36 | 1.11 |
| 60 %ILE ($\mu$eq L$^{-1}$) | 1.55 | 1.29 | 1.45 | 1.41 |
| 80 %ILE ($\mu$eq L$^{-1}$) | 1.64 | 1.69 | 1.92 | 1.62 |

| Sample Sizes | | | Sample Weighted Statistics ($\mu$eq L$^{-1}$) | | | |
|---|---|---|---|---|---|---|
| Actual | Unique | Effective | Min | Max | Mean | SD |
| 54 | 51 | 84 | 0.82 | 5.24 | 1.51 | 0.61 |

**Figure A.14.** **Population distribution estimate for dissolved iron, based on spring downstream averages.**

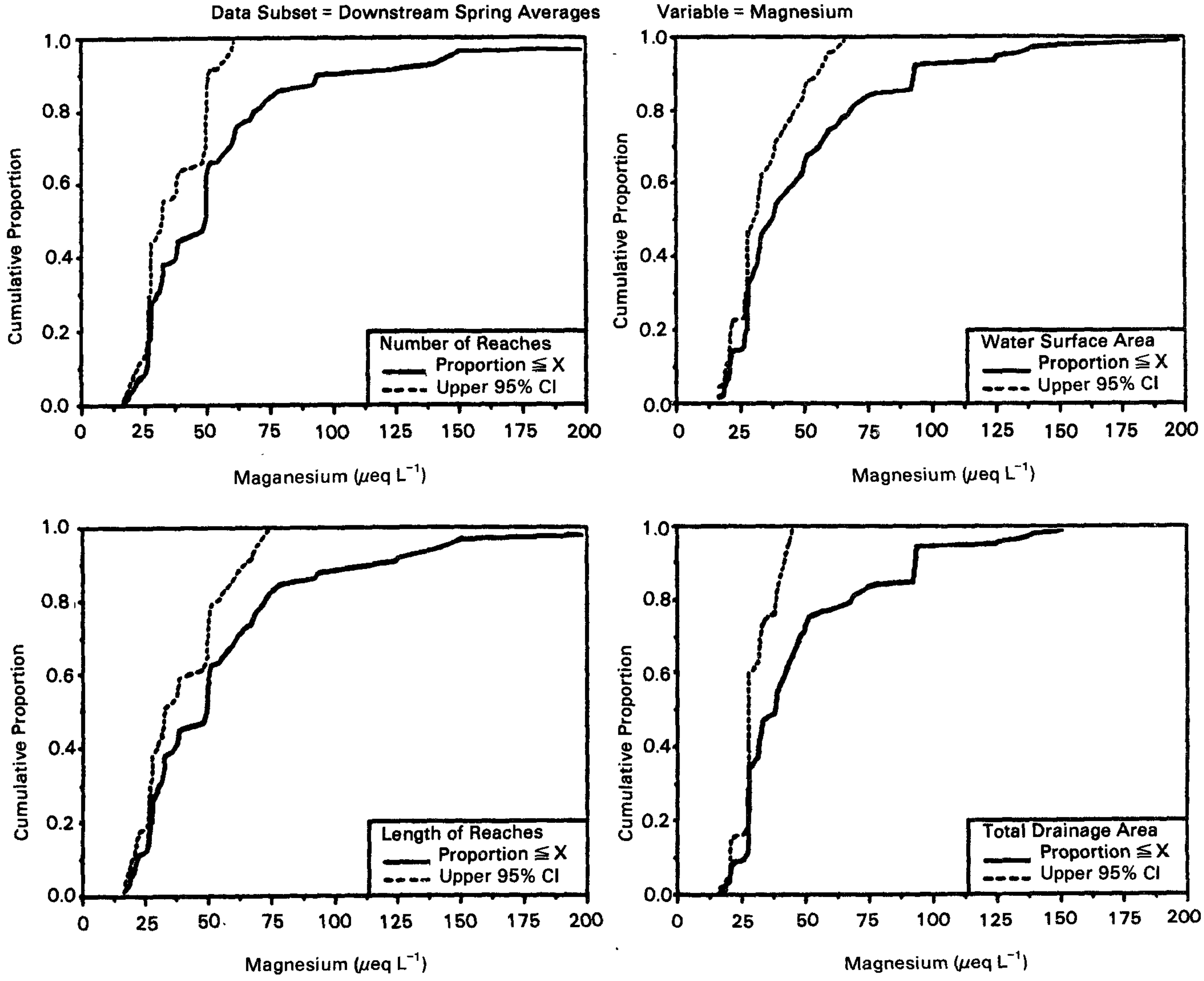


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu g\ L^{-1}$) | 6.85 | 6.85 | 6.95 | 11.15 |
| 40 %ILE ($\mu g\ L^{-1}$) | 19.03 | 17.18 | 17.30 | 17.30 |
| Median ($\mu g\ L^{-1}$) | 27.46 | 23.42 | 26.57 | 25.47 |
| 60 %ILE ($\mu g\ L^{-1}$) | 34.43 | 26.48 | 34.41 | 25.77 |
| 80 %ILE ($\mu g\ L^{-1}$) | 43.43 | 42.53 | 58.29 | 38.33 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics ($\mu g\ L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 0.37 | 216.02 | 35.35 | 36.39 |

**Figure A.15. Population distribution estimate for magnesium, based on spring downstream averages.**

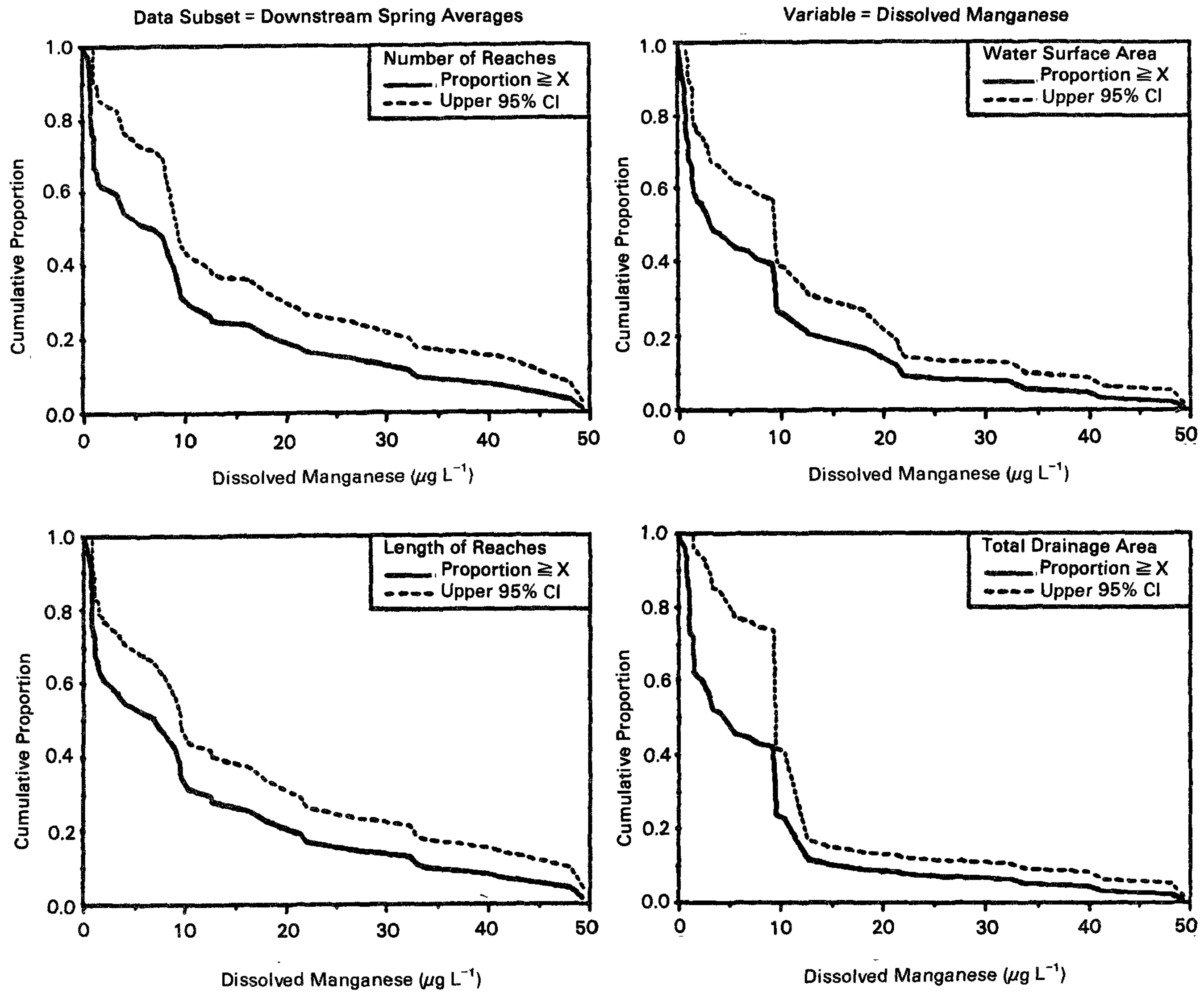


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (µeq $L^{-1}$) | 27.64 | 27.45 | 27.35 | 27.67 |
| 40 %ILE (µeq $L^{-1}$) | 37.92 | 32.06 | 36.76 | 31.92 |
| Median (µeq $L^{-1}$) | 49.33 | 37.27 | 49.38 | 38.06 |
| 60 %ILE (µeq $L^{-1}$) | 49.74 | 46.34 | 50.53 | 42.06 |
| 80 %ILE (µeq $L^{-1}$) | 68.63 | 68.41 | 72.36 | 67.83 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics (µeq $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 16.51 | 253.09 | 58.80 | 47.83 |

**Figure A.16. Population distribution estimate for dissolved manganese, based on spring downstream averages.**

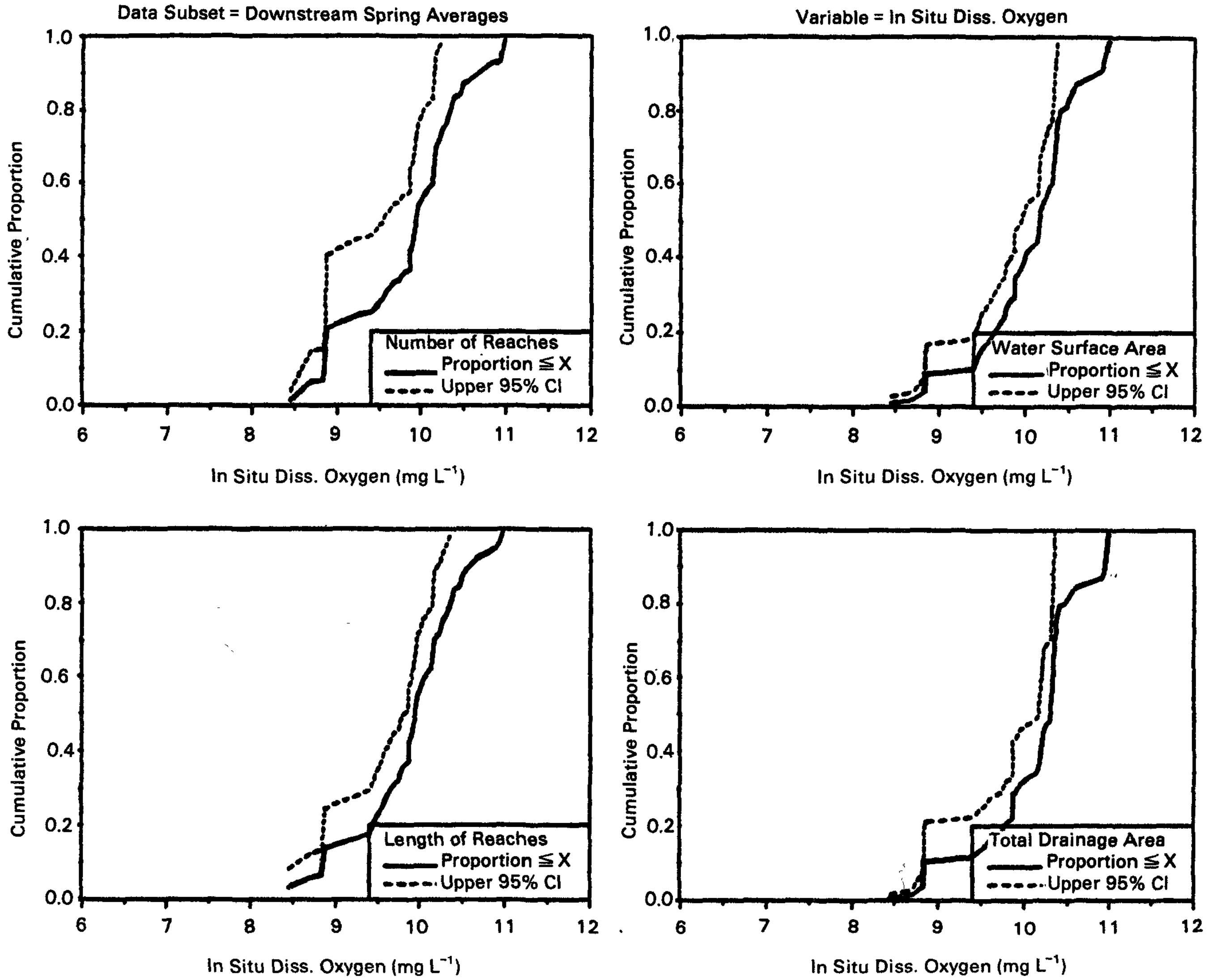


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu g\ L^{-1}$) | 0.77 | 0.67 | 0.73 | 0.90 |
| 40 %ILE ($\mu g\ L^{-1}$) | 2.71 | 1.42 | 1.83 | 1.89 |
| Median ($\mu g\ L^{-1}$) | 5.75 | 2.85 | 5.96 | 3.50 |
| 60 %ILE ($\mu g\ L^{-1}$) | 7.79 | 7.69 | 9.19 | 9.18 |
| 80 %ILE ($\mu g\ L^{-1}$) | 16.86 | 12.56 | 17.64 | 9.83 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 47 | 84 |

| Sample Weighted Statistics ($\mu g\ L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 0.00 | 49.33 | 10.37 | 12.99 |

**Figure A.17.** **Population distribution estimate for in-situ dissolved oxygen, based on spring downstream averages.**

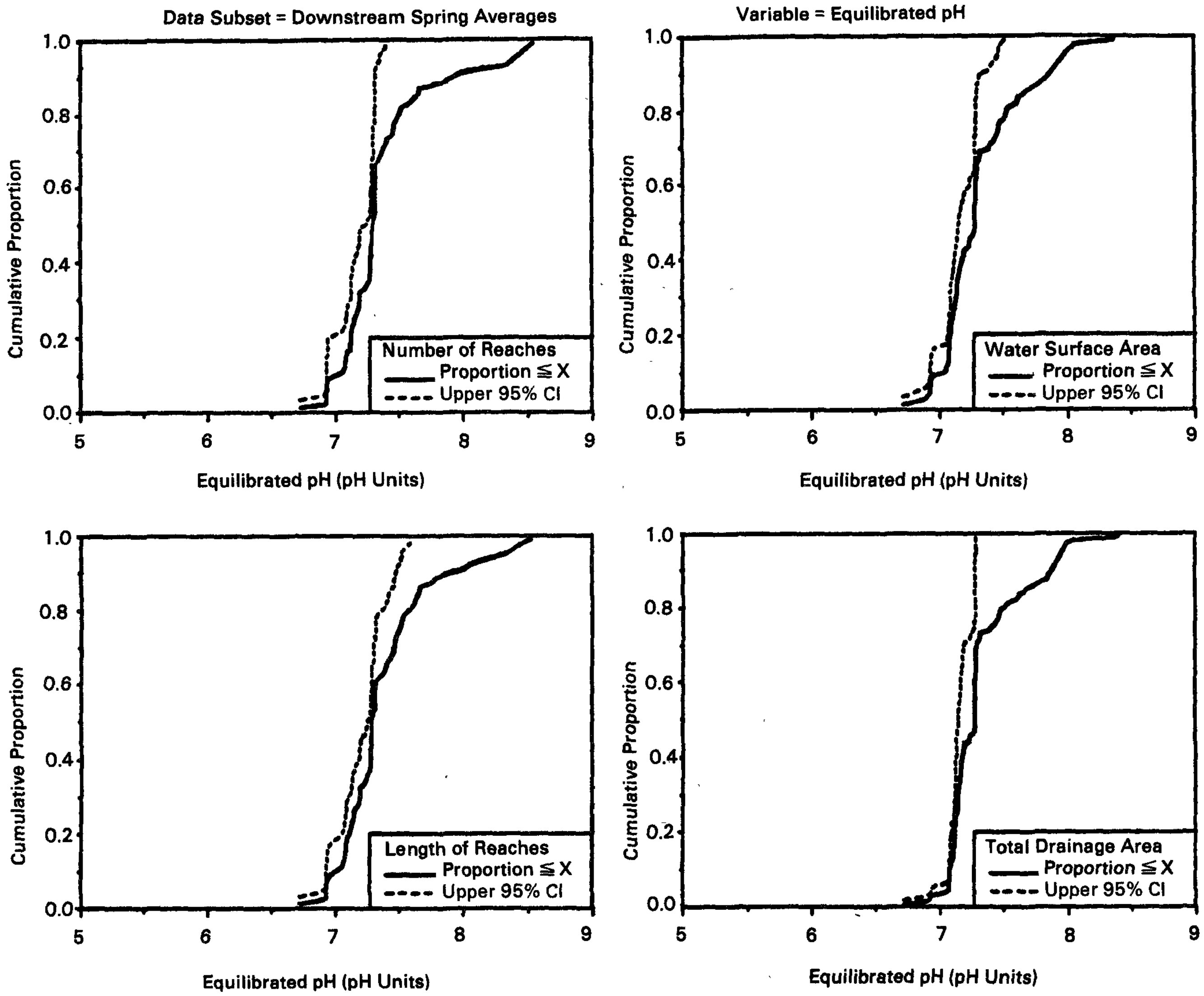


|  | Population Estimates |  |  |  |
|---|---|---|---|---|
|  | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (mg L$^{-1}$) | 8.87 | 9.64 | 9.44 | 9.77 |
| 40 %ILE (mg L$^{-1}$) | 9.87 | 9.98 | 9.87 | 10.19 |
| Median (mg L$^{-1}$) | 9.94 | 10.16 | 9.94 | 10.31 |
| 60 %ILE (mg L$^{-1}$) | 10.13 | 10.30 | 10.07 | 10.34 |
| 80 %ILE (mg L$^{-1}$) | 10.35 | 10.41 | 10.35 | 10.44 |

| Sample Sizes |  |  |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 39 | 84 |

| Sample Weighted Statistics (mg L$^{-1}$) |  |  |  |
|---|---|---|---|
| Min | Max | Mean | SD |
| 8.45 | 11.00 | 9.86 | 0.67 |

**Figure A.18.** **Population distribution estimate for equilibrated pH, based on spring downstream averages.**

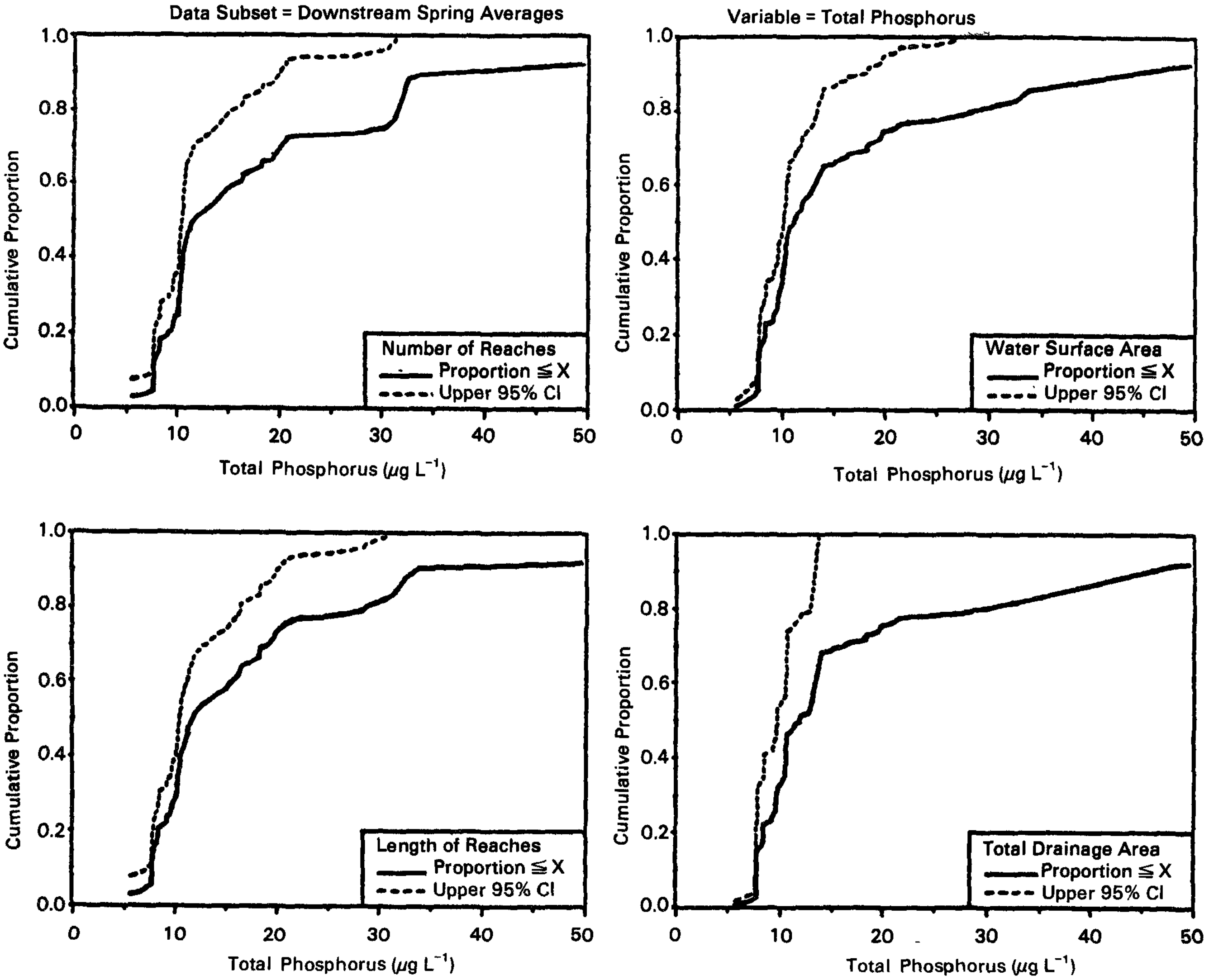


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (pH Units) | 7.12 | 7.09 | 7.11 | 7.12 |
| 40 %ILE (pH Units) | 7.27 | 7.19 | 7.27 | 7.18 |
| Median (pH Units) | 7.30 | 7.27 | 7.29 | 7.27 |
| 60 %ILE (pH Units) | 7.31 | 7.28 | 7.31 | 7.28 |
| 80 %ILE (pH Units) | 7.51 | 7.52 | 7.58 | 7.50 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 50 | 84 |

| Sample Weighted Statistics (pH Units) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 6.72 | 8.58 | 7.39 | 0.40 |

**Figure A.19. Population distribution estimate for total phosphorus, based on spring downstream averages.**

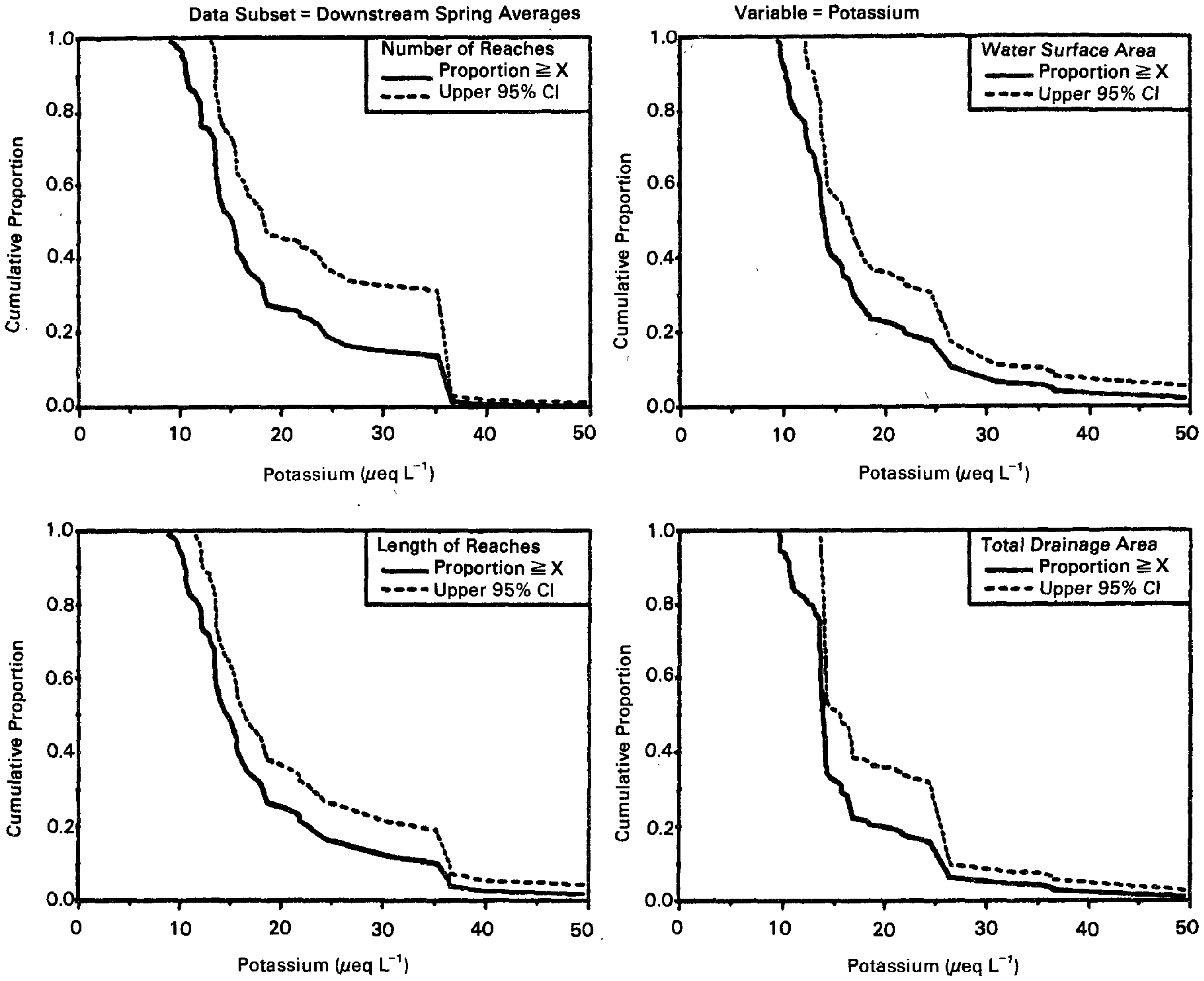


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu g\ L^{-1}$) | 9.26 | 8.43 | 8.44 | 8.44 |
| 40 %ILE ($\mu g\ L^{-1}$) | 10.64 | 10.25 | 10.64 | 10.55 |
| Median ($\mu g\ L^{-1}$) | 11.66 | 11.14 | 11.72 | 11.83 |
| 60 %ILE ($\mu g\ L^{-1}$) | 15.89 | 13.16 | 15.60 | 13.38 |
| 80 %ILE ($\mu g\ L^{-1}$) | 31.52 | 28.55 | 28.48 | 29.37 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 52 | 84 |

| Sample Weighted Statistics ($\mu g\ L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 5.67 | 503.33 | 41.10 | 103.07 |

**Figure A.20. Population distribution estimate for potassium, based on spring downstream averages.**

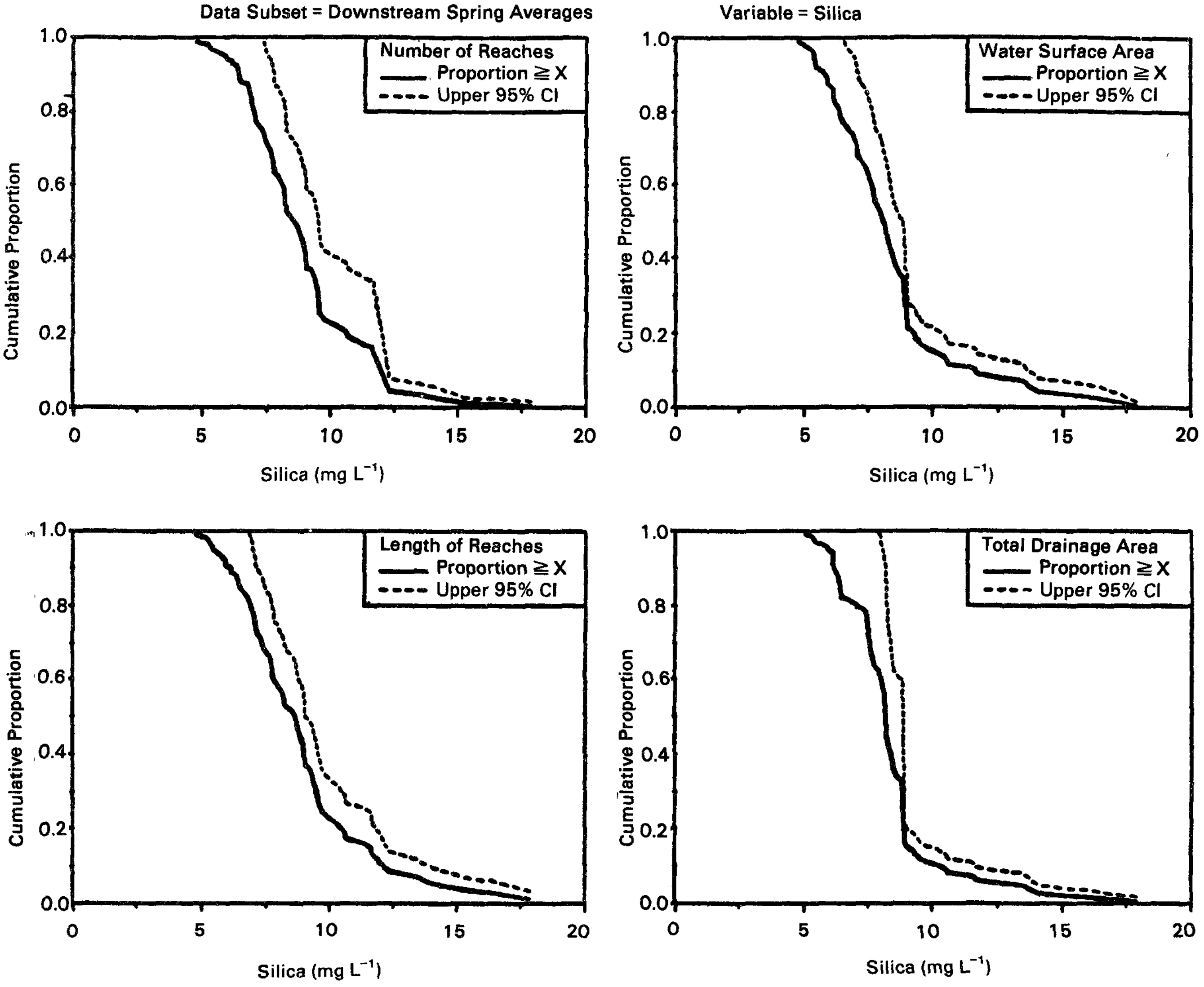


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu$eq L$^{-1}$) | 11.70 | 10.74 | 11.34 | 12.20 |
| 40 %ILE ($\mu$eq L$^{-1}$) | 13.54 | 13.43 | 13.51 | 13.52 |
| Median ($\mu$eq L$^{-1}$) | 14.74 | 13.83 | 14.44 | 13.83 |
| 60 %ILE ($\mu$eq L$^{-1}$) | 15.73 | 14.55 | 15.62 | 13.85 |
| 80 %ILE ($\mu$eq L$^{-1}$) | 23.20 | 21.61 | 21.94 | 18.52 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics ($\mu$eq L$^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 8.41 | 52.84 | 18.08 | 8.44 |

Figure A.21. **Population distribution estimate for silica, based on spring downstream averages.**

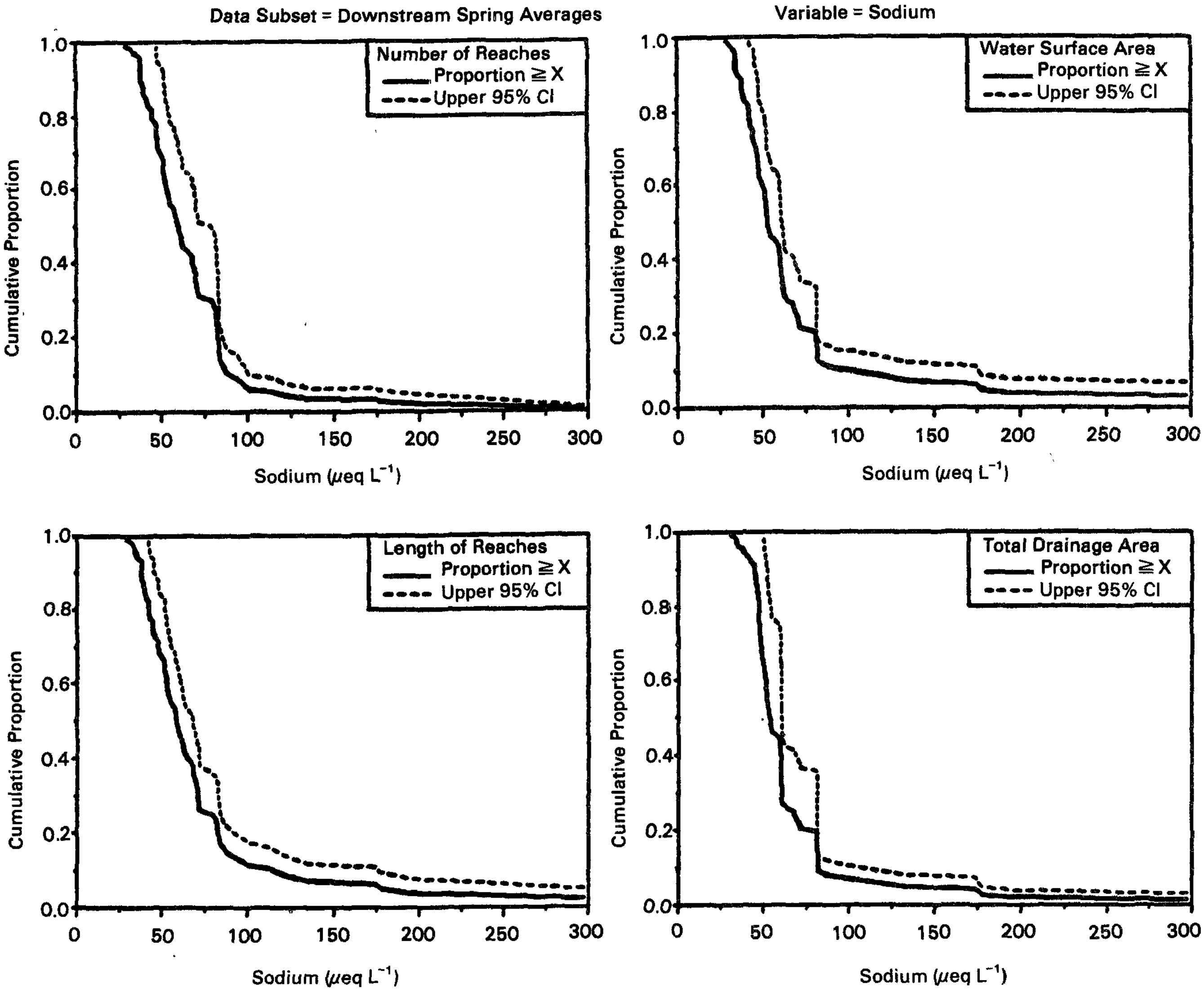


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (mg $L^{-1}$) | 6.85 | 6.20 | 6.78 | 6.96 |
| 40 %ILE (mg $L^{-1}$) | 7.93 | 7.46 | 7.77 | 7.91 |
| Median (mg $L^{-1}$) | 8.26 | 7.94 | 8.53 | 8.08 |
| 60 %ILE (mg $L^{-1}$) | 8.94 | 8.24 | 8.94 | 8.22 |
| 80 %ILE (mg $L^{-1}$) | 10.49 | 9.13 | 10.29 | 8.82 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics (mg $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 4.53 | 17.90 | 8.74 | 2.17 |

**Figure A.22.** Population distribution estimate for sodium, based on spring downstream averages.

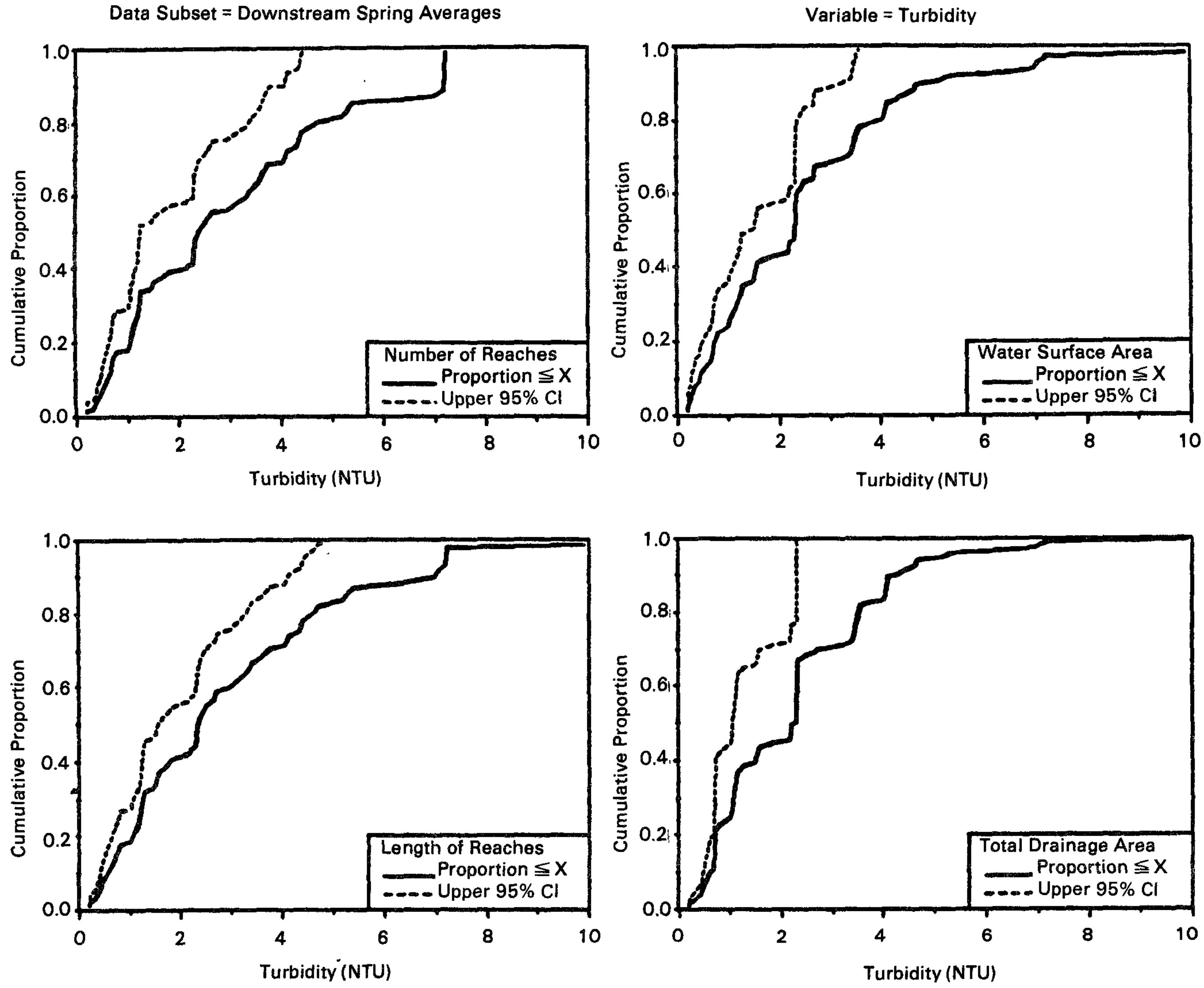


| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE ($\mu$eq $L^{-1}$) | 44.28 | 41.30 | 41.67 | 47.18 |
| 40 %ILE ($\mu$eq $L^{-1}$) | 52.86 | 47.75 | 52.39 | 47.84 |
| Median ($\mu$eq $L^{-1}$) | 58.99 | 52.73 | 57.38 | 52.92 |
| 60 %ILE ($\mu$eq $L^{-1}$) | 67.62 | 59.17 | 62.75 | 58.97 |
| 80 %ILE ($\mu$eq $L^{-1}$) | 81.51 | 76.67 | 81.53 | 71.57 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics ($\mu$eq $L^{-1}$) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 27.86 | 726.45 | 67.43 | 44.66 |

**Figure A.23. Population distribution estimate for turbidity, based on spring downstream averages.**



| | Population Estimates | | | |
|---|---|---|---|---|
| | Number of Reaches | Water Surface Area (Hectares) | Reach Length (km) | Total Watershed Area (sq km) |
| Totals | 2021 | 4633 | 8963 | 51215 |
| 20 %ILE (NTU) | 1.06 | 0.74 | 1.06 | 0.72 |
| 40 %ILE (NTU) | 2.17 | 1.55 | 1.79 | 1.51 |
| Median (NTU) | 2.40 | 2.30 | 2.34 | 2.27 |
| 60 %ILE (NTU) | 3.37 | 2.33 | 2.97 | 2.30 |
| 80 %ILE (NTU) | 4.82 | 4.02 | 4.59 | 3.54 |

| Sample Sizes | | |
|---|---|---|
| Actual | Unique | Effective |
| 54 | 54 | 84 |

| Sample Weighted Statistics (NTU) | | | |
|---|---|---|---|
| Min | Max | Mean | SD |
| 0.20 | 16.82 | 3.21 | 2.64 |

# Appendix B
# Geographic Data for Stage II Sites

**Table B.1. Geographic Data for Phase I—Pilot Survey Second Stage sampling sites.**

| Reach ID# | Stream Name | County of Location | Grid Site | | 7-1/2 Minute Map Stream Location | Number of Reaches | Drainage Area (Mi.$^2$) | Crew ID Code |
|---|---|---|---|---|---|---|---|---|
| | | | Latitude | Longitude | | | | |
| Chattanooga | | | | | | | | |
| 2A00701 | Sugar Cove Branch | Monroe/FC | 35°19′56″ | 84°03′46″ | Big Junction (TN-NC) | 1 | 7-1/2 | W1R |
| 2A07702 | Childers Creek | Polk | 35°12′30″ | 84°28′30″ | McFarland (TN) | 1 | 6 | M1G |
| 2A07703 | Hall Creek | Polk | 35°05′56″ | 84°19′47″ | Isabella (TN-NC) | 1 | 3-1/2 | T2G |
| Knoxville | | | | | | | | |
| 2A07801 | Big Fork | Cocke | 35°54′43″ | 83°06′03″ | Neddy Mtn. (TN) | 15 | 33 | S2G |
| 2A07802 | Puncheon Fork | Madison | 35°55′35″ | 82°32′19″ | Sams Gap (NC-TN) | 1 | 7 | TH2G |
| 2A07803 | Unnamed Trib. of Ellejoy Crk. | Blount | 35°46′40″ | 83°47′47″ | Wildwood (TN) | 1 | 2 | TH2G |
| 2A07805 | Cosby Creek | Cocke | 35°47′37″ | 83°14′09″ | Hartford (TN-NC) | 1 | 5 | S2G |
| 2A07806 | Roaring Fork | Madison | 35°48′11″ | 82°57′24″ | Lemon Gap (NC-TN) | 1 | 5 | S1G |
| 2A07807 | North Fork | Buncombe | 35°48′57″ | 82°23′39″ | Barnardsville (NC)<br>Mt. Mitchell (NC) | 1 | 14 | T1G |
| 2A07808 | Armstrong Creek | McDowell | 35°49′20″ | 82°06′57″ | Little Switzerland (NC)<br>Celo (NC) | 1 | 22 | W1B |
| 2A07810 | Little River Gorge | Sevier/P | 35°40′04″ | 83°38′52″ | Wear Cove (TN)<br>Gatlinburg (TN) | 5 | 50 | W2G |
| 2A07811 | False Gap Prong | Sevier/P | 35°40′35″ | 83°22′11″ | Mt. Le Conte (TN-NC)<br>Mt. Guyot, (TN-NC) | 1 | 5 | TH2R |
| 2A07812 | Correll Branch | Haywood/P | 35°41′01″ | 83°05′28″ | Cove Creek Gap (NC) | 1 | 3 | M2G |
| 2A07813 | Little Sandy Mush Creek | Madison | 35°41′24″ | 82°48′42″ | Sandymush (NC) | 1 | 17 | S1G |
| 2A07814 | Reems Creek | Buncombe | 35°41′50″ | 82°31′54″ | Weaverville (NC) | 3 | 32 | T1G |
| 2A07815 | Curtis Creek | McDowell | 35°42′18″ | 82°15′09″ | Marion (15′ map) (NC) | 1 | 17 | W1B |
| 2A07816 | Eagle Creek (Gunna Creek) | Swain/P | 35°32′57″ | 83°46′59″ | Fontana Dam (NC)<br>Thunderhead Mt. (NC-TN) | 1 | 11 | M2B |
| 2A07817 | Forney Creek | Swain/P | 35°33′28″ | 83°13′11″ | Silers Bald (NC-TN) | 1 | 7 | W1G |
| 2A07818 | Bunches Creek | Swain/I | 35°33′52″ | 83°30′31″ | Bunches Bald (NC) | 5 | 15-1/2 | M2G |
| 2A07819 | Crooked Creek | McDowell | 35°35′39″ | 82°06′33″ | Marion (15′ map) (NC)<br>Black Mountain (NC) | 1 | 33 | W1B |
| 2A07820 | Pigeon River | Haywood | 35°27′48″ | 82°48′06″ | Cruso (NC) (15′ map) | 7 | 44 | S1B |
| 2A07821 | Grassy Creek | Henderson | 35°28′36″ | 82°14′44″ | Bat Cave (NC)<br>Lake Cure (15′ map) | 1 | 2-1/2 | TH1B |
| 2A07881 | Walnut Creek | Madison | 35°48′41″ | 82°40′28″ | Marshall (NC) | 5 | 37 | TH2G |
| 2A07882 | Little Branch Cr. | Haywood | 35°27′16″ | 83°04′47″ | Hazelwood (NC) | 1 | 4 | T2R |
| 2A07822 | Sweetwater Creek | Graham | 35°19′15″ | 83°46′07″ | Robinsville (NC) | 3 | 13 | TH2B |
| 2A07823 | Brush Creek | Swain | 35°19′46″ | 83°29′31″ | Alarka (NC)<br>Wesser (NC) | 1 | 6-1/2 | TH2B |
| 2A07824 | Middle Prong | Haywood/FP | 35°20′41″ | 82°56′05″ | Sam Knob (NC) | 1 | 8 | T2B |
| 2A07825 | S. Fork Mills R. | Tran./FP | 35°21′07″ | 82°39′21″ | Pisgah Forest (NC)<br>Shining Rock (NC) | 1 | 18 | S1B |
| 2A07826 | Henderson Creek | Henderson | 35°21′33″ | 82°22′36″ | Hendersonville (NC)<br>Cliffield Mtn. (NC)<br>Horse Shoe (NC) | 1 | 3-1/2 | TH1B |
| 2A07827 | Welch Mill Creek | Cherokee | 35°12′00″ | 83°54′09″ | Marble (NC) | 1 | 3 | W1R |
| 2A07828 | Whiteoak Creek | Macon/FN | 35°12′35″ | 83°22′36″ | Wayah Bald (NC) | 1 | 7-1/2 | S1R |
| 2A07829 | Catheys Creek | Tran. | 35°13′57″ | 82°47′23″ | Shining Rock (NC)<br>Rosman (NC) | 1 | 7-1/2 | S2B |

**Table B.1. (continued)**

| Reach ID# | Stream Name | County of Location | Grid Site Latitude | Grid Site Longitude | 7-1/2 Minute Map Stream Location | Number of Reaches | Drainage Area (Mi.$^2$) | Crew ID Code |
|---|---|---|---|---|---|---|---|---|
| Knoxville (continued) | | | | | | | | |
| 2A07830 | Mud Creek | Henderson | 35°14′32″ | 82°30′48″ | Hendersonville (NC)<br>Standingstone Mtn. (NC)<br>Horse Shoe (NC) | 1 | 6 | T1B |
| 2A07831 | N. Pacolet River | Polk | 35°14′54″ | 82°14′00″ | Inman (SC-NC) (15′ map)<br>Tigersville (SC-NC) (15′ map) | 1 | 25 | T1B |
| 2A07832 | Tusquitee Cr. | Clay | 35°05′37″ | 82°45′23″ | Hayesville (NC)<br>Shooting Creek (NC) | 1 | 40 | W2R |
| 2A07833 | Allison Creek | Macon | 35°06′08″ | 83°28′42″ | Prentiss (NC)<br>Rainbow Springs (NC) | 11 | 6 | W2R |
| 2A07834 | Brush Creek | Macon | 35°06′35″ | 83°12′13″ | Scaly Mountain (NC)<br>Highlands (NC-GA) | 1 | 4 | T1R |
| 2A07835 | Middle River | Greenville | 35°07′30″ | 82°39′00″ | Cleveland (SC)<br>Table Rock (SC-NC) | 1 | 11 | S2B |
| 2A07881 | Walnut Creek | Madison | 35°48′27″ | 83°43′36″ | Marshall (NC) | 5 | 37 | TH2G |
| 2A07882 | Little Branch Cr. | Haywood | 35°03′39″ | 83°27′04″ | Hazelwood (NC) | 1 | 4 | T2R |
| 2A07891* | Cosby Creek | Cocke/P | 35°44′50″ | 83°12′00″ | Hartford (TN-NC)<br>Luftee Knob (NC-TN) | 1 | 3-1/2 | TH2R |
| 2A07892* | Twentymile Creek | Swain/P | 35°28′00″ | 83°52′25″ | Fontana Dam (NC)<br>Cades Cove (TN-NC) | 1 | 7 | M2B |
| 2A07893* | Jarrett Creek | Macon/FN | 35°08′50″ | 83°37′00″ | Wayah Bald (NC)<br>Topton (NC) | 1 | 6 | S1R |
| 2A07894* | Slope Fork | Macon | 35°03′48″ | 83°26′11″ | Prentiss (NC) | — | — | S2R |
| 2A07895* | Moses Creek | Jackson | 35°19′30″ | 83°06′15″ | Tuckasegee (NC)<br>Sam Knob (NC) | 1 | 11 | T2B |
| 2A07896* | Pinnacle Branch | Macon | 35°03′27″ | 83°28′03″ | Prentiss (NC) | ? | ? | S2R |
| Rome | | | | | | | | |
| 2A08801 | Unnamed Trib. to Perry Creek | Murray | 34°57′15″ | 84°43′33″ | Tennga (GA-TN) | 1 | 1-3/4 | M1G |
| 2A08802 | Dunn Mill Creek | Fannin | 34°57′48″ | 84°26′57″ | Epworth (GA-TN) | 1 | 2 | T2G |
| 2A08803 | Owenby Creek | Fannin | 34°58′07″ | 84°10′21″ | Culberson (GA-NC) | 3 | 4 | TH1G |
| 2A08804 | Bear Creek | Gilmer/Fch | 35°50′45″ | 84°35′04″ | Dyer Gap (GA) | 1 | 1 | M2R |
| 2A08805 | Weaver Creek | Fannin | 34°51′07″ | 84°18′33″ | Blue Ridge (GA) | 1 | 3 | TH1G |
| 2A08806 | Unnamed Trib. to Kiutuestia Creek | Union | 34°51′33″ | 84°01′55″ | Mulkey Gap (GA) | 1 | 3/4 | TH1R |
| 2A08808 | Whitpath Creek | Gilmer | 34°44′04″ | 84°26′22″ | Ellijay (GA) | 1 | 3 | TH1G |
| 2A08809 | Tickanetley Creek | Gilmer | 34°37′27″ | 84°17′45″ | Tickanetley (GA) | 13 | 18 | M1B |
| 2A08810 | Bryant Creek | Lumpkin/Fch | 34°37′48″ | 84°01′15″ | Suches, Dahlonega Campbell Mtn. (GA) | 1 | 2 | W2B |
| 2A08811 | Hinton Creek | Pickens | 34°30′26″ | 84°25′41″ | Jasper (GA)<br>Dyke (GA) | 1 | 1/4 | M1B |
| 2A08891* | Chester Creek | Fannin/Fch | 34°39′30″ | 84°10′40″ | Noontootla (GA) | 1 | 2 | W2B |
| Greenville | | | | | | | | |
| 2A08901 | Persimmon Cr. | Rabun | 34°56′56″ | 83°29′08″ | Hightower Bald (GA-NC)<br>Dillard (GA-NC) | 1 | 6-1/2 | S2R |
| 2A08902 | West Fork | Rabun | 34°57′25″ | 83°12′46″ | Satulah (GA-SC-NC) | 12 | 45 | T1R |
| 2A08903 | Nottely River | Union | 34°49′07″ | 83°53′46″ | Coosa Bald (GA) | 27 | 58 | TH1R |
| 2A08904 | She Creek | Rabun | 34°50′19″ | 83°20′37″ | Rainy Mountain (GA-SC) | 1 | 6 | M1R |
| 2A08905 | Chattahoochee River | White | 34°42′35″ | 83°44′59″ | Cowrock (GA)<br>Helen (GA) | 5 | 32 | T2R |
| 2A08906 | Deep Creek | Hebersham | 34°43′16″ | 83°28′27″ | Tallulah Falls (GA) | 1 | 4-1/2 | M1R |

*Special interest points.

# *Appendix C*
# *Geographic Data*

SAS

| STREAM ID | WEIGHT (1/A1) | SHREVE ORDER | AREA (SQ KM) | ELEVATION (M) | GRADIENT (%) | LENGTH (KM) | WIDTH (M) | DEPTH (M) |
|---|---|---|---|---|---|---|---|---|
| 2A07701L | 0.120627 | 1 | 21.47 | 610 | 5.76 | 7.36 | 10.6 | 0.42 |
| 2A07701U | 0.120627 | - | 0.28 | 1036 | - | - | 1.8 | 0.05 |
| 2A07702L | 0.236967 | 1 | 10.93 | 232 | 1.04 | 9.33 | 2.8 | 0.28 |
| 2A07702U | 0.236967 | - | 0.08 | 329 | - | - | 0.8 | 0.03 |
| 2A07703L | 0.255102 | 1 | 10.15 | 488 | 0.43 | 5.58 | 2.9 | 0.21 |
| 2A07703U | 0.255102 | - | 1.42 | 512 | - | - | 1.5 | 0.13 |
| 2A07801L | 0.423729 | 8 | 91.14 | 415 | 0.54 | 2.24 | 13.0 | 0.27 |
| 2A07801U | 0.423729 | - | 85.03 | 427 | - | - | 40.0 | 0.46 |
| 2A07802L | 0.136426 | 1 | 18.93 | 914 | 2.50 | 7.28 | 6.3 | 0.15 |
| 2A07802U | 0.136426 | - | 1.01 | 1097 | - | - | 1.2 | 0.09 |
| 2A07803L | 0.505051 | 1 | 5.13 | 280 | 0.92 | 2.64 | 2.0 | 0.13 |
| 2A07803U | 0.505051 | - | 0.39 | 305 | - | - | 0.3 | 0.09 |
| 2A07805L | 0.729927 | 3 | 29.91 | 436 | 1.92 | 3.31 | 4.5 | 0.40 |
| 2A07805U | 0.729927 | - | 26.37 | 500 | - | - | 5.0 | 0.15 |
| 2A07806L | 0.178571 | 1 | 14.50 | 671 | 6.22 | 5.17 | 5.1 | 0.21 |
| 2A07806U | 0.178571 | - | 2.43 | 994 | - | - | 3.7 | 0.08 |
| 2A07807L | 0.066313 | 1 | 39.06 | 671 | 3.53 | 9.95 | 5.8 | 0.22 |
| 2A07807U | 0.066313 | - | 1.50 | 1024 | - | - | 3.1 | 0.15 |
| 2A07808L | 0.038212 | 1 | 67.78 | 445 | 1.53 | 15.06 | 10.1 | 0.34 |
| 2A07808U | 0.038212 | - | 0.23 | 677 | - | - | 1.2 | 0.15 |
| 2A07810L | 0.036563 | 3 | 138.88 | 433 | 1.74 | 21.65 | 12.0 | 0.85 |
| 2A07810U | 0.036563 | - | 68.04 | 811 | - | - | 25.0 | 0.30 |
| 2A07811L | 0.208768 | 1 | 12.41 | 549 | 6.91 | 4.03 | 6.7 | 0.30 |
| 2A07811U | 0.208768 | - | 2.23 | 829 | - | - | 4.6 | 0.52 |
| 2A07812L | 0.341297 | 1 | 7.59 | 884 | 7.42 | 4.74 | 2.7 | 0.16 |
| 2A07812U | 0.341297 | - | 0.26 | 1237 | - | - | 0.6 | 0.05 |
| 2A07813L | 0.104275 | 1 | 24.84 | 622 | 2.72 | 8.46 | 4.0 | 0.61 |
| 2A07813U | 0.104275 | - | 0.26 | 853 | - | - | 1.2 | 0.09 |
| 2A07814L | 0.072516 | 2 | 81.30 | 597 | 0.65 | 9.84 | 10.3 | 0.27 |
| 2A07814U | 0.072516 | - | 45.58 | 661 | - | - | 6.1 | 0.24 |
| 2A07815L | 0.059952 | 1 | 43.20 | 427 | 2.28 | 11.18 | 7.6 | 0.24 |
| 2A07815U | 0.059952 | - | 4.51 | 683 | - | - | 4.6 | 0.61 |
| 2A07816L | 0.084602 | 1 | 30.61 | 579 | 6.00 | 10.82 | 11.0 | 0.25 |
| 2A07816U | 0.084602 | - | 1.04 | 1231 | - | - | 3.0 | 0.30 |
| 2A07817L | 0.096618 | 1 | 26.81 | 732 | 8.89 | 6.27 | 9.1 | 0.61 |
| 2A07817U | 0.096618 | - | 3.13 | 1292 | - | - | 9.1 | 0.09 |
| 2A07818L | 0.990099 | 3 | 44.65 | 732 | 2.28 | 2.13 | 8.8 | 0.23 |
| 2A07818U | 0.990099 | - | 42.04 | 780 | - | - | 3.0 | 0.46 |
| 2A07819L | 0.027739 | 1 | 93.37 | 427 | 0.64 | 22.88 | 9.8 | 0.30 |
| 2A07819U | 0.027739 | - | 0.28 | 573 | - | - | 1.2 | 0.21 |
| 2A07820L | 0.081566 | 4 | 115.67 | 829 | 0.79 | 7.68 | 15.2 | 0.61 |
| 2A07820U | 0.081566 | - | 83.92 | 890 | - | - | 8.5 | 0.24 |
| 2A07821L | 0.393701 | 1 | 6.58 | 552 | 12.61 | 2.46 | 3.0 | 0.20 |
| 2A07821U | 0.393701 | - | 3.83 | 864 | - | - | 0.9 | 0.15 |
| 2A07822L | 0.151976 | 2 | 36.36 | 610 | 0.74 | 6.78 | 6.7 | 0.17 |
| 2A07822U | 0.151976 | - | 19.32 | 660 | - | - | 4.6 | 0.15 |
| 2A07823L | 0.132275 | 1 | 19.58 | 549 | 4.88 | 6.21 | 5.2 | 0.12 |
| 2A07823U | 0.132275 | - | 0.91 | 853 | - | - | 0.9 | 0.15 |
| 2A07824L | 0.080775 | 1 | 32.06 | 951 | 5.58 | 6.35 | 14.3 | 0.19 |
| 2A07824U | 0.080775 | - | 2.93 | 1308 | - | - | 6.1 | 0.46 |
| 2A07825L | 0.043995 | 1 | 58.87 | 732 | 0.86 | 31.97 | 14.6 | 0.25 |
| 2A07825U | 0.043995 | - | 0.23 | 1009 | - | - | 3.0 | 0.18 |
| 2A07826L | 0.245098 | 1 | 10.57 | 646 | 0.32 | 4.77 | 4.0 | 0.15 |
| 2A07826U | 0.245098 | - | 0.80 | 661 | - | - | 0.9 | 0.08 |
| 2A07827L | 0.252525 | 1 | 10.26 | 503 | 1.28 | 6.53 | 6.5 | 0.10 |

| STREAM ID | WEIGHT (1/A1) | SHREVE ORDER | AREA (SQ KM) | SAS ELEVATION (M) | GRADIENT (%) | LENGTH (KM) | WIDTH (M) | DEPTH (M) |
|---|---|---|---|---|---|---|---|---|
| 2A07827U | 0.252525 | - | 0.44 | 587 | - | - | 3.7 | 0.15 |
| 2A07828L | 0.135870 | 1 | 19.06 | 960 | 4.53 | 7.42 | 6.7 | 0.28 |
| 2A07828U | 0.135870 | - | 1.89 | 1298 | - | - | 3.7 | 0.09 |
| 2A07829L | 0.118203 | 1 | 21.91 | 689 | 3.10 | 5.28 | 6.7 | 0.18 |
| 2A07829U | 0.118203 | - | 5.21 | 853 | - | - | 6.7 | 0.18 |
| 2A07830L | 0.184843 | 1 | 14.01 | 652 | 1.22 | 6.43 | 2.9 | 0.20 |
| 2A07830U | 0.184843 | - | 0.41 | 732 | - | - | 1.5 | 0.05 |
| 2A07831L | 0.035842 | 1 | 72.26 | 268 | 1.66 | 16.77 | 12.8 | 0.43 |
| 2A07831U | 0.035842 | - | 2.56 | 549 | - | - | 3.7 | 0.18 |
| 2A07832L | 0.056625 | 6 | 110.41 | 543 | 0.66 | 9.63 | 12.6 | 0.37 |
| 2A07832U | 0.056625 | - | 64.67 | 607 | - | - | 15.2 | 0.23 |
| 2A07833L | 0.167785 | 1 | 15.44 | 683 | 5.42 | 6.37 | 4.2 | 0.17 |
| 2A07833U | 0.167785 | - | 0.28 | 1030 | - | - | 0.5 | 0.05 |
| 2A07834L | 0.222222 | 1 | 11.65 | 838 | 5.86 | 6.26 | 0.8 | 0.12 |
| 2A07834U | 0.222222 | - | 1.58 | 1207 | - | - | 3.0 | 0.09 |
| 2A07835L | 0.093721 | 1 | 27.64 | 329 | 3.59 | 8.10 | 9.8 | 0.26 |
| 2A07835U | 0.093721 | - | 5.13 | 622 | - | - | 1.8 | 0.30 |
| 2A07881L | 0.074963 | 3 | 43.87 | 500 | 0.85 | 14.24 | 8.0 | 0.20 |
| 2A07881U | 0.074963 | - | 9.32 | 622 | - | - | 4.6 | 0.15 |
| 2A07882L | 0.450450 | 1 | 5.75 | 936 | 6.12 | 3.71 | 3.3 | 0.19 |
| 2A07882U | 0.450450 | - | 0.93 | 1164 | - | - | 1.8 | 0.15 |
| 2A07891L | - | 3 | 29.91 | 756 | - | 3.76 | 9.1 | 0.21 |
| 2A07892L | - | 1 | 20.95 | 439 | - | 5.30 | 6.7 | 0.52 |
| 2A07893L | - | 1 | 14.19 | 939 | - | 6.90 | 4.6 | 0.23 |
| 2A07894L | - | 1 | 9.38 | 695 | - | 3.44 | 4.6 | 0.15 |
| 2A07895L | - | 1 | 23.44 | 707 | 2.47 | 9.58 | 3.8 | 0.27 |
| 2A07895U | - | - | 0.23 | 945 | - | - | 4.6 | 0.21 |
| 2A07896L | - | 1 | 1.11 | 951 | - | 1.01 | 1.2 | 0.08 |
| 2A08801L | 0.591716 | 1 | 4.38 | 244 | 2.87 | 3.17 | 2.2 | 0.12 |
| 2A08801U | 0.591716 | - | 0.21 | 335 | - | - | 0.6 | 0.05 |
| 2A08802L | 0.456621 | 1 | 5.67 | 506 | 0.80 | 4.54 | 3.7 | 0.13 |
| 2A08802U | 0.456621 | - | 0.00 | 543 | - | - | 0.3 | 0.05 |
| 2A08803L | 0.393701 | 2 | 17.87 | 488 | 0.48 | 5.09 | 4.3 | 0.16 |
| 2A08803U | 0.393701 | - | 11.29 | 512 | - | - | 2.0 | 0.09 |
| 2A08804L | 1.010101 | 1 | 2.56 | 567 | 5.44 | 3.34 | 4.0 | 0.05 |
| 2A08804U | 1.010101 | - | 0.05 | 750 | - | - | 3.0 | 0.09 |
| 2A08805L | 0.302115 | 1 | 8.57 | 488 | 0.92 | 7.22 | 2.5 | 0.23 |
| 2A08805U | 0.302115 | - | 0.28 | 555 | - | - | 0.6 | 0.09 |
| 2A08806L | 1.666667 | 1 | 1.55 | 561 | 1.23 | 1.97 | 1.3 | 0.07 |
| 2A08806U | 1.666667 | - | 0.03 | 585 | - | - | 0.6 | 0.08 |
| 2A08808L | 0.311526 | 1 | 8.31 | 408 | 2.38 | 4.83 | 3.4 | 0.19 |
| 2A08808U | 0.311526 | - | 0.80 | 524 | - | - | 1.0 | 0.08 |
| 2A08809L | 0.510204 | 7 | 48.23 | 512 | 0.62 | 3.41 | 9.1 | 0.51 |
| 2A08809U | 0.510204 | - | 43.15 | 533 | - | - | 8.2 | 0.36 |
| 2A08810L | 0.531915 | 1 | 4.87 | 448 | 1.82 | 4.32 | 10.7 | 0.18 |
| 2A08810U | 0.531915 | - | 0.03 | 527 | - | - | 4.6 | 0.01 |
| 2A08811L | 0.775194 | 1 | 3.34 | 375 | 1.51 | 2.21 | 2.4 | 0.13 |
| 2A08811U | 0.775194 | - | 0.83 | 408 | - | - | 0.9 | 0.08 |
| 2A08891L | - | 1 | 7.33 | 774 | 3.81 | 3.02 | 7.6 | 0.22 |
| 2A08891U | - | - | 0.23 | 890 | - | - | 1.2 | 0.09 |
| 2A08901L | 0.133511 | 1 | 19.40 | 596 | 3.70 | 8.22 | 7.0 | 0.24 |
| 2A08901U | 0.133511 | - | 0.18 | 902 | - | - | 0.9 | 0.09 |
| 2A08902L | 0.124844 | 12 | 133.39 | 485 | 0.62 | 5.82 | 19.6 | 0.52 |
| 2A08902U | 0.124844 | - | 112.64 | 521 | - | - | 9.1 | 0.30 |
| 2A08903L | 0.440529 | 27 | 148.74 | 561 | 0.18 | 3.42 | 20.8 | 0.27 |

SAS

| STREAM ID | WEIGHT (1/A1) | SHREVE ORDER | AREA (SQ KM) | ELEVATION (M) | GRADIENT (%) | LENGTH (KM) | WIDTH (M) | DEPTH (M) |
|---|---|---|---|---|---|---|---|---|
| 2A08903U | 0.440529 | - | 142.86 | 567 | - | - | 15.2 | 0.76 |
| 2A08904L | 0.199203 | 1 | 13.00 | 442 | 1.22 | 5.60 | 5.3 | 0.01 |
| 2A08904U | 0.199203 | - | 0.31 | 511 | - | - | 0.9 | 0.02 |
| 2A08905L | 0.507614 | 5 | 83.81 | 436 | 0.87 | 2.45 | 12.6 | 0.44 |
| 2A08905U | 0.507614 | - | 78.71 | 457 | - | - | 12.2 | 0.21 |
| 2A08906L | 0.196850 | 1 | 13.16 | 430 | 0.48 | 8.22 | 9.3 | 0.02 |
| 2A08906U | 0.196850 | - | 1.32 | 469 | - | - | 2.9 | 0.15 |

## *Appendix D*
## *Chemical Data*

### Glossary for Chemical Data

The variable SAMPLE identifies the sampling time intervals. Codes 0, 1, 2, 3, and 4 refer, respectively, to sampling intervals SPO, SP1, SP2, SP3, and SP4 in Table 3-1 of this report. Streams corresponding to the stream identification numbers (STRM-ID) are listed in Appendix B. Other variables are identified below. For calculating spring index values, observations marked with "E" after SAMPLE number should be replaced by the average of the remaining two observations in SAMPLEs 1 through 3. SAMPLEs numbered 0 are not included in the calculation of index values.

The variable "WGT" is equal to $1/a_1$. Whenever making explicit population estimates and their variances, WGT must be multiplied by the Stage II grid point density (128 $mi^2$/data point) to obtain values of "w" used in Equations 2.1 and 2.6.

| Variable Name | Chemical Definition | Units |
|---|---|---|
| NA16 | Sodium | $\mu eq\ L^{-1}$ |
| K16 | Potassium | $\mu eq\ L^{-1}$ |
| CA16 | Calcium | $\mu eq\ L^{-1}$ |
| MG16 | Magnesium | $\mu eq\ L^{-1}$ |
| FE11 | Iron | $\mu eq\ L^{-1}$ |
| MN11 | Manganese | $\mu eq\ L^{-1}$ |
| H16 | Hydrogen ion activity | $\mu eq\ L^{-1}$ |
| ALKA11 | Alkalinity | $\mu eq\ L^{-1}$ |
| SO416 | Sulfate ion | $\mu eq\ L^{-1}$ |
| NO316 | Nitrate ion | $\mu eq\ L^{-1}$ |
| CL16 | Chloride ion | $\mu eq\ L^{-1}$ |
| FTL16 | Fluoride ion, Total | $\mu eq\ L^{-1}$ |
| SI0211 | Silica | $mg\ L^{-1}$ |
| COND11 | Conductivity | $\mu S\ cm^{-1}$ |
| ALTL11 | Aluminum, total | $\mu g\ L^{-1}$ |
| ALEX11 | Aluminum, extractable | $\mu g\ L^{-1}$ |
| ALOR11 | Aluminum, organic | $\mu g\ L^{-1}$ |
| DOC11 | Dissolved organic carbon | $mg\ L^{-1}$ |
| COLVAL | Color value | alpha units |
| TURVAL | Turbidity value | NTU |
| ORGION | Organic ion | $\mu eq\ L^{-1}$ |
| PTL11 | Total phosphorous | $\mu g\ L^{-1}$ |
| NH416 | Ammonium ion | $\mu eq\ L^{-1}$ |
| CONIS | Conductivity, *in situ* | $\mu S\ cm^{-1}$ |
| TMPSTR | Stream temperature | degrees C |
| PH-CLO | pH, routine closed | pH units |
| PH-OPN | pH, routine open | pH units |
| PHSTVL | pH, station value | pH units |
| DICVAL | Dissolved inorganic carbon | $mg\ L^{-1}$ |
| ALKA11 | Alkalinity | $\mu eq\ L^{-1}$ |
| PHEQ11 | pH, air equilibrated | pH units |
| PHAC11 | pH, initial acidity | pH units |
| PHAL11 | pH, initial alkalinity | pH units |
| DICE11 | Dissolved inorganic carbon (equil.) | $mg\ L^{-1}$ |

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                                                      SAS

STRM_ID           WGT      SAMPLE       NA16       K16       CA16      MG16       FE11      MN11       H16

2A07701L     0.120627      1            38.3      12.1       81.3      26.9        5.0       1.5      0.08
                           2            38.1      12.8       71.4      30.6        0.2       0.0      0.13
                           3            38.6      13.8       91.3      30.1        5.0       0.0      0.13
                           4            39.5      13.8      107.8      33.0       12.0       2.0      0.11

2A07701U     0.120627      3            31.0      11.9       45.7      17.8        0.7       0.0      0.37
                           4            32.9      10.3       43.3      18.2        1.0       0.0      0.35

2A07702L     0.236967      0            71.5      11.7     1177.6     121.6        7.5       0.6      0.00
                           1            72.0      13.0     1122.8     121.3        9.0       0.5      0.00
                           2E           73.9      14.5      983.0     118.5       33.0       1.0      0.02
                           3            69.6      13.8     1157.7     127.5       11.0       1.0      0.01
                           4            65.3      15.0     1447.1     127.5        7.0       2.0      0.01

2A07702U     0.236967      4            80.5      13.8      266.5     172.7        8.0      31.0      0.07

2A07703L     0.255102      1            65.7      22.6       89.9      49.4       30.0      22.0      0.09
                           2            61.1      22.2       87.6      51.4       56.0      25.0      0.14
                           3            66.6      22.7       82.8      48.1       17.0      19.0      0.14
                           4            63.1      23.0       97.3      51.3       34.0      27.0      0.13

2A07703U     0.255102      3            68.3      24.6       46.4      37.2       49.0       2.0      0.12
                           4            65.7      22.9       50.9      38.7       43.0       5.0      0.21

2A07801L     0.423729      1            80.3      23.6      349.3     100.4       10.0       1.3      0.02
                           2            83.5      24.2      291.9      92.1       18.0       2.0      0.03
                           3            80.0      25.6      302.4      88.3       24.0       1.0      0.03
                           4            99.8      31.5      683.6     160.0       24.0       4.0      0.00

2A07801U     0.423729      3            77.4      24.4      300.4      83.1       20.0       1.0      0.04
                           4           104.4      30.7      543.9     137.4       34.0       6.0      0.01

2A07802L     0.136426      1           122.9      22.0      147.2      71.0       41.0       8.5      0.07
                           2           120.1      20.9      125.2      71.4      594.0      12.0      0.17
                           3           123.5      22.4      131.2      71.9       13.0       7.0      0.10
                           4           125.3      24.5      135.2      70.2       59.0       6.0      0.07

2A07802U     0.136426      4           124.0      23.4      145.2      69.8       55.0      13.0      0.07

2A07803L     0.505051      1            96.6      22.3     1781.4     259.9       39.5      22.0      0.01
                           2            83.5      20.8     1297.4     223.7       25.0      27.0      0.01
                           3           100.0      27.4     1686.6     275.6       14.0      30.0      0.02
                           4           136.6      51.4     2410.2     367.7       17.0      74.0      0.01

2A07803U     0.505051      3           114.4      25.8     1841.3     297.0        5.0       2.0      0.02
                           4           136.2      23.6     2455.1     364.4        4.0       3.0      0.01

2A07805L     0.729927      1            53.5      10.6       79.3      38.3       13.0       2.3      0.11
                           2            50.0      10.5       83.8      38.5       10.5       0.0      0.26
                           3            55.1      10.6       93.3      39.5       13.0       0.0      0.15
                           4            79.6      10.9      127.7      56.4       39.0       7.0      0.11
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                                                SAS

STRM_ID          WGT      SAMPLE        NA16       K16       CA16      MG16      FE11      MN11       H16

2A07805U    0.729927      4             55.7       8.4       73.4      35.9       8.0       1.0      0.15

2A07806L    0.178571      0             63.6      12.8       67.6      20.9       7.8       0.7      0.15
                          1             67.9      14.3       67.9      22.4       6.0       0.0      0.13
                          2             76.6      13.4       67.4      21.6       5.0       1.0      0.35
                          3             70.5      15.0       70.4      22.8       9.0       1.0      0.16
                          4             75.7      14.2       75.8      24.9       7.0       2.0      0.11

2A07806U    0.178571      4             50.5      12.3       52.4      16.5       8.0       2.0      0.17

2A07807L    0.066313      0            102.3      20.2      120.8      74.7       7.0       2.4      0.10
                          1            103.1      20.7      102.3      71.2      11.5       1.5      0.06
                          2             95.7      21.7      104.3      65.8      19.0       0.0      0.14
                          3            105.3      22.9      106.3      72.1      21.0       4.0      0.17
                          4            109.2      27.4      109.8      70.4      17.0       3.0      0.12

2A07807U    0.066313      4             62.2      13.8       72.9      42.9       1.0       1.0      0.14

2A07808L    0.038212      1             63.7      14.0      108.8      65.8       9.0       1.3      0.05
                          2             67.0      14.5       96.8      70.1       8.0       1.0      0.15
                          3             52.2      14.7      101.8      65.5      17.0       0.0      0.28
                          4             69.2      18.3      118.8      77.9      25.0       4.0      0.12

2A07808U    0.038212      4             47.4      11.9      131.7      50.0      15.0       1.0      0.09

2A07810L    0.036563      1             33.8      11.8       69.4      26.8       1.0       0.0      0.19
                          2             33.7      11.2       57.9      27.6       0.7       0.0      0.18
                          3             35.9      13.4       64.4      29.0       2.0       0.0      0.30
                          4             41.8      13.5       77.8      33.6      10.0       4.0      0.19

2A07810U    0.036563      4             32.8      10.6       58.9      26.1       1.0       2.0      0.42

2A07811L    0.208768      1             26.8      10.8       59.4      33.7       0.0       0.0      0.81
                          2             27.3       9.8       50.4      29.9       0.7       0.0      0.60
                          3             29.4      10.2       48.9      27.1       0.4       0.0      0.60
                          4             34.0       7.7       45.7      25.1       0.5       2.5      0.45

2A07811U    0.208768      4             29.9       7.0       49.9      23.1       0.0       1.0      0.66

2A07812L    0.341297      1             55.7      12.5       53.9      27.0       5.0       2.0      0.15
                          2             56.5      12.8       52.4      25.9       0.7       0.0      0.17
                          3             63.9      14.8       54.4      26.7       0.8       1.0      0.20
                          4             70.0      16.0       72.9      35.7       4.0       1.0      0.09

2A07812U    0.341297      4             48.7      10.3       57.9      33.2       1.0       0.0      0.19

2A07813L    0.104275      0            165.2      34.5      243.5     132.6      36.6       7.7      0.04
                          1            177.0      37.3      228.5     133.3      31.9       6.0      0.04
                          2            172.3      34.5      226.5     130.0      35.0       5.0      0.06
                          3            183.1      38.0      221.1     136.6      41.0       9.5      0.05
                          4            180.5      45.8      242.5     140.7      51.0       8.0      0.04
```

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                                              SAS

STRM_ID              WGT     SAMPLE        NA16        K16       CA16      MG16       FE11      MN11        H16

2A07813U        0.104275     3            109.2       23.9      134.7      76.7       45.0       9.0       0.06
                             4             92.2       47.3      153.7      88.0       49.0       2.0       0.14

2A07814L        0.072516     0            164.7       36.0      212.6     143.1       98.0      49.3       0.04
                             1            206.6       39.9      196.6     149.7      104.0      32.0       0.02
                             2            151.4       40.5      175.4     130.8       82.5      35.5       0.10
                             3            164.4       39.9      181.6     139.8      101.0      52.0       0.10
                             4            193.6       77.2      223.1     160.4       72.0      43.0       0.09

2A07814U        0.072516     3            118.3       31.2      122.3      96.2       31.0      11.0       0.10
                             4            158.3       45.1      168.9     124.6       39.5      13.0       0.07

2A07815L        0.059952     1             54.1       11.9       59.9      30.0       14.0       2.4       0.11
                             2             59.2       12.2       51.9      33.0       13.0       1.0       0.14
                             3             45.2       12.9       58.9      31.3       15.0       1.0       0.39
                             4             52.6       15.1       59.9      35.2       21.0       8.0       0.18

2A07815U        0.059952     4             40.5       13.1       55.9      33.2        3.0       2.0       0.27

2A07816L        0.084602     1             33.3        9.5       34.8      16.7        3.0       3.0       0.19
                             2             34.1       10.9       32.6      16.6        1.0       0.0       0.28
                             3             36.2       11.1       33.5      16.2        2.0       0.0       0.41
                             4             38.1       10.8       37.5      13.4        7.0       1.0       0.17

2A07816U        0.084602     4             26.1        6.4       35.6      19.1        2.0       0.0       0.41

2A07817L        0.096618     1             31.0        9.1       38.8      17.4        3.0       1.5       0.16
                             2             30.1        9.1       35.8      20.1        0.0       0.0       0.31
                             3             28.1       10.0       44.1      20.0        2.0       0.5       0.40
                             4             28.7        8.2       43.4      20.9        5.0       1.5       0.35

2A07817U        0.096618     4             27.0        8.3       71.4      24.8        1.0       6.0       1.12

2A07818L        0.990099     1             46.3       12.9       49.4      27.4        9.0       3.0       0.12
                             2             46.5       13.0       46.4      27.9        2.0       0.0       0.23
                             3             50.0       14.7       43.4      28.3       10.0       0.0       0.35
                             4             54.8       15.9       56.9      31.7       16.0       4.0       0.19

2A07818U        0.990099     3             49.6       14.4       44.4      27.6        7.0       0.0       0.32
                             4             53.9       15.5       56.4      31.6       13.0       2.0       0.19

2A07819L        0.027739     1            127.0       20.3      126.2      52.3       37.0      14.5       0.04
                             2            142.2       20.6      110.5      56.0      110.5      15.0       0.07
                             3E           105.3       23.5      107.3      51.3       58.0      10.0       0.22
                             4            131.4       29.4      121.8      53.7      144.0      11.0       0.12

2A07819U        0.027739     4            147.0       23.4      186.1      34.7       29.0       3.0       0.09
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                                                   SAS

STRM_ID          WGT     SAMPLE      NA16      K16        CA16      MG16      FE11      MN11       H16

2A07820L    0.081566     0           45.6      12.3       65.4      33.9      14.4       6.5      0.16
                         1           45.5      13.9       54.9      34.6      13.9       3.0      0.16
                         2           43.3      12.8       56.4      30.1      14.0       1.0      0.21
                         3           46.1      13.8       52.4      34.9      17.0       3.0      0.15
                         4           50.0      15.2       55.9      35.2      17.0       7.0      0.19

2A07820U    0.081566     3           36.7      10.7       37.5      24.6       2.0       0.0      0.20
                         4           38.7      11.5       41.9      25.9       3.0       2.0      0.23

2A07821L    0.393701     1           80.5      13.6       63.4      25.3      22.0       1.3      0.11
                         2           86.3      13.7       56.4      25.1      26.0       0.0      0.15
                         3           70.0      14.2       57.4      27.5      44.0       1.0      0.10
                         4           81.8      14.7       63.4      29.0      42.5       2.0      0.13

2A07821U    0.393701     4           80.5      15.0       64.4      27.6      52.0       7.0      0.09

2A07822L    0.151976     1           67.9      16.2      118.3      52.2      24.0      15.0      0.13
                         2           65.3      14.3      104.3      49.5      28.0      12.0      0.15
                         3           71.8      16.3      113.3      52.2      24.0      11.0      0.11
                         4           81.3      19.9      142.7      65.1      61.0      15.0      0.10

2A07822U    0.151976     4           82.2      18.8      146.2      62.0      40.0      10.0      0.13

2A07823L    0.132275     1           70.0      21.5       77.8      52.3      13.1       7.5      0.14
                         2           67.4      19.3       69.9      51.6       4.0       8.0      0.14
                         3           72.6      22.6       67.4      46.9       7.0       7.0      0.11
                         4           85.3      35.5      183.1      79.5      27.0      12.0      0.06

2A07823U    0.132275     3           66.1      18.2       41.4      22.5      14.0       0.0      0.10
                         4           72.2      28.1      296.4      66.4      20.0       2.0      0.05

2A07824L    0.080775     1           35.1      10.4       46.9      27.4       3.5       2.5      0.19
                         2           34.4      10.7       40.5      28.5       1.3       0.0      0.16
                         3           36.0      11.8       39.5      26.7       4.0       0.0      0.17
                         4           41.4      12.3       48.2      29.2       6.0       2.0      0.15

2A07824U    0.080775     4           33.1       7.8       34.9      19.8      12.0       2.0      0.20

2A07825L    0.043995     0           42.2       8.4       30.4      20.4      13.7       1.3      0.19
                         1           43.9      10.2       31.6      22.0      13.1       0.0      0.23
                         2           41.6       9.3       30.1      21.8      14.0       1.0      0.23
                         3           42.5       9.7       28.6      21.5      19.0       0.0      0.16
                         4           45.7      12.3       35.1      25.5      25.0       4.0      0.21

2A07825U    0.043995     3           55.7       9.6       40.5      26.5       0.8       0.0      0.25
                         4           52.2      10.7       44.8      31.0      13.0       2.0      0.36

2A07826L    0.245098     1          189.5      35.8      232.5      89.6     104.0      27.8      0.06
                         2          214.9      35.0      213.1      89.7     143.0      26.0      0.11
                         3          175.7      38.6      233.0      97.9     164.0      48.0      0.06
                         4          212.7      39.1      236.0      92.1     137.0      43.0      0.12
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                                                      SAS

STRM_ID            WGT        SAMPLE       NA16      K16      CA16      MG16      FE11      MN11      H16

2A07826U       0.245098       3           206.6     35.5     202.1      78.7      66.0      17.0      0.13
                              4            96.6     94.6     313.9     108.6     174.0     121.0      0.68

2A07827L       0.252525       1            43.1     12.6     234.5      66.6      30.0       8.6      0.05
                              2            40.7     14.4     151.7      64.2      41.0       8.0      0.06
                              3            41.6     12.2     170.2      64.2      54.0      12.0      0.09
                              4            46.1     19.2     223.6      87.2      62.0      20.0      0.09

2A07827U       0.252525       4            44.8     11.9      38.4      27.1       9.0       1.0      0.21

2A07828L       0.135870       0            31.7      9.0      31.4      19.2       1.8       1.8      0.30
                              1            32.6     10.1      30.6      21.0      10.3       0.0      0.24
                              2            30.8      9.6      29.5      19.7      10.0       0.0      0.28
                              3            33.6     10.5      29.1      21.1      18.0       2.0      0.19
                              4            35.5     16.2     108.3      39.2      39.0      12.0      0.17

2A07828U       0.135870       3            27.9      8.6      16.3      15.4      14.0       1.0      0.35
                              4            26.9      8.4      25.4      18.7       4.0       1.0      0.55

2A07829L       0.118203       1            44.8     10.9      30.3      19.2      11.0       0.7      0.17
                              2            41.8     11.3      30.2      18.1      13.0       0.0      0.33
                              3            42.2     11.4      32.5      19.0      13.0       0.0      0.30
                              4            47.8     12.5      39.7      23.2      24.0       1.0      0.21

2A07829U       0.118203       3            42.1     10.4      24.8      16.5      16.0       0.0      0.21
                              4            46.5     11.4      29.4      19.7      49.0       3.0      0.20

2A07830L       0.134843       0           105.7     20.7     121.8      59.9      68.0      20.7      0.06
                              1           109.2     19.8     108.8      61.8      73.0      16.0      0.10
                              2           123.5     52.2     176.6      93.8      60.0      11.0      0.46
                              3           107.4     20.7     114.3      63.9      96.5      22.0      0.26
                              4            68.3     12.6      29.8      17.3      16.0       2.0      0.18

2A07830U       0.134843       4           130.9     31.7     148.7      75.1      89.0      17.0      0.22

2A07831L       0.035842       0           263.5     23.0     206.1     113.5      49.0      29.2      0.06
                              1           487.2     25.8     132.1     118.5      68.0      30.0      0.05
                              2E          253.2     28.4     176.6     114.3     103.0      20.0      0.15
                              3           965.7     33.2     191.6     132.4      73.0      36.0      0.14
                              4           134.0     28.1     193.6     111.1      40.0      20.0      0.11

2A07831U       0.035842       3            94.4     19.0     110.8      73.3      33.0       4.0      0.19
                              4           109.2     25.3     127.7      79.0      39.0       3.0      0.16

2A07832L       0.056625       1            46.5     12.4      57.9      33.6      19.9       1.0      0.13
                              2            46.1     12.1      52.9      36.4      12.0       4.0      0.16
                              3            48.7     14.2      56.4      37.2      37.0       3.0      0.41
                              4            52.2     20.9      66.4      41.5      66.0      10.0      0.22

2A07832U       0.056625       3            46.5     13.3      51.4      33.2      16.0       4.0      0.28
                              4            50.9     14.9      58.9      35.9      29.0       5.0      0.16
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                                                SAS

STRM_ID          WGT     SAMPLE      NA16      K16      CA16      MG16      FE11      MN11      H16

2A07833L    0.167785     1           54.4     12.6     138.5      73.2      22.9       5.0     0.05
                         2           53.1     12.6     126.2      76.3      16.0       8.0     0.08
                         3           56.3     18.5     130.2      75.5       5.0       4.0     0.08
                         4           69.6     20.3     179.1     103.6      37.0      18.0     0.07

2A07833U    0.167785     3           93.1     16.9     143.7      61.8       0.0       0.0     0.17
                         4          113.5     19.2     161.7      68.5       0.0       0.0     0.13

2A07834L    0.222222     0           41.9      7.6      22.2      16.0      43.0       0.9     0.22
                         1           41.6      8.2      24.1      18.5      45.5       0.0     0.23
                         2           36.9      8.4      30.6      19.0      39.0       1.0     0.38
                         3           41.8      8.6      27.2      18.7      99.0       3.0     0.40
                         4           43.9     10.1      32.3      20.8      34.0       2.0     0.27

2A07834U    0.222222     4           58.3     13.0      45.9      30.4      19.0       4.0     0.42

2A07835L    0.093721     1           72.2      9.5      40.7      28.6      12.5       2.4     0.09
                         2           70.9     10.3      43.9      30.3      11.0       2.0     0.13
                         3           71.3     11.0      39.5      30.7      11.0       1.0     0.12
                         4           79.6     12.5      60.6      37.9      26.0       7.5     0.13

2A07835U    0.093721     4           65.7     10.0      46.9      28.2      18.0       1.0     0.13

2A07881L    0.074963     1          299.7     50.9     432.6     228.7      60.3       8.0     0.04
                         2          273.8     49.1     405.7     216.8      48.5       7.5     0.06
                         3          303.2     58.6     410.2     215.5      51.0      13.0     0.04
                         4          508.9     81.8     623.8     312.6     162.0      16.0     0.02

2A07881U    0.074963     3          208.4     41.7     296.9     158.8      34.0      11.0     0.07
                         4          266.2     62.1     436.6     233.6      61.0      28.0     0.04

2A07882L    0.450450     1           52.2     11.1      65.1      34.3       3.0       1.5     0.10
                         2           47.4     10.9      51.9      29.8       0.7       0.0     0.11
                         3           54.4     12.6      64.4      34.1       3.0       0.0     0.23
                         4           67.4     15.2      89.3      48.5       6.0       1.0     0.16

2A07882U    0.450450     4           45.7     10.0      42.8      22.5       1.0       1.0     0.28

2A07891L       -         1           30.2      9.9      71.9      41.8       0.0       0.0     0.43
                         2           30.2      8.9      66.9      40.9       0.7       0.0     0.65
                         3           32.3      9.4      69.4      41.2       0.0       0.0     0.38
                         4           36.4      8.2      72.9      44.0       1.0       1.0     0.43

2A07892L       -         1           39.9     11.9      31.7      17.8       7.0       2.0     0.16
                         2           39.8     12.0      31.0      17.6       1.5       0.0     0.28
                         3           43.5     13.9      34.5      18.0       4.0       0.0     0.32
                         4           43.5     14.0      40.6      22.3      17.0       1.0     0.19
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                                                       SAS
STRM_ID           WGT       SAMPLE       NA16         K16        CA16        MG16        FE11        MN11        H16

2A07893L          -           0          50.8         9.2        43.0        32.6         1.1         1.1        0.21
                              1          51.8        10.4        39.9        35.8        10.9         0.0        0.11
                              2          50.0         9.7        39.2        33.5        10.0         1.0        0.19
                              3          53.9        10.8        38.9        36.2        20.0         2.0        0.14
                              4          55.7        10.6        45.2        41.9        13.0         3.0        0.11

2A07894L          -           1          36.0         9.7        38.8        25.2         3.0         0.3        0.11
                              2          35.1        10.1        36.0        25.1         3.0         0.0        0.16
                              3          37.3        10.8        44.6        26.6         2.0         2.0        0.14
                              4          40.0        10.9        53.9        31.7         6.0         0.0        0.13

2A07895L          -           1          56.1        13.7        74.8        47.1        19.0         3.0        0.06
                              2          52.6        12.8        56.9        44.5         5.0         0.0        0.07
                              3          56.3        15.2        62.9        43.6        12.0         0.5        0.07
                              4          62.0        15.9        80.6        54.1        18.0         2.5        0.09

2A07895U          -           3          50.0        13.7        46.4        38.1        12.0         0.0        0.10

2A07896L          -           1          34.6         7.7        27.5        20.9         3.0         0.3        0.21
                              2          32.9         8.3        26.3        19.7         1.0         0.0        0.19
                              3          34.1         8.5        29.6        20.6         0.0         0.0        0.19
                              4          37.5         8.0        35.6        25.3         1.0         0.0        0.22

2A08801L     0.591716         0          96.7        12.5      1596.8       183.9        37.8        24.6        0.01
                              1          97.4        14.4      1526.9       176.9        50.0        28.0        0.01
                              2          79.2        23.7      1127.7       140.7       111.0        32.0        0.03
                              3          73.9        15.9      1037.9       134.1        63.0        64.0        0.01
                              4          93.1        20.4      1566.9       178.5        42.0        41.0        0.01

2A08801U     0.591716         4          60.9        11.7      1492.0       171.9        24.0         6.0        0.02

2A08802L     0.456621         1          39.5        13.5        41.1        40.9        30.0        16.0        0.13
                              2          39.0        17.3        33.7        67.4        21.0        19.0        0.21
                              3          39.4        14.0        34.5        39.8         7.0        14.0        0.21
                              4          39.5        13.2        35.3        40.6        36.0        16.0        0.26

2A08802U     0.456621         4          60.9        16.1        36.9        28.7        20.0        11.0        0.18

2A08803L     0.393701         1          45.1        10.2       122.8        67.6        48.0        47.1        0.02
                              2          45.2        10.3       112.3        66.9       120.0        49.0        0.08
                              3          43.9        11.1       127.2        71.4       154.0        48.0        0.07
                              4          46.5        12.0       139.7        78.4       101.0        61.0        0.09

2A08803U     0.393701         4          47.4        10.3       147.2       100.4        53.0        24.0        0.12

2A08804L     1.010101         1          37.8        11.3        27.5        27.1         6.0         2.0        0.18
                              2          37.4        11.8        28.4        26.6         2.0         0.0        0.26
                              3          39.2        12.9        28.1        27.0         7.5         0.0        0.35
                              4          39.0        13.3        32.5        30.5        12.0         1.0        0.27

2A08804U     1.010101         4          38.6        12.0        29.7        23.1         7.0         1.0        0.26
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SAS

| STRM_ID | WGT | SAMPLE | NA16 | K16 | CA16 | MG16 | FE11 | MN11 | H16 |
|---|---|---|---|---|---|---|---|---|---|
| 2A08805L | 0.302115 | 1 | 55.5 | 15.6 | 68.4 | 52.0 | 42.0 | 10.9 | 0.16 |
| | | 2 | 62.0 | 15.2 | 60.9 | 48.1 | 42.0 | 9.0 | 0.15 |
| | | 3 | 54.4 | 16.4 | 70.4 | 51.8 | 69.0 | 9.0 | 0.11 |
| | | 4 | 55.2 | 17.5 | 88.8 | 62.1 | 46.0 | 13.0 | 0.19 |
| 2A08805U | 0.302115 | 4 | 36.0 | 10.0 | 30.6 | 37.5 | 48.0 | 29.0 | 0.55 |
| 2A08806L | 1.666667 | 1 | 80.1 | 39.3 | 65.9 | 52.9 | 30.0 | 7.7 | 0.28 |
| | | 2 | 85.7 | 27.1 | 61.4 | 46.2 | 61.0 | 7.0 | 0.15 |
| | | 3 | 79.6 | 39.4 | 68.4 | 50.2 | 32.0 | 9.0 | 0.19 |
| | | 4 | 82.6 | 29.4 | 75.3 | 57.6 | 45.0 | 10.0 | 0.22 |
| 2A08806U | 1.666667 | 4 | 65.7 | 26.8 | 54.4 | 47.1 | 50.0 | 7.0 | 0.17 |
| 2A08808L | 0.311526 | 1 | 62.5 | 21.0 | 293.2 | 78.6 | 37.5 | 32.5 | 0.10 |
| | | 2 | 71.3 | 16.2 | 267.5 | 78.5 | 62.0 | 33.0 | 0.05 |
| | | 3 | 69.6 | 18.0 | 296.9 | 78.5 | 85.0 | 31.0 | 0.05 |
| | | 4 | 77.9 | 23.8 | 425.4 | 99.9 | 93.5 | 34.0 | 0.07 |
| 2A08808U | 0.311526 | 4 | 70.5 | 15.9 | 71.4 | 54.0 | 53.0 | 3.0 | 0.18 |
| 2A08809L | 0.510204 | 0 | 49.6 | 14.0 | 39.8 | 29.8 | 21.9 | 4.0 | 0.21 |
| | | 1 | 50.5 | 15.8 | 36.8 | 32.0 | 52.0 | 3.0 | 0.19 |
| | | 2E | 46.1 | 18.8 | 49.0 | 34.0 | 93.0 | 10.0 | 0.32 |
| | | 3 | 52.9 | 16.8 | 37.5 | 32.8 | 36.5 | 5.0 | 0.16 |
| | | 4 | 51.3 | 17.0 | 42.5 | 33.6 | 12.0 | 6.0 | 0.23 |
| 2A08809U | 0.510204 | 4 | 48.7 | 16.4 | 37.3 | 31.6 | 47.0 | 5.0 | 0.26 |
| 2A08810L | 0.531915 | 1 | 64.8 | 16.1 | 76.8 | 58.6 | 48.9 | 11.0 | 0.08 |
| | | 2 | 57.0 | 15.8 | 67.9 | 59.1 | 43.0 | 14.0 | 0.18 |
| | | 3 | 63.1 | 18.4 | 71.4 | 61.1 | 7.0 | 12.0 | 0.19 |
| | | 4 | 66.3 | 26.3 | 95.6 | 72.0 | 163.5 | 31.5 | 0.11 |
| 2A08810U | 0.531915 | 4 | 57.9 | 12.9 | 68.4 | 72.6 | 0.0 | 0.0 | 0.09 |
| 2A08811L | 0.775194 | 0 | 64.9 | 12.9 | 95.6 | 57.1 | 21.7 | 4.0 | 0.08 |
| | | 1 | 68.3 | 14.4 | 85.8 | 60.1 | 29.0 | 3.0 | 0.10 |
| | | 2 | 68.7 | 15.5 | 110.8 | 63.3 | 48.0 | 4.0 | 0.14 |
| | | 3 | 70.9 | 16.2 | 94.3 | 63.0 | 28.0 | 3.0 | 0.11 |
| | | 4 | 70.3 | 17.5 | 123.5 | 71.8 | 22.5 | 4.0 | 0.11 |
| 2A08811U | 0.775194 | 4 | 72.6 | 18.3 | 70.9 | 55.9 | 19.0 | 3.0 | 0.18 |
| 2A08891L | - | 1 | 31.5 | 9.6 | 18.0 | 19.1 | 10.6 | 0.0 | 0.21 |
| | | 2 | 31.2 | 9.4 | 18.0 | 19.3 | 6.5 | 0.0 | 0.27 |
| | | 3 | 31.9 | 10.4 | 18.9 | 19.1 | 19.0 | 0.0 | 0.40 |
| | | 4 | 36.2 | 11.4 | 20.9 | 21.8 | 33.0 | 4.0 | 0.28 |
| 2A08891U | - | 3 | 35.0 | 11.3 | 24.8 | 22.0 | 22.0 | 0.0 | 0.38 |

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                                                  SAS

STRM_ID            WGT      SAMPLE       NA16       K16       CA16      MG16      FE11      MN11      H16

2A08901L      0.133511      1            65.3      14.1       50.4      32.7      17.0       1.5     0.09
                            2            58.3      15.8       57.4      33.7      37.0      13.0     0.17
                            3            64.8      17.0       63.9      32.0      34.0       6.0     0.13
                            4            67.0      18.5       77.3      41.0      40.0      17.0     0.09

2A08901U      0.133511      3            42.0      10.7       27.6      19.3       4.0       1.0     0.19
                            4            41.6       9.0       29.6      21.8      12.0       1.0     0.16

2A08902L      0.124844      0            44.5       8.7       27.2      21.6      20.0       2.5     0.13
                            1            45.2       9.5       24.7      23.1      38.0       1.0     0.15
                            2E           39.6       9.8       26.3      23.3      36.0       0.0     0.27
                            3            46.1       9.9       26.2      18.7      41.0       5.0     0.25
                            4            47.8      11.7       33.0      25.8      32.0       6.0     0.16

2A08902U      0.124844      4            51.3      12.0       42.0      30.5     107.0      11.0     0.21

2A08903L      0.440529      1            59.0      13.7       57.9      48.3      14.0       8.8     0.30
                            2            64.8      13.8       60.4      49.2      35.0       9.0     0.17
                            3            55.5      14.1       61.4      47.3      28.5      10.0     0.13
                            4            62.2      17.1       78.3      60.0      48.0      12.0     0.17

2A08903U      0.440529      3            52.2      13.9       56.4      42.6      40.0       8.0     0.12
                            4            59.6      16.4       30.3      60.6      57.0      11.0     0.20

2A08904L      0.199203      0            87.4      17.1       94.8      54.2      46.1      13.4     0.06
                            1            88.7      17.5       86.8      55.4      93.0      11.0     0.10
                            2E           66.3      32.1       82.8      48.5     139.0      19.0     0.66
                            3            85.7      19.7       83.8      55.6      53.0      14.0     0.14
                            4            83.1      23.7       91.8      56.5      51.0      24.0     0.18

2A08904U      0.199203      3           110.1      19.8       48.8      48.8       7.0       0.0     0.16
                            4            97.0      20.5       55.4      52.2       6.0       1.0     0.18

2A08905L      0.507614      1            47.0      12.6       34.8      26.8      31.0      12.0     0.14
                            2            47.4      13.2       27.3      27.7      23.0      10.0     0.23
                            3            49.2      14.8       29.6      28.5      30.0       9.0     0.17
                            4            54.4      15.5       32.2      29.9      22.0       4.0     0.15

2A08905U      0.507614      3            43.5      13.5       25.6      25.6      13.0       2.0     0.15
                            4            47.8      14.4       28.3      23.0      19.0       3.0     0.17

2A08906L      0.196850      0            53.5      18.6       38.8      37.8      42.9      21.5     0.10
                            1            52.0      23.8       33.2      37.0     118.0      17.5     0.33
                            2E           45.7      58.8       31.7      32.3     178.0      52.0     2.00
                            3            53.5      29.1       34.0      38.7     258.0      25.0     0.49
                            4            42.2      19.6       23.6      27.7      32.0      24.0     0.50

2A08906U      0.196850      4            47.4      30.2       34.3      36.1      81.0      40.0     0.76
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                                                  SAS

STRM_ID            WGT    SAMPLE     ALKA11      SO416      NO316       CL16      FTL16      SIO211       COND11

2A07701L      0.120627    1            90.0       25.8       12.0       15.5       1.05        5.85        16.30
                          2            84.5       27.8       14.6       16.5       1.05        6.65        17.00
                          3            93.3       28.1       12.3       15.2       1.32        5.22        17.90
                          4           147.0       29.8       11.9       14.9       1.10        6.40        21.30

2A07701U      0.120627    3            38.0       33.5       11.7       14.5       1.26        4.62        12.50
                          4            55.0       31.0       11.7       14.9       0.95        5.50        12.40

2A07702L      0.236967    0          1174.0       96.2        0.2       28.8       2.16        7.30       126.44
                          1          1137.5       97.8        0.0       29.1       2.24        8.65       123.20
                          2E          967.0       94.1        2.5       29.1       2.11        6.72       106.40
                          3          1300.0       90.4        5.3       25.9       2.42        8.62       138.40
                          4          1542.0       86.6        5.9       25.9       2.74        9.67       157.10

2A07702U      0.236967    4           458.0       87.7       10.7       19.2       2.05        9.95        55.50

2A07703L      0.255102    1           147.0       42.3        5.0       18.2       1.37        9.15        22.90
                          2           145.5       43.6        6.5       25.6       1.34        9.00        24.50
                          3           143.0       35.2        3.8       27.6       1.42        9.45        22.90
                          4           181.0       31.4        6.0       24.7       1.58        9.75        25.10

2A07703U      0.255102    3            97.9       36.4        1.7       15.8       1.42       10.60        18.90
                          4           132.0       31.9        2.6       16.6       1.58       11.30        19.40

2A07801L      0.423729    1           450.0       64.2       13.4       19.6       2.47        8.02        55.30
                          2           384.0       57.3        7.3       22.2       2.26        8.65        50.70
                          3           370.0       62.7       11.9       16.6       2.26        8.10        48.20
                          4           886.0       64.4       12.6       21.6       2.89        9.05        95.60

2A07801U      0.423729    3           364.0       60.4       11.7       23.1       2.26        8.20        47.40
                          4           729.0       60.4       12.6       19.1       2.89       10.50        81.20

2A07802L      0.136426    1           219.5       28.3       22.4       64.7       2.47       12.05        36.80
                          2           211.0       30.8       26.8       79.8       2.42       12.30        36.30
                          3           228.0       27.1       19.0       62.6       2.74       12.70        36.80
                          4           278.0       24.4        5.7       62.3       3.11       13.20        37.20

2A07802U      0.136426    4           281.0       21.7       29.2       50.8       3.11       14.30        38.30

2A07803L      0.505051    1          1719.5      126.6        1.0       39.1       2.79        5.62       179.10
                          2          1483.0      118.0        4.4       37.8       2.53        6.72       163.30
                          3          1929.0      112.8        7.6       41.5       3.05        7.95       200.60
                          4          2896.0      106.8       11.0       56.4       4.26        9.50       281.40

2A07803U      0.505051    3          2201.0      112.0        6.9       27.3       3.79       10.90       223.50
                          4          3019.0      109.7        6.8       29.3       4.42       12.90       283.60

2A07805L      0.729927    1           106.0       43.1       26.1       20.6       1.42        5.60        20.70
                          2            85.5       41.8       26.9       21.5       1.39        6.82        20.55
                          3           105.0       37.5       21.3       22.3       1.58        6.50        21.20
                          4           189.0       37.3       18.4       29.3       1.79        8.55        29.20
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                                                     SAS

STRM_ID          WGT     SAMPLE     ALKA11     SO416     NO316     CL16     FTL16     SIO211     COND11

2A07805U    0.729927     4           111.0      32.3      18.4     11.0      1.63       7.95      18.80

2A07806L    0.178571     0           116.0      26.0      17.4     14.5      2.95       8.97      17.00
                         1           118.0      28.9      15.1     13.5      3.53       9.40      18.20
                         2            99.4      28.3      16.1     15.2      3.37       8.80      18.00
                         3            95.7      28.3      17.4     13.0      3.42       9.75      18.90
                         4           133.0      29.6      17.3     12.3      3.58      10.90      20.30

2A07806U    0.178571     4            83.0      17.6      16.5     12.3      2.32       8.15      14.50

2A07807L    0.066313     0           158.0      62.3      41.9     46.3      1.32      10.70      33.81
                         1           177.0      62.3      30.7     38.2      1.47      10.85      31.75
                         2           159.0      61.4      26.1     41.2      1.53      11.30      30.60
                         3           189.0      50.4      24.8     38.1      1.63      12.00      33.00
                         4           228.0      48.1      19.4     34.1      1.79      12.80      33.90

2A07807U    0.066313     4           172.0      23.9      14.4     16.0      1.10      10.50      20.30

2A07808L    0.038212     1           162.0      36.4       8.3     28.8      1.21       9.50      25.74
                         2           173.0      42.9      13.1     32.7      1.47      11.30      25.70
                         3           127.0      62.0      12.5     28.2      1.42       6.26      25.20
                         4           213.0      36.0      21.8     31.3      1.47      10.30      30.50

2A07808U    0.033212     4           202.0      26.0       7.2     13.1      1.32       8.81      25.30

2A07810L    0.036563     1            68.5      36.2      17.6     11.7      1.21       5.10      15.00
                         2            60.9      37.7      18.1     14.5      1.21       5.28      15.30
                         3            68.6      33.5      14.9     13.9      1.42       5.70      15.80
                         4           113.0      34.1      12.3     11.8      1.32       5.06      18.40

2A07810U    0.036563     4            64.9      37.7      25.0     10.8      1.16       5.46      15.10

2A07811L    0.208763     1            13.4      48.3      45.8     12.3      1.26       4.21      16.30
                         2            17.5      40.6      39.4     13.8      1.26       4.32      14.80
                         3            17.6      41.8      33.1     12.0      1.37       5.07      14.20
                         4            37.0      41.4      24.5     12.2      1.34       5.62      13.50

2A07811U    0.208768     4            23.5      47.3      33.4     13.3      1.21       4.94      14.30

2A07812L    0.341297     1            99.7      23.7       4.2     12.7      1.53       8.05      15.80
                         2           100.3      23.8       3.6     11.9      1.55       9.60      15.60
                         3           108.0      22.1       3.3     11.7      1.58       8.50      16.40
                         4           153.0      21.7      12.3     11.1      1.58      10.80      20.20

2A07812U    0.341297     4            85.4      33.1      25.2     11.0      1.10       8.10      16.50

2A07813L    0.104275     0           358.0      71.2      37.4     75.0      3.47      16.70      58.32
                         1           363.0      78.3      29.7     81.2      4.11      17.30      60.30
                         2           357.0      68.9      31.1     78.4      3.68      18.10      58.10
                         3           395.0      76.3      28.7     73.1      3.95      18.30      61.35
                         4           448.0      68.1      27.3     69.7      4.32      19.40      64.20
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                                                 SAS

STRM_ID          WGT      SAMPLE     ALKA11     SO416     NO316      CL16     FTL16     SIO211     COND11

2A07813U    0.104275      3           254.0      30.2      33.1      19.3      2.74      14.50      35.90
                          4           293.0      55.8      37.1      23.4      3.11      11.60      40.40

2A07814L    0.072516      0           322.0      94.5      30.3      85.2      2.26      13.80      57.12
                          1           373.0      88.1      24.4      83.8      2.47      13.10      60.10
                          2           297.0      86.5      26.9      71.8      2.47      13.80      52.30
                          3           352.0      75.8      25.8      66.3      2.63      14.10      55.60
                          4           444.0     105.6      26.1     101.3      3.58      15.20      70.20

2A07814U    0.072516      3           229.0      65.4      20.3      44.0      2.11      12.70      39.50
                          4           368.0      72.6      13.8      60.7      2.74      16.35      52.45

2A07815L    0.059952      1            95.5      43.5       1.4      16.4      1.32       8.10      16.63
                          2            94.1      47.5       2.5      18.1      1.26       9.00      16.80
                          3            70.3      66.0       4.0      17.4      1.37       6.50      17.00
                          4           103.0      45.4       5.0      15.2      1.47      11.10      18.10

2A07815U    0.059952      4            84.3      43.1       6.5      14.7      1.21       6.70      15.90

2A07816L    0.084602      1            46.4      24.2       8.7      11.8      1.16       5.10      10.30
                          2            64.9      19.4       8.7      11.9      1.05       6.15      10.00
                          3            58.2      16.6       5.3      11.7      1.16       6.00      10.50
                          4            72.1      17.7       8.1      11.1      1.10       6.50      11.00

2A07816U    0.084602      4            31.7      24.6      28.7      12.6      0.95       4.08      10.60

2A07817L    0.096618      1            36.0      19.2      14.8      10.7      0.84       5.05      10.43
                          2            27.5      23.9      23.4      11.2      1.00       5.40      12.10
                          3            27.6      27.7      24.2      12.0      1.16       4.05      11.95
                          4            40.0      34.9      22.1      10.2      1.03       4.81      12.10

2A07817U    0.096618      4            12.0      53.1      57.7      12.8      1.16       3.88      17.20

2A07818L    0.990099      1            81.2      24.2      14.4      11.4      1.39       7.37      14.00
                          2            86.3      22.3      14.7      11.9      1.42       8.85      14.60
                          3            92.4      21.2      12.7      11.7      1.47       8.30      15.30
                          4           115.0      24.8      11.5      11.4      1.42       8.95      16.70

2A07818U    0.990099      3            97.2      20.8      12.7      10.1      1.42       8.15      14.90
                          4           113.0      26.6      12.5      12.0      1.42       8.90      16.60

2A07819L    0.027739      1           244.0      21.2       7.6      29.9      2.21      15.60      31.90
                          2           251.0      21.4       7.3      32.6      2.32      14.95      31.30
                          3E          201.0      38.1      15.9      35.0      2.11      13.50      29.90
                          4           294.0      20.5      10.5      33.3      2.84      15.90      35.80

2A07819U    0.027739      4           393.0      30.8      14.4      35.0      3.58      18.20      45.90
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                                             SAS

STRM_ID           WGT   SAMPLE   ALKA11   SO416   NO316   CL16   FTL16   SIO211   COND11

2A07820L     0.081566   0          108.0    30.4    12.2   20.7    1.00     6.10    15.98
                        1           70.1    28.7     9.4   18.5    1.13     6.17    16.05
                        2           75.9    39.8    10.4   19.9    1.00     5.76    16.00
                        3           80.6    27.1     8.9   18.6    0.95     6.50    16.50
                        4          102.0    27.5     9.8   19.2    1.10     6.60    17.60

2A07820U     0.081566   3           55.8    22.3     6.8   15.8    0.89     5.75    12.40
                        4           67.0    26.0     7.8   14.3    0.84     4.81    13.50

2A07821L     0.393701   1          127.0    12.4     7.1   24.4    1.74    11.50    18.36
                        2          137.5    16.8     7.5   26.1    1.63    12.25    19.05
                        3          115.0    22.9     8.2   29.3    1.53     8.16    18.20
                        4          158.0    11.6     7.2   26.1    1.63    12.15    20.10

2A07821U     0.393701   4          158.0     9.3     7.1   26.5    1.58    11.80    20.00

2A07822L     0.151976   1          149.0    30.4    12.9   28.2    1.37     8.55    25.70
                        2          158.0    29.6     8.6   31.3    1.42     7.92    24.90
                        3          169.0    27.3    11.0   27.1    1.58     9.10    26.10
                        4          241.0    27.3    15.0   32.4    1.58     9.75    32.20

2A07822U     0.151976   4          237.0    32.7    20.5   34.4    1.68    10.30    32.30

2A07823L     0.132275   1           91.4    72.2     4.5   24.9    1.97     9.80    23.55
                        2          110.0    60.0     3.1   26.7    1.95     9.20    23.40
                        3          106.0    65.0     2.6   22.9    2.11    10.20    22.90
                        4          271.0    93.7     3.6   32.4    2.89    11.40    41.10

2A07823U     0.132275   3           99.7    16.9     1.5   15.8    1.58    10.60    15.50
                        4          408.0    42.9     4.9   19.4    2.21    10.90    46.50

2A07824L     0.080775   1           45.2    28.3    20.6   13.2    0.92     5.90    12.70
                        2           52.1    29.7    22.0   16.5    0.92     5.70    13.65
                        3           50.2    28.3    18.5   13.7    0.89     6.20    13.30
                        4           72.0    32.5    15.9   12.6    0.95     6.95    14.50

2A07824U     0.080775   4           53.0    29.8    10.0   11.4    0.95     5.55    10.90

2A07825L     0.043995   0           80.0    15.4     1.5   14.8    0.68     6.90    10.47
                        1           58.6    15.8     0.2   14.9    1.00     6.80    11.10
                        2           52.9    22.8     1.2   16.9    0.84     5.98    11.25
                        3           60.6    15.2     0.6   15.1    0.84     6.65    11.10
                        4           76.0    22.9     2.1   14.3    0.89     7.10    12.90

2A07825U     0.043995   3           40.3    21.4     4.1   55.6    0.74     5.20    15.30
                        4           51.0    26.9     4.2   45.1    0.84     6.20    16.30

2A07826L     0.245098   1          357.0    32.5    45.5   93.7    2.63    14.60    55.08
                        2          359.0    26.0    35.8   88.3    2.63    14.30    56.50
                        3          327.0    47.9    44.2   87.7    2.63    13.30    56.60
                        4          412.0    33.7    54.4   98.7    3.32    17.80    61.50
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| STRM_ID | WGT | SAMPLE | ALKA11 | SO416 | NO316 | CL16 | FTL16 | SIO211 | COND11 |
|---|---|---|---|---|---|---|---|---|---|
| 2A07826U | 0.245098 | 3 | 298.0 | 44.3 | 48.6 | 99.0 | 2.16 | 15.60 | 54.80 |
| | | 4 | 221.0 | 98.9 | 40.0 | 330.1 | 2.42 | 4.41 | 79.00 |
| 2A07827L | 0.252525 | 1 | 279.0 | 30.6 | 3.7 | 18.3 | 1.05 | 6.95 | 34.45 |
| | | 2 | 220.0 | 32.3 | 3.6 | 20.2 | 1.05 | 7.80 | 29.10 |
| | | 3 | 205.0 | 33.5 | 3.0 | 18.9 | 1.05 | 6.58 | 28.60 |
| | | 4 | 318.0 | 35.4 | 6.2 | 22.1 | 1.10 | 7.65 | 39.10 |
| 2A07827U | 0.252525 | 4 | 77.0 | 33.9 | 2.5 | 12.8 | 1.10 | 7.90 | 13.70 |
| 2A07828L | 0.135870 | 0 | 44.0 | 17.8 | 4.7 | 14.1 | 0.68 | 5.35 | 9.69 |
| | | 1 | 47.6 | 17.6 | 4.5 | 13.5 | 0.89 | 5.50 | 10.20 |
| | | 2 | 43.0 | 20.6 | 4.0 | 14.2 | 0.79 | 5.20 | 9.91 |
| | | 3 | 54.1 | 15.9 | 4.4 | 13.0 | 0.84 | 5.75 | 10.50 |
| | | 4 | 155.0 | 27.9 | 7.9 | 15.3 | 1.32 | 4.60 | 22.00 |
| 2A07828U | 0.135870 | 3 | 31.9 | 9.3 | 4.7 | 10.9 | 0.68 | 7.90 | 7.58 |
| | | 4 | 40.5 | 19.1 | 4.6 | 10.3 | 0.74 | 4.79 | 9.05 |
| 2A07829L | 0.118203 | 1 | 66.9 | 14.8 | 8.9 | 16.0 | 0.89 | 7.55 | 11.50 |
| | | 2 | 65.3 | 15.9 | 9.3 | 17.5 | 0.95 | 8.35 | 11.70 |
| | | 3 | 62.1 | 13.5 | 11.1 | 15.8 | 0.89 | 7.45 | 11.70 |
| | | 4 | 82.5 | 12.5 | 15.1 | 15.4 | 0.95 | 8.50 | 13.60 |
| 2A07829U | 0.118203 | 3 | 63.7 | 6.2 | 0.0 | 13.4 | 0.84 | 8.35 | 9.69 |
| | | 4 | 89.6 | 6.5 | 1.1 | 12.9 | 0.79 | 8.80 | 11.20 |
| 2A07830L | 0.184843 | 0 | 189.0 | 34.4 | 26.1 | 51.6 | 1.63 | 11.40 | 31.60 |
| | | 1 | 197.0 | 31.2 | 21.6 | 41.8 | 1.84 | 11.90 | 31.40 |
| | | 2 | 251.0 | 65.2 | 26.8 | 84.3 | 2.05 | 8.26 | 47.80 |
| | | 3 | 203.5 | 30.1 | 21.7 | 47.5 | 1.84 | 11.55 | 32.40 |
| | | 4 | 95.0 | 15.3 | 1.6 | 17.0 | 1.10 | 10.80 | 13.80 |
| 2A07830U | 0.184843 | 4 | 257.0 | 32.9 | 32.7 | 59.8 | 2.11 | 12.10 | 42.80 |
| 2A07831L | 0.035842 | 0 | 327.0 | 62.3 | 17.9 | 192.1 | 1.63 | 13.30 | 63.74 |
| | | 1 | 320.0 | 83.5 | 15.3 | 403.4 | 1.79 | 13.20 | 86.00 |
| | | 2E | 274.0 | 85.6 | 24.8 | 171.0 | 1.74 | 12.30 | 61.00 |
| | | 3 | 382.0 | 89.7 | 16.6 | 840.7 | 2.21 | 13.70 | 142.30 |
| | | 4 | 338.0 | 55.0 | 18.7 | 63.2 | 1.89 | 13.70 | 48.40 |
| 2A07831U | 0.035842 | 3 | 207.0 | 25.8 | 18.5 | 42.9 | 1.47 | 10.40 | 31.40 |
| | | 4 | 251.0 | 35.0 | 26.6 | 55.0 | 1.63 | 11.40 | 36.80 |
| 2A07832L | 0.056625 | 1 | 88.7 | 26.4 | 6.7 | 19.2 | 1.16 | 6.95 | 15.40 |
| | | 2 | 81.2 | 27.5 | 15.0 | 33.3 | 1.00 | 8.40 | 16.50 |
| | | 3 | 92.7 | 26.9 | 8.7 | 20.3 | 1.05 | 7.85 | 16.90 |
| | | 4 | 116.0 | 37.1 | 9.9 | 23.3 | 1.16 | 7.65 | 19.70 |
| 2A07832U | 0.056625 | 3 | 110.0 | 27.7 | 2.9 | 16.2 | 1.10 | 8.15 | 15.60 |
| | | 4 | 118.0 | 29.1 | 4.5 | 16.2 | 1.16 | 8.20 | 17.10 |

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                                              SAS

STRM_ID          WGT     SAMPLE    ALKA11    SO416    NO316     CL16    FTL16     SIO211     COND41

2A07833L     0.167785      1        211.5     26.0      5.0     21.3     1.21       9.87      27.40
                           2        201.0     31.0      6.4     25.1     1.21      10.40      27.70
                           3        223.0     25.8      6.6     24.4     1.37      10.50      29.40
                           4        314.0     38.3     10.0     25.4     1.53      11.60      38.40

2A07833U     0.167785      3        202.0      9.6      8.1     91.7     0.84       9.65      33.70
                           4        232.0     11.9      8.1    139.1     0.95      10.00      40.10

2A07834L     0.222222      0         44.0     18.9      2.7     21.8     0.95       5.75       9.61
                           1         49.6     15.7      2.6     22.8     0.95       5.67      10.40
                           2         37.2     20.7      2.0     23.9     0.79       4.42      10.20
                           3         42.9     15.5      4.0     20.8     0.84       5.56      10.70
                           4         66.0     19.8      3.3     22.1     0.84       5.95      11.90

2A07834U     0.222222      4         50.0     25.2     14.7     60.4     0.79       4.97      17.90

2A07835L     0.093721      1         97.7     25.1      1.3     23.1     1.08       9.80      15.80
                           2         93.7     24.6      1.5     27.1     1.10      11.60      16.90
                           3         97.4     24.8      1.5     25.4     1.00      10.00      16.80
                           4        147.0     21.7      5.5     23.7     1.16      11.35      20.00

2A07835U     0.093721      4        113.0     14.2      3.7     24.8     0.95       9.90      16.00

2A07881L     0.074963      1        538.0    174.9     27.9    183.4     5.42      16.00     104.60
                           2        513.0    203.5     29.8    180.5     4.66      16.50      99.25
                           3        587.0    174.9     21.0    184.2     5.63      16.90     103.10
                           4        973.0    156.6      9.5    394.9     8.00      18.30     157.60

2A07881U     0.074963      3        429.0    150.3     21.6     75.0     5.00      18.60      73.60
                           4        758.0    125.8     23.1    117.1     6.42      22.10     101.10

2A07882L     0.450450      1        105.5     22.4     16.3     16.4     1.16       7.70      16.70
                           2         96.1     22.1     14.6     20.3     0.10       7.20      15.80
                           3        118.0     21.0     15.6     20.0     1.21       8.40      17.80
                           4        160.0     20.7     26.1     20.6     1.37      10.60      23.50

2A07882U     0.450450      4         83.0     22.3     16.0     13.0     1.16       8.00      13.40

2A07891L         -         1         33.2     60.0     46.3     11.6     0.95       4.16      18.50
                           2         36.9     45.2     46.9     13.1     0.95       4.12      17.80
                           3         40.9     46.8     45.8     11.7     1.00       5.00      18.10
                           4         65.4     46.8     49.0     13.2     1.16       5.66      19.10

2A07892L         -         1         59.7     25.0      3.5     12.9     1.24       6.57      10.90
                           2         58.8     18.6      3.4     13.8     1.32       8.15      10.80
                           3         66.4     14.7      3.2     13.3     1.37       7.65      11.60
                           4         81.8     21.2      7.0     10.6     1.16       7.21      13.00
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                                                   SAS

STRM_ID          WGT     SAMPLE     ALKA11     SO416     NO316      CL16     FTL16     SIO211     COND11

2A07893L          -        0          82.0      13.0       0.0      28.8      0.63       7.40      13.45
                           1          89.9      12.4       0.6      28.5      0.76       7.50      14.40
                           2          82.4      16.4       0.0      29.9      0.74       6.92      14.20
                           3          87.6      12.5       1.3      29.1      0.79       7.90      15.10
                           4         111.0      12.5       2.2      28.8      0.79       4.88      16.50

2A07894L          -        1          81.5      13.8       1.4      13.5      0.79       7.10      11.60
                           2          66.3      16.1       2.0      15.7      1.00       7.70      11.70
                           3          81.0      12.1       1.2      14.6      0.89       7.55      12.40
                           4         103.0      14.0       3.5      13.3      0.84       7.75      14.50

2A07895L          -        1         137.0      22.5       2.0      13.9      1.21       9.40      17.80
                           2         126.0      20.0       2.4      14.2      1.10       8.64      17.80
                           3         139.0      20.7       0.7      13.3      1.10       9.87      18.35
                           4         181.0      21.9       3.8      12.8      1.16      11.15      22.00

2A07895U          -        3         113.0      17.4       0.4      11.9      1.00       9.45      15.30

2A07896L          -        1          51.7      22.3       1.3      15.4      0.74       6.25      10.10
                           2          45.4      22.9       0.9      16.7      0.95       6.60      10.10
                           3          44.2      21.7       1.7      15.8      0.89       6.30      10.30
                           4          67.1      24.4       2.4      13.6      0.95       6.90      11.80

2A08801L      0.591716     0        1662.0      55.6       1.6      40.6      1.68       8.70     168.95
                           1        1604.0      67.0       1.8      37.5      1.89      10.10     164.20
                           2        1092.0      80.4       1.8      41.2      1.84       7.46     120.50
                           3        1797.0      43.9       2.4      38.6      2.11      10.50     180.40
                           4        1750.0      53.7       4.7      40.3      2.21      10.80     177.80

2A08801U      0.591716     4        1650.0      49.6       1.7      32.7      1.95       8.77     164.20

2A08802L      0.456621     1          92.0      15.2       6.2      18.9      1.16       7.50      13.70
                           2          85.0      14.7       7.0      18.7      1.05       6.88      13.80
                           3          86.3      15.1       5.5      19.0      1.10       7.55      13.70
                           4          93.5      11.0       7.1      18.6      1.16       7.65      13.80

2A08802U      0.456621     4         112.0      15.0       1.1      15.3      1.47      10.60      15.00

2A08803L      0.393701     1         136.2      25.2       2.7      18.6      1.42       7.30      23.65
                           2         194.0      24.8       2.6      22.8      1.32       8.10      24.80
                           3         183.0      26.9       2.4      18.1      1.37       7.56      25.20
                           4         231.0      29.8       6.2      20.2      1.47       7.95      29.30

2A08803U      0.393701     4         268.0      21.2       9.5      22.8      1.58       7.70      31.60

2A08804L      1.010101     1          58.8      24.8       2.5      19.7      1.10       6.45      11.50
                           2          53.8      22.9       3.9      18.9      1.26       7.30      11.70
                           3          63.2      20.5       3.1      18.9      1.08       6.92      12.05
                           4          75.5      24.3       5.5      17.7      1.00       6.75      12.95

2A08804U      1.010101     4          62.9      22.7       5.3      18.1      1.00       6.30      11.70
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                                              SAS

STRM_ID          WGT    SAMPLE      ALKA11     SO416     NO316      CL16     FTL16      SIO211     COND11

2A08805L    0.302115    1            124.0      35.2       8.0      27.0      1.37        8.10      20.08
                        2            117.5      32.1       6.0      30.2      1.42       11.70      20.50
                        3            113.0      32.1       7.0      24.0      1.42        8.86      20.50
                        4            151.0      38.9       9.2      27.3      1.47        7.75      24.40

2A08805U    0.302115    4             61.5      32.1       0.8      18.2      1.10        7.55      13.40

2A08806L    1.666667    1            161.0      15.6      26.3      34.7      1.53       11.20      26.24
                        2            175.0      13.8      20.8      27.4      1.58       13.20      23.00
                        3            157.0      30.0      42.6      31.6      1.58       10.60      25.60
                        4            192.0      11.9      24.0      28.5      1.63       12.90      26.30

2A08806U    1.666667    4            154.0      11.7       7.6      22.3      1.63       11.80      20.10

2A08808L    0.311526    1            177.5     167.9       5.4      28.6      1.66        8.25      46.17
                        2            226.0     169.9       4.1      30.7      1.63        9.75      47.80
                        3            205.0     198.0       5.0      26.5      1.68        8.81      50.40
                        4            318.0     273.8       8.5      26.4      2.08        9.01      69.15

2A08808U    0.311526    4            139.0      43.7       8.0      21.9      1.37       10.00      22.70

2A08809L    0.510204    0             84.0      19.5       1.6      21.7      0.84        7.55      13.71
                        1             90.4      18.0       1.8      22.4      0.95        7.80      14.50
                        2E            75.1      30.2       5.2      21.3      1.26        6.22      16.10
                        3             90.9      17.0       2.2      21.0      1.08        8.13      15.20
                        4             97.0      21.9       3.5      20.1      1.26        8.40      16.00

2A08809U    0.510204    4             87.0      26.4       3.8      20.1      1.10        8.00      14.90

2A08810L    0.531915    1            134.0      18.4      14.7      30.2      1.10        8.85      20.80
                        2            133.0      27.3      15.1      29.9      1.00        8.40      21.80
                        3            147.0      18.6      14.5      32.2      1.10        9.70      22.60
                        4            183.5      28.4      21.7      34.1      1.18        9.27      28.10

2A08810U    0.531915    4            182.0      14.3       2.0      22.3      1.00       11.70      21.80

2A08811L    0.775194    0            112.5      62.8       2.7      33.3      1.34        8.77      24.03
                        1            118.0      70.4       3.2      35.5      1.58        9.85      24.80
                        2            112.0      76.6       7.5      45.7      1.58        8.50      27.70
                        3            134.0      70.2       3.6      32.4      1.63       10.10      26.80
                        4            179.5      66.4       6.7      34.8      1.87       10.60      31.25

2A08811U    0.775194    4            135.0      50.0       4.6      23.8      1.58       11.30      24.30

2A08891L        -       1             44.1      14.6       0.2      17.3      0.74        5.60       8.85
                        2             39.6      16.8       0.5      19.2      0.66        5.20       8.85
                        3             39.8      14.0       0.5      18.9      0.76        5.75       8.95
                        4             64.0      15.6       0.8      18.4      0.84        6.41      10.10

2A08891U        -       3             51.2      11.7       1.5      21.8      0.74        6.45      10.10
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STRM_ID           WGT     SAMPLE     ALKA11     SO416     NO316     CL16     FTL16     SIO211     COND11

2A08901L     0.133511     1           129.0     15.8       6.0      20.6      1.00       9.50      17.70
                          2           107.5     20.2       9.0      24.7      0.92      10.35      17.95
                          3           125.0     13.7       5.2      21.5      1.00      10.00      18.00
                          4           161.0     18.5       8.2      22.5      0.95      10.10      21.50

2A08901U     0.133511     3            55.9     13.6       0.0      19.8      0.84       7.30      10.70
                          4            65.1     15.7       0.6      17.5      0.84       6.90      11.30

2A08902L     0.124844     0            62.0     15.2       2.0      21.4      0.71       6.45      10.76
                          1            68.5     13.3       1.6      23.2      0.84       6.60      11.40
                          2E           40.8     23.9       3.1      21.0      0.79       4.98      11.30
                          3            58.2     12.4       1.5      20.8      0.79       5.66      11.40
                          4            83.1     14.6       1.6      20.9      0.79       7.10      12.60

2A08902U     0.124844     4            96.3     19.9       3.8      23.7      0.79       7.25      14.50

2A08903L     0.440529     1           112.0     22.9      10.7      32.7      1.05       8.15      19.44
                          2           116.0     21.9      10.0      32.7      1.00       9.45      20.00
                          3           105.0     25.5       9.1      28.8      1.03       8.96      19.00
                          4           140.0     28.3      19.4      33.6      1.10       9.95      23.80

2A08903U     0.440529     3            98.3     27.1       8.0      25.8      0.95       8.91      17.70
                          4           139.0     28.9      20.5      32.2      1.00       9.85      24.20

2A08904L     0.199203     0           173.0     23.9       9.1      30.2      1.10      10.10      25.05
                          1           183.0     23.1       8.1      31.3      1.26      11.60      25.30
                          2E          132.5     42.2      16.5      34.6      1.47       6.58      26.25
                          3           190.0     21.2       6.3      26.9      1.37      11.70      26.20
                          4           191.0     29.8      14.0      29.3      1.32      10.90      27.80

2A08904U     0.199203     3           166.0     12.5       3.2      22.7      1.21      13.20      21.90
                          4           191.0     15.3       4.0      23.2      1.26      13.50      23.50

2A08905L     0.507614     1            71.0     19.1       0.0      19.8      0.89       7.45      11.90
                          2            71.7     17.7       1.5      25.7      0.79       7.04      13.00
                          3            76.0     18.0       1.4      22.3      0.84       7.80      13.10
                          4            97.2     15.8       0.9      21.7      1.05       8.41      14.20

2A08905U     0.507614     3            66.7     17.0       0.4      18.1      0.84       8.00      11.60
                          4            86.3     20.3       0.2      18.0      0.89       8.31      12.80

2A08906L     0.196850     0            69.0     16.4      22.4      34.1      0.84       6.70      16.74
                          1            70.4     16.4      20.9      34.7      0.92       7.05      17.30
                          2E           52.2     35.4      32.6      37.0      1.10       4.14      21.70
                          3            74.9     16.3      19.5      33.9      1.00       7.06      17.90
                          4            50.0     31.9      45.2      23.1      0.95       7.20      13.70

2A08906U     0.196850     4            47.0     37.5      26.1      31.6      0.95       6.30      18.90
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                                                    SAS

STRM_ID              WGT    SAMPLE      ALTL11    ALEX11    ALOR11    DOC11    COLVAL    TURVAL    ORGION

2A07701L        0.120627    1             25.7       0.0       0.0      0.7        15       0.2       2.5
                            2             44.5       3.5       3.0      1.0        15       0.8       4.0
                            3             73.0       2.0       1.0      0.5         5       1.3       2.1
                            4             54.0       5.0       1.0      0.6        20       0.7       2.4

2A07701U        0.120627    3             61.0       3.0       3.0      0.3        10       0.8       1.9
                            4             76.0       2.0       2.0      0.4        10       0.1       2.1

2A07702L        0.236967    0             23.5       3.0       2.0      0.4         5       0.5       0.6
                            1             52.5       2.5       2.0      0.6        10       0.8       1.1
144                         2E           113.0       5.0       4.0      1.4        15      10.0       3.5
                            3             30.0       3.0       2.0      0.6         0       1.6       1.3
                            4             55.0       3.0       5.0      0.3        10       2.2       0.8

2A07702U        0.236967    4             42.0       1.0       1.0      0.3         5       1.8       1.1

2A07703L        0.255102    1            228.0       4.0       3.0      0.9        20       3.0       3.3
                            2            114.0       1.0       0.8      0.7        15       7.9       2.9
                            3            154.0       3.0       1.0      0.5        20       4.9       2.2
                            4            192.0       1.0       0.0      0.8        25       6.2       3.4

2A07703U        0.255102    3            192.0       5.0       4.0      0.6        15       2.0       2.4
                            4            244.0       6.0       3.0      1.0        20       3.4       4.5

2A07801L        0.423729    1            117.0       6.0       6.5      1.6        23       6.9       4.3
                            2             47.0      10.0       9.0      1.7        20       1.4       4.9
                            3             61.0      10.0       7.0      1.2        10       2.4       3.2
                            4            235.0      33.0      34.5      1.4        20      14.5       2.4

2A07801U        0.423729    3             68.0      10.0      10.0      1.2        20       3.3       3.6
                            4            195.0      26.0      23.0      1.4        15      10.5       2.9

2A07802L        0.136426    1             81.2       5.0       1.5      0.6        18       1.4       2.2
                            2             96.0       4.0       2.0      0.6        15       3.1       2.6
                            3            215.0       8.0       1.0      0.9        20       2.0       3.4
                            4            197.0      26.0      18.0      1.1        15       7.4       3.8

2A07802U        0.136426    4            552.0       8.0       4.0      0.9        15       7.8       3.2

2A07803L        0.505051    1             53.5       4.0       3.5      0.9        20       2.0       1.6
                            2             23.0       2.0       2.0      1.1        10       2.1       2.5
                            3             76.0       3.0       3.0      1.2        20       3.9       3.3
                            4            266.0      13.0      14.0      2.0        25      14.2       4.6

2A07803U        0.505051    3            113.0       3.0       2.0      0.6        10       1.8       1.6
                            4            187.0       6.0       6.0      1.0        15       3.0       2.2

2A07805L        0.729927    1             64.0       0.0       3.0      1.0        15       0.5       4.1
                            2             35.0       6.0       3.0      0.8        10       0.4       3.8
                            3             33.0       5.0       2.0      0.7        10       0.9       3.0
                            4            115.0       4.0       2.0      0.8        15       1.5       3.2
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STRM_ID          WGT    SAMPLE      ALTL11    ALEX11    ALOR11   DOC11   COLVAL   TURVAL   ORGION

2A07805U    0.729927    4             47.0       3.0       2.0     0.8       10      0.8      3.3
2A07806L    0.178571    0            118.8       5.5       4.5     0.6       10      0.6      2.6
                        1            262.0       5.0       5.0     0.8       10      1.1      3.3
                        2            102.0       9.0       4.0     0.7       10      3.9      3.7
                        3            335.0       5.0       4.0     0.8       10      8.0      3.3
                        4            244.0       5.0       3.0     0.9       30      2.3      3.5
2A07806U    0.178571    4            173.0       7.0       7.0     1.0       25      1.8      4.6
2A07807L    0.066313    0             68.2       1.0       0.0     0.4       10      0.5      1.6
                        1             83.0       3.5       4.0     1.0       18      1.1      3.5
                        2            126.0       0.0       0.0     1.0       10      2.5      4.5
                        3            124.0       2.0       1.0     0.8       10      3.3      3.4
                        4            372.0       1.0       4.0     0.9       25      6.7      3.8
2A07807U    0.066313    4            179.0       2.0       2.0     0.8       20      2.2      3.4
2A07808L    0.038212    1             22.8       2.0       0.0     0.3        5      0.3      1.1
                        2             34.0       4.0       0.5     0.6       10      0.7      2.7
                        3             99.0       2.0       1.0     0.6        5      3.3      2.8
                        4            126.0       7.0       3.0     0.7       15      1.3      2.7
2A07808U    0.038212    4             91.0       3.0       3.0     0.5       15      0.5      1.8
2A07810L    0.036563    1            145.0       4.0       2.0     0.7       15      0.3      3.0
                        2             16.0       3.0       1.0     0.5       10      0.5      2.4
                        3             49.0       4.0       3.0     0.7       15      0.2      3.5
                        4             50.0       9.0       4.0     0.9       15      0.3      4.1
2A07810U    0.036563    4             32.0       6.0       5.0     0.6        5      0.3      3.3
2A07811L    0.203768    1            496.0      10.0       6.0     0.5       15      0.1      3.4
                        2             29.0       8.0       4.0     0.4       10      0.3      2.3
                        3             54.5      10.5       7.5     0.4       10      0.2      2.6
                        4             51.0       8.5       7.5     0.5       10      0.3      2.8
2A07811U    0.203768    4              8.0      12.0       8.0     0.5        5      0.2      3.1
2A07812L    0.341297    1            106.0       1.0       1.0     1.1       20      0.3      4.8
                        2             25.0       3.5       3.0     0.7       10      0.2      3.3
                        3             33.0       2.0       1.0     0.4       10      0.8      1.8
                        4             77.0       3.0       2.0     0.9        5      0.4      3.2
2A07812U    0.341297    4             81.0       3.0       3.0     0.7       10      0.2      3.1
2A07813L    0.104275    0            127.0       7.0       2.0     0.9       15      3.7      2.8
                        1            114.0       6.0       5.0     1.0       20      2.8      3.2
                        2            112.0      12.0      11.0     0.9       15      5.8      3.3
                        3            183.0       7.5       5.5     1.0       20     10.4      3.2
                        4            660.0       1.0       1.0     1.6       20     22.0      5.1
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                                                SAS

STRM_ID           WGT     SAMPLE      ALTL11     ALEX11     ALOR11     DOC11     COLVAL     TURVAL     ORGION

2A07813U      0.104275    3            716.0        5.0        2.0       1.1         15       24.0        3.8
                          4           1280.0        7.0        4.0       4.8         55       38.0       20.5

2A07814L      0.072516    0             51.3        1.0        1.0       0.8         15        1.9        2.3
                          1             64.0        3.0        3.0       1.2         20        2.8        3.2
                          2            118.0        5.5        2.0       1.5         18        7.2        6.0
                          3            126.0        1.0        1.0       0.9         15        4.1        3.4
                          4           2320.0        1.0        3.0       2.8         50       76.0       10.7

2A07814U      0.072516    3            116.0        2.0        1.0       1.1          5        3.9        4.4
                          4            366.0        1.5        3.0       1.1         23        7.6        4.0

2A07815L      0.059952    1             24.0        0.0        0.0       0.5         13        0.3        1.8
                          2             44.0        3.0        2.0       0.5         15        0.7        2.0
                          3            125.0        3.0        2.0       0.6          5        3.5        3.5
                          4             96.0        4.0        3.0       0.8         10        1.8        3.5

2A07815U      0.059952    4             98.0        5.0        4.0       0.7         10        1.3        3.5

2A07816L      0.084602    1             41.0        1.0        1.0       1.1         10        0.2        5.3
                          2             29.0        3.0        2.0       0.5         10        0.4        2.6
                          3             46.0        3.0        3.0       0.7         10        0.7        3.8
                          4             71.0        4.0        3.0       0.6         10        0.4        2.7

2A07816U      0.084602    4            127.0        6.0        5.0       0.5          5        0.5        2.7

2A07817L      0.096618    1             23.7        2.0        5.0       0.4         10        0.1        1.9
                          2             52.0        8.0        6.0       0.5         10        0.3        2.8
                          3             51.0        8.0        8.0       0.6          5        0.6        3.3
                          4             60.0        6.0        6.0       0.8         10        0.2        4.1

2A07817U      0.096618    4             62.0       20.0       11.0       0.6         10        0.1        4.1

2A07818L      0.990099    1            105.5        1.0        1.0       0.6         15        0.9        2.4
                          2             56.0        4.0        1.0       0.6         10        0.8        3.0
                          3             66.0        3.0        1.0       0.6         10        1.8        3.3
                          4            124.0        6.0        4.0       0.8         15        3.7        3.8

2A07818U      0.990099    3             76.0        4.0        2.0       0.6         15        1.9        3.2
                          4             88.0        5.0        4.0       0.7         15        3.2        3.1

2A07819L      0.027739    1             82.0        2.0        0.0       0.5         10        2.8        1.4
                          2            112.0        7.5        2.5       0.6         10        3.1        2.0
                          3E           579.0        2.0        1.0       1.0         25       31.0        4.6
                          4            196.0       13.0        3.0       0.8         20        7.9        3.5

2A07819U      0.027739    4            477.0        6.0        3.0       0.4         15        5.8        1.6
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                                                   SAS

STRM_ID            WGT    SAMPLE    ALTL11    ALEX11    ALOR11     DOC11    COLVAL    TURVAL    ORGION

2A07820L      0.081566    0           46.8       4.0       0.0       0.5         5       0.5       2.4
                          1          110.1       2.0       6.5       0.5        15       0.5       2.2
                          2           34.0       5.0       2.0       0.7        10       0.8       3.1
                          3           81.0       2.0       2.0       0.5        10       1.8       2.0
                          4           98.0       4.0       2.0       0.7        15       1.3       3.2

2A07820U      0.081566    3           50.0       4.0       3.0       0.4         5       0.5       2.1
                          4           91.0       7.0       5.0       0.9        20       0.4       4.4

2A07821L      0.393701    1           92.4       7.0       5.0       0.8        10       1.7       3.0
                          2          192.0       6.5       3.0       0.5        13       4.6       2.1
                          3          462.0       4.0       2.0       0.7        10       9.8       2.7
                          4          714.0       3.5       1.5       0.6        15       9.3       2.7

2A07821U      0.393701    4          230.0       3.0       1.0       0.7        15       5.9       2.5

2A07822L      0.151976    1          103.0       2.0       1.0       0.5        15       1.3       2.1
                          2           50.0       6.0       0.0       0.5        10       1.9       2.0
                          3           99.0       4.0       1.0       0.5        10       1.4       1.9
                          4           81.0       6.0       2.0       0.8        15       2.0       3.0

2A07822U      0.151976    4          113.0       5.0       2.0       0.5        10       1.8       2.1

2A07823L      0.132275    1          174.5      25.0      15.6       0.4        15       1.1       1.8
                          2          128.0      17.0      16.0       0.4        10       1.8       1.9
                          3          166.0      28.0      14.0       0.3        15       1.6       1.4
                          4          270.0      38.0      12.0       0.7        20       6.0       2.6

2A07823U      0.132275    3          228.0       2.0      71.0       0.3        10       2.0       1.2
                          4         1410.0       6.0       2.0       0.5        20      25.0       1.8

2A07824L      0.080775    1          118.0      10.5       9.0       0.8        15       0.2       3.8
                          2           32.0       9.5       8.5       1.0         8       0.2       4.3
                          3           49.0      15.0       8.0       1.0        10       0.2       4.6
                          4           73.0      12.0      10.0       1.0         5       0.8       4.4

2A07824U      0.080775    4          102.0      26.0      22.0       1.4         5       0.3       6.4

2A07825L      0.043995    0           36.7       5.0       4.0       0.7        15       0.3       3.1
                          1          954.0       4.0       4.0       0.9        10       0.5       4.2
                          2           52.0       9.0       6.5       0.9        18       0.6       4.5
                          3           60.0       6.0       5.0       0.8        15       7.0       3.3
                          4          187.0      11.0      10.0       2.4        15       1.1      11.1

2A07825U      0.043995    3           63.0       3.0       2.0       0.4        10       0.6       2.1
                          4          330.0       8.0       7.0       1.9        20       5.6       9.9

2A07826L      0.245098    1           78.9       3.0       3.0       1.1        15       2.0       3.6
                          2           56.0       3.0       3.0       0.9        25       2.2       3.7
                          3          100.0       3.0       1.0       1.5        20       6.0       5.3
                          4          121.0       2.0       1.0       1.4        25       5.0       5.8
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                                              SAS
STRM_ID         WGT      SAMPLE    ALTL11    ALEX11    ALOR11    DOC11    COLVAL    TURVAL    ORGION

2A07826U     0.245098     3         128.0       4.0       3.0      1.4       20        7.4       5.8
                          4       74000.0       5.0       4.0      7.7      750     1800.0      46.5

2A07827L     0.252525     1          70.5       7.0       2.0      0.5       15        2.4       1.6
                          2         104.0       6.0       3.0      1.3       15        1.6       4.5
                          3          73.0       3.0       1.0      0.5       10        3.5       2.0
                          4         101.0       4.0       1.0      0.9       20        2.3       3.3

2A07827U     0.252525     4          47.0       2.0       2.0      0.6       15        0.6       3.0

2A07828L     0.135870     0          43.4       5.0       4.0      0.6       10        0.3       3.1
                          1          78.1       6.0       6.0      0.6       10        0.4       2.8
                          2          55.0       8.0       6.0      0.6       10        1.6       3.0
                          3         102.0       6.0       5.0      0.7       15        1.6       3.3
                          4        1820.0       7.0       5.0      2.3       35       42.0      10.3

2A07828U     0.135870     3          84.0       7.0       5.0      1.2       15        0.9       6.5
                          4         209.5      13.5      14.0      1.7       18        3.0       9.9

2A07829L     0.118203     1          49.0       1.0       1.0      0.8       15        0.4       3.6
                          2          92.0       6.0       6.0      0.9       15        1.1       4.5
                          3          98.0       4.0       4.0      0.6       10        1.6       3.2
                          4         185.0       4.0       4.0      0.8       10        3.2       3.7

2A07829U     0.118203     3          76.0       5.0       5.0      0.6       15        2.1       2.7
                          4         144.0       7.0       6.0      0.8       10        3.0       3.5

2A07830L     0.184843     0         236.0       4.0       0.0      0.9       15        4.7       3.2
                          1         162.0       4.0       4.0      1.1       20        5.2       4.4
                          2         201.0       9.0       8.0      3.3       30        7.9      18.1
                          3         166.5       3.5       2.0      1.7       20        8.4       8.6
                          4         145.0       6.0       6.0      1.1       25        2.6       5.2

2A07830U     0.184843     4         300.0       2.0       3.0      1.8       35        8.8       8.7

2A07831L     0.035842     0          73.7       0.0       0.0      0.5       15        2.0       1.7
                          1         124.0       3.0       2.0      1.0       20        2.7       3.5
                          2E        372.0       2.0       1.0      1.2       30       42.0       5.0
                          3         143.0       2.0       1.0      1.3       15        5.4       5.3
                          4        1890.0       3.0       1.0      1.0       25       38.0       4.2

2A07831U     0.035842     3         121.0       2.0       1.0      1.0       10        6.1       4.6
                          4        2000.0       1.0       4.0      1.4       40       57.0       6.1

2A07832L     0.056625     1         214.0       4.0       2.0      0.6       10        1.0       2.4
                          2          50.0       0.5       0.3      0.5       10        2.0       2.4
                          3         163.0       2.0       2.0      0.6       10        1.7       3.1
                          4          54.0       6.0       4.0      1.2       25       49.0       5.7

2A07832U     0.056625     3         158.0       3.0       2.0      0.7       15        1.2       3.4
                          4         240.0       7.0       4.0      0.6       10        2.8       2.5
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                                                  SAS
STRM_ID          WGT      SAMPLE       ALTL11      ALEX11      ALOR11      DOC11      COLVAL       TURVAL      ORGION
2A07833L    0.167785      1             231.5         2.5         1.0        0.3          13          1.0         1.0
                          2              52.0         1.0         0.9        0.5          10          2.4         1.7
                          3             124.0         7.0         6.0        0.6          10          1.7         2.2
                          4             144.0         6.0         3.0        0.6          15          6.6         2.0

2A07833U    0.167785      3             147.0         1.0         0.0        0.2          10          0.4         1.0
                          4             135.0         4.0         3.0        0.1          10          1.4         0.6

2A07834L    0.222222      0              60.9         4.0         4.0        0.5          15          0.7         2.3
                          1              78.5         7.5         7.0        1.0          20          1.1         4.8
                          2             136.0        18.0        16.0        1.6          25          2.9         8.4
                          3              93.0         4.0         3.0        1.1          10          1.5         6.1
                          4             123.0         7.0         6.0        1.4          25          1.8         7.2

2A07834U    0.222222      4             220.0         7.0         6.0        0.9          20          3.2         4.9

2A07835L    0.093721      1              35.0         0.0         0.0        0.6          20          0.4         2.1
                          2              30.0         4.0         2.0        1.0          20          0.6         4.3
                          3              65.0         3.0         1.0        0.8          15          1.4         3.4
                          4              89.5         4.0         3.5        0.7          13          2.8         2.9

2A07835U    0.093721      4             192.0         5.0         4.0        0.5          10          3.0         2.2

2A07881L    0.074963      1             136.0         5.0         4.0        1.4          10          3.5         4.4
                          2             182.5         6.0         6.0        1.5          25          9.6         5.3
                          3             190.0        10.0         4.0        1.1          25          8.0         3.6
                          4             194.0        10.0         8.0        2.1          20         14.0         5.0

2A07881U    0.074963      3             158.0         7.0         5.0        1.1          25          4.8         4.0
                          4             138.0         6.0         5.0        2.0          20          3.9         6.2

2A07882L    0.450450      1             109.0         4.5         3.0        0.6          15          0.3         2.5
                          2              38.0         2.0         2.0        0.7           5          1.4         2.9
                          3              43.0         3.0         2.0        0.9          15          0.4         4.4
                          4             162.0         2.0         0.0        0.6          10          0.6         2.8

2A07882U    0.450450      4             120.0         3.0         2.0        0.7          10          1.6         3.3

2A07891L           -      1             193.0         6.0         4.0        0.5          15          0.1         2.7
                          2              16.0         2.0         3.0        0.3          10          0.3         2.0
                          3              36.0         4.0         0.0        0.3           5          0.1         1.8
                          4              36.0         5.0         4.0        0.5           5          0.1         2.5

2A07892L           -      1              82.5         1.0         1.0        0.8          15          0.5         3.3
                          2              37.0         4.0         5.0        0.6          10          0.4         3.0
                          3              71.0         3.0         2.0        1.1          10          1.3         5.6
                          4             163.0         8.0         7.0        1.7          15          2.7         7.8
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                                                  SAS
STRM_ID            WGT    SAMPLE     ALTL11     ALEX11     ALOR11      DOC11     COLVAL     TURVAL     ORGION
2A07893L      -           0            31.7        2.0        1.0        0.4         10        0.3        2.0
                          1            78.5        3.0        4.0        0.5         20        0.3        2.0
                          2            30.0        4.0        5.0        0.4         10        0.5        2.0
                          3            93.0        4.0        2.0        0.7         15        1.7        2.9
                          4            70.0        3.0        2.0        0.5         15        0.8        2.1

2A07894L      -           1            70.0        2.0        0.0        0.7         15        0.3        2.7
                          2            65.0        2.0        2.0        0.5         10        0.8        2.1
                          3            73.5        2.0        1.5        0.5         10        1.5        2.1
                          4           208.0        3.0        3.0        0.7         10        2.5        2.9

2A07895L      -           1           166.0        3.0        2.0        0.7         15        0.8        2.4
                          2            28.0        2.0        1.0        0.8          5        1.1        2.9
                          3            96.0        4.0        1.0        0.8         15        1.0        2.7
                          4           213.0        1.5        0.0        0.6         15        1.5        2.1

2A07895U      -           3            82.0        2.0        2.0        0.6         15        1.1        2.3

2A07896L      -           1            75.0        0.0        0.0        0.4         20        0.2        2.1
                          2            34.0        5.0        4.0        0.6         20        0.2        2.6
                          3            54.0        3.0        7.0        0.3         15        0.6        1.4
                          4            99.0        4.0        4.0        0.6         10        1.2        2.9

2A08801L      0.591716    0            31.4        0.0        1.0        0.7         10        1.0        1.4
                          1            70.0        2.0        2.0        1.1         10        2.0        2.5
                          2           196.0        6.0        4.0        4.3         45        9.1       11.7
                          3            46.0        7.0        5.0        0.7         15        2.1        1.5
                          4           258.0        5.0        5.0        1.7         25       20.0        3.7

2A08801U      0.591716    4            57.0        3.0        2.0        1.4         15        1.4        3.4

2A08802L      0.456621    1           164.0        3.0        2.0        0.4         15        1.6        1.9
                          2            44.0        2.0        0.8        0.4         10        3.3        1.8
                          3            52.0        2.0        1.0        0.4         15        2.3        1.9
                          4           123.0        0.0        0.0        0.4         10        2.9        2.1

2A08802U      0.456621    4           320.0        4.0        1.0        0.9         20        5.4        3.9

2A08803L      0.393701    1            43.3        8.0        1.0        0.7         15        2.4        1.7
                          2            41.0        2.0        1.0        0.6         20        4.9        2.2
                          3            45.0        1.0        1.0        0.9         20        6.7        3.3
                          4            90.0        1.0        0.0        0.8         30        9.5        3.2

2A08803U      0.393701    4            46.0        1.0        1.0        0.8         20        4.8        3.1

2A08804L      1.010101    1           107.0        0.0        0.0        0.4         15        0.6        2.0
                          2            72.0        2.0        2.0        0.5          5        0.9        2.6
                          3           110.5        2.5        2.0        0.4         13        2.3        1.9
                          4           171.0        3.0        3.0        0.5         15        1.5        2.7

2A08804U      1.010101    4            78.0        3.0        3.0        0.4         15        2.2        2.2
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                                                     SAS

STRM_ID             WGT   SAMPLE      ALTL11     ALEX11     ALOR11     DOC11     COLVAL     TURVAL     ORGION

2A08805L       0.302115   1             67.6        4.0        2.0       0.6         15        2.2        2.7
                          2             64.5        2.5        2.5       0.6         10        2.5        2.8
                          3             88.0        2.0        1.0       0.9         15        5.3        3.5
                          4            159.0        1.0        1.0       0.9         20        4.8        4.2

2A08805U       0.302115   4            103.0        6.0        4.0       0.9         20        5.9        5.0

2A08806L       1.666667   1            102.1        4.0        3.0       1.4         20        2.0        6.9
                          2            157.0        4.0        4.0       0.6         20        7.2        2.7
                          3            172.0        2.0        2.0       1.1         20       12.5        5.1
                          4            134.0        2.0        1.0       1.0         20       11.0        5.0

2A08806U       1.666667   4            139.0        3.0        3.0       1.0         20        4.8        4.6

2A08808L       0.311526   1             78.7        4.0        2.5       0.9         13        2.2        3.5
                          2             59.0        3.0        2.0       0.5          5        1.7        1.6
                          3             86.0        2.0        1.0       0.6         10        5.5        1.9
                          4            182.0        4.5        2.5       1.2         20       15.9        4.3

2A08808U       0.311526   4            242.0        6.0        4.0       1.1         25       10.8        5.0

2A08809L       0.510204   0             42.8        1.0        0.0       0.3          5        1.0        1.6
                          1            108.0        2.0        1.0       0.7         20        2.3        3.3
                          2E           648.0        8.0        8.0       2.0         40       40.0       10.3
                          3            125.0        1.0        1.5       0.8         15        5.9        3.3
                          4            324.0        2.0        2.0       1.3         30        9.5        6.0

2A08809U       0.510204   4            282.0        2.0        2.0       1.2         25        6.3        6.1

2A08810L       0.531915   1            115.0        1.0        0.0       0.4         15        1.6        1.5
                          2             48.0        0.6        0.4       0.6         15        2.9        2.6
                          3             84.0        2.0        1.0       0.7         10        2.5        3.1
                          4            186.0        3.0        2.0       1.0         15        7.1        4.0

2A08810U       0.531915   4             91.0        2.0        2.0       0.5         10        0.8        1.8

2A08811L       0.775194   0             62.9        2.0        0.5       0.3          8        1.4        1.2
                          1             61.0        3.0        2.0       0.5         20        1.3        2.1
                          2            103.0        5.0        2.0       0.7         15        7.3        2.8
                          3             73.0        4.0        1.0       0.7         10        2.7        2.9
                          4             95.5        4.5        1.5       1.0         20        2.0        4.0

2A08811U       0.775194   4            114.0        1.0        1.0       0.7         20        3.5        3.0

2A08891L           -      1            160.0        3.0        3.0       0.3         10        0.5        1.6
                          2             46.5        2.5        3.0       0.5         10        0.8        2.4
                          3             89.0        5.0        5.0       0.4         10        0.8        2.4
                          4             61.0        6.0        6.0       0.8         15        1.4        3.9

2A08891U           -      3            196.0        4.0        3.0       0.5         10        1.9        2.9
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                                                    SAS
STRM_ID             WGT    SAMPLE      ALTL11     ALEX11     ALOR11     DOC11     COLVAL     TURVAL     ORGION
2A08901L        0.133511    1             86.0        1.0        0.0       0.6         15        2.3        2.4
                            2            371.5        5.0        4.0       1.0         25       12.4        4.2
                            3            400.0        4.0        2.0       0.7         10        6.2        2.9
                            4            189.0        5.0        2.0       0.8         20       10.0        3.1

2A08901U        0.133511    3            168.0        3.0        2.0       0.5         15        2.3        2.1
                            4            336.0        4.0        4.0       1.0         10        4.5        4.6

2A08902L        0.124844    0             46.2        2.5        2.0       0.3         13        0.9        1.4
                            1             59.0        7.0        5.0       0.7         15        1.6        3.2
                            2E           162.0       10.0        8.0       1.1         15        9.5        5.4
                            3            102.0        4.0        2.0       1.1         10        2.8        5.4
                            4            200.0        5.0        4.0       1.2         20        5.2        5.3

2A08902U        0.124844    4            194.0        4.0        3.0       1.0         15        7.0        4.7

2A08903L        0.440529    1             54.8        6.0        3.0       0.6         10        1.0        3.0
                            2              5.0        2.0        2.0       0.5         15        1.6        2.3
                            3            112.0        2.5        1.5       0.7          8        4.3        2.8
                            4            119.0        2.0        1.0       0.7         10        3.8        3.3

2A08903U        0.440529    3            114.0        2.0        1.0       0.6         10        4.6        2.4
                            4            184.0        2.0        1.0       0.7         15        4.5        3.1

2A08904L        0.199203    0             84.3        1.0        0.0       0.8         15        5.9        2.9
                            1             99.0        3.0        2.0       0.6         15        3.8        2.4
                            2E          6840.0        5.0        3.0       3.4        400     1550.0       20.2
                            3            109.0        3.0        1.0       0.6         10        6.5        2.6
                            4            492.0        1.0        1.0       1.1         30       20.0        4.8

2A08904U        0.199203    3            118.0        2.0        1.0       0.5          5        4.0        2.4
                            4            185.0        1.0        1.0       0.7         15        4.0        3.0

2A08905L        0.507614    1            146.0        3.0        3.0       0.6          5        0.5        2.6
                            2             37.0        3.0        3.0       0.6          5        1.0        2.7
                            3             48.0        5.0        2.0       0.4         15        0.7        2.0
                            4             73.0        6.0        4.0       0.6         10        1.1        2.6

2A08905U        0.507614    3             58.0        3.0        2.0       0.6         10        0.5        2.5
                            4            108.0        6.0        3.0       0.6         15        1.4        2.7

2A08906L        0.196850    0            159.0        2.0        1.0       1.1         20        5.4        4.5
                            1            286.0        6.0        3.0       1.0         30       11.6        4.9
                            2E          3920.0       22.0       20.0       5.4        350     1000.0       39.3
                            3            270.0       12.0        3.0       1.4         30       22.0        7.8
                            4           1420.0        5.0        4.0       1.3         30       25.0        7.7

2A08906U        0.196850    4           1730.0        5.0        4.0       1.8         40       55.0       10.8
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                                     SAS
STRM_ID          WGT    SAMPLE     PTL11     NH416     TURVAL     CONIS     TMPSTR

2A07701L    0.120627    1              9       0.0        0.2        12        7.6
                        2              4       0.4        0.8        10        8.0
                        3             14       0.6        1.3        15       13.8
                        4             11       0.2        0.7        18       18.0

2A07701U    0.120627    3             13       1.9        0.8        10       12.0
                        4             10       0.1        0.1         7       12.0

2A07702L    0.236967    0              8       0.4        0.5        90       13.0
                        1             12       1.2        0.8        92       17.2
                        2E            26       0.3       10.0        85       16.0
                        3             20       0.8        1.6       119       19.9
                        4             21       0.9        2.2       135       20.0

2A07702U    0.236967    4              4       0.3        1.8        50       21.0

2A07703L    0.255102    1             14       0.8        3.0        12       11.5
                        2             19       1.2        7.9        15       11.0
                        3             16       0.8        4.9        20       17.0
                        4             17       0.8        6.2        23       18.5

2A07703U    0.255102    3             21       0.8        2.0        15       15.0
                        4             15       0.7        3.4        16       17.0

2A07801L    0.423729    1             15       0.6        6.9        34        9.1
                        2            105       0.7        1.4        35       10.3
                        3             26       1.3        2.4        39       18.0
                        4             46       1.1       14.5        87       22.0

2A07801U    0.423729    3             26       0.9        3.3        40       19.8
                        4             44       1.6       10.5        75       20.5

2A07802L    0.136426    1             12       0.9        1.4        20        8.3
                        2             18       0.6        3.1        24        7.0
                        3             25       0.8        2.0        28       13.0
                        4             31       0.7        7.4        32       22.0

2A07802U    0.136426    4             63       0.8        7.8        32       18.0

2A07803L    0.505051    1              9       0.9        2.0       132       14.5
                        2             15       0.7        2.1       111       12.0
                        3             21       1.2        3.9       165       18.4
                        4             73       1.6       14.2       211       27.5

2A07803U    0.505051    3             37       1.0        1.8       164       16.0
                        4             50       0.5        3.0       204       21.5

2A07805L    0.729927    1             22       1.2        0.5        11       10.0
                        2           1470       0.8        0.4        11        9.0
                        3             18       4.2        0.9        15       15.0
                        4             31       1.2        1.5        22       18.0
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                                                  SAS
STRM_ID           WGT       SAMPLE             PTL11      NH416      TURVAL       CONIS       TMPSTR
2A07805U     0.729927       4                     17        1.1         0.8          16         16.0
2A07806L     0.178571       0                     40        1.6         0.6          10          8.0
                            1                     44        0.7         1.1          10         12.9
                            2                     49        0.9         3.9          11         12.5
                            3                     70        0.8         8.0          17         13.9
                            4                     71        0.4         2.3          10         16.0
2A07806U     0.178571       4                     45        0.3         1.8           9         14.0
2A07807L     0.066313       0                     10        0.1         0.5          20          6.0
                            1                      8        0.5         1.1          19          8.5
                            2                     17        1.6         2.5          21         11.8
                            3                     21        0.8         3.3          25         12.0
                            4                     35        0.2         6.7          24         16.0
2A07807U     0.066313       4                     11        0.2         2.2          15         13.0
2A07808L     0.038212       1                     25        0.4         0.3          15          7.0
                            2                     23        0.9         0.7          20          7.0
                            3                     27        0.9         3.3          22         13.6
                            4                     48        0.5         1.3          27         20.0
2A07808U     0.038212       4                     13        0.4         0.5          13         16.0
2A07810L     0.036563       1                      9        1.4         0.3           9          7.8
                            2                     10        0.0         0.5           9          5.7
                            3                     11        0.8         0.2          12         15.0
                            4                     10        0.5         0.3          17         20.0
2A07810U     0.036563       4                      7        0.4         0.3          13         15.7
2A07811L     0.208768       1                      4        0.8         0.1          11         10.5
                            2                      9        0.4         0.3          10          7.8
                            3                     11        0.7         0.2          10         13.5
                            4                      5        1.1         0.3          11         19.0
2A07811U     0.208768       4                      5        0.2         0.2          12         16.0
2A07812L     0.341297       1                     16        0.9         0.3           8          6.0
                            2                     18        0.6         0.2           9          7.8
                            3                     20        1.1         0.8          11         15.0
                            4                     27        0.7         0.4          17         14.0
2A07812U     0.341297       4                     15        0.3         0.2          11         14.0
2A07813L     0.104275       0                     27        0.6         3.7          39         12.0
                            1                     23        0.8         2.8          38         13.5
                            2                     28        0.6         5.8          41         14.8
                            3                     34        1.1        10.4          50         17.2
                            4                     59        0.7        22.0          37         16.0
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                                              SAS
STRM_ID          WGT       SAMPLE          PTL11     NH416      TURVAL      CONIS      TMPSTR

2A07813U    0.104275       3                  69       2.5        24.0         29        15.3
                           4                 361       1.8        38.0         25        15.8

2A07814L    0.072516       0                  11       0.5         1.9         35         9.0
                           1                  11       1.2         2.8         35        10.0
                           2                  26       1.0         7.2         50        10.4
                           3                  27       1.9         4.1         44        16.3
                           4                 173       1.9        76.0         52        19.0

2A07814U    0.072516       3                  15       0.7         3.9         31        13.9
                           4                  18       0.6         7.6         42        18.5

2A07815L    0.059952       1                   5       0.4         0.3         13        12.0
                           2                   5       0.6         0.7         15        11.2
                           3                  24       0.8         3.5         17        15.9
                           4                  15       0.8         1.8         16        20.0

2A07815U    0.059952       4                  13       2.1         1.3         15        19.0

2A07816L    0.084602       1                   6       0.7         0.2          9         6.0
                           2                   7       0.5         0.4         10         7.0
                           3                  10       0.7         0.7         10        14.1
                           4                  15       0.6         0.4          7        18.0

2A07816U    0.084602       4                   8       0.9         0.5          2        14.0

2A07817L    0.096618       1                   3       0.4         0.1          5         6.0
                           2                   6       0.4         0.3          8         7.1
                           3                  14       0.8         0.6          9        12.2
                           4                   6       0.5         0.2          7        12.0

2A07817U    0.096618       4                   2       0.7         0.1         10        12.0

2A07818L    0.990099       1                   7       0.6         0.9          6         5.0
                           2                  13       0.4         0.8          8         6.8
                           3                  12       0.8         1.8         11        11.5
                           4                  19       1.6         3.7         12        18.0

2A07818U    0.990099       3                  12       0.8         1.9         12        12.0
                           4                  24       0.9         3.2         12        17.0

2A07819L    0.027739       1                  19       0.4         2.8         21        10.0
                           2                  19       0.4         3.1         25        10.2
                           3E                 65       1.1        31.0         25        16.9
                           4                  47       1.0         7.9         24        23.0

2A07819U    0.027739       4                  63       0.5         5.8         26        18.0
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                                                SAS

STRM_ID          WGT        SAMPLE          PTL11     NH416      TURVAL    CONIS     TMPSTR

2A07820L    0.081566        0                  28       0.5         0.5       11       10.8
                            1                   6       1.0         0.5       17       14.3
                            2                  11       0.6         0.8       11       11.1
                            3                  12       0.8         1.8       14       13.9
                            4                  17       0.2         1.3        9       18.0

2A07820U    0.081566        3                   6       0.4         0.5        9       13.8
                            4                   7       0.4         0.4        7       17.0

2A07821L    0.393701        1                  13       0.0         1.7       12        7.0
                            2                  56       0.5         4.6       18       10.5
                            3                  25       0.6         9.8       12       16.0
                            4                  28       0.7         9.3       10       16.0

2A07821U    0.393701        4                  16       0.9         5.9       16       15.8

2A07822L    0.151976        1                   9       1.1         1.3       22       12.0
                            2                  13       0.3         1.9       15        9.9
                            3                  37       0.8         1.4       24       15.0
                            4                  21       1.0         2.0       27       18.5

2A07822U    0.151976        4                  33       1.6         1.8       29       18.5

2A07823L    0.132275        1                   7       0.4         1.1       16       10.5
                            2                  11       0.6         1.8       16        7.4
                            3                  37       1.2         1.6       22       18.5
                            4                  19       0.7         6.0       24       22.0

2A07823U    0.132275        3                  42       1.2         2.0       14       14.0
                            4                  20       0.5        25.0       39       19.0

2A07824L    0.080775        1                   6       0.0         0.2        8        5.0
                            2                   6       0.4         0.2       10        3.9
                            3                   8       0.7         0.2       10       11.4
                            4                   6       0.5         0.8       13       18.0

2A07824U    0.080775        4                   8       0.4         0.3        9       14.0

2A07825L    0.043995        0                  10       1.1         0.3        8        8.0
                            1                   4       0.6         0.5       13       14.0
                            2                  10       0.6         0.6        9       11.4
                            3                   9       0.6         7.0       10       15.8
                            4                  18       0.1         1.1        8       17.0

2A07825U    0.043995        3                   9       0.5         0.6       10       13.0
                            4                  20       0.4         5.6        7       15.0

2A07826L    0.245098        1                  16       0.4         2.0       38        9.0
                            2                  17       0.6         2.2       36        9.0
                            3                  26       2.5         6.0       50       14.8
                            4                  84       2.6         5.0       52       17.0
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                                                  SAS

STRM_ID           WGT      SAMPLE          PTL11      NH416        TURVAL       CONIS       TMPSTR

2A07826U     0.245098      3                  61        1.9           7.4          49         15.8
                           4                  31        9.0        1800.0          46         18.0

2A07827L     0.252525      1                  11        3.0           2.4          25         13.0
                           2                  14        1.9           1.6          20         15.0
                           3                  13        0.4           3.5          20         12.8
                           4                  27        0.8           2.3          29         19.0

2A07827U     0.252525      4                  10        0.1           0.6          12         16.0

2A07828L     0.135870      0                   8        1.1           0.3           7          7.8
                           1                   7        0.5           0.4           8         10.5
                           2                  11        0.1           1.6           8         11.5
                           3                  12        1.8           1.6           9         13.5
                           4                 108        1.8          42.0          16         14.0

2A07828U     0.135870      3                  10        0.4           0.9           6         13.0
                           4                  20        0.5           3.0           8         15.2

2A07829L     0.118203      1                 194        1.9           0.4           9          8.8
                           2                 166        4.3           1.1           9          8.0
                           3                  53        2.4           1.6          10         14.5
                           4                  59        0.2           3.2          12         16.0

2A07829U     0.118203      3                  12        0.0           2.1           9         12.2
                           4                  12        0.8           3.0           9         14.0

2A07830L     0.184843      0                  29        1.2           4.7          23         12.0
                           1                  27        1.6           5.2          25         12.5
                           2                 120        6.6           7.9          34         13.0
                           3                  43        2.1           8.4          22         15.3
                           4                  11        1.1           2.6          39         20.0

2A07830U     0.184843      4                  90         20           8.8          12         16.0

2A07831L     0.035842      0                  26        0.5           2.0          42          8.0
                           1                  51        0.9           2.7          60         11.0
                           2E                 48        1.3          42.0          42         13.5
                           3                 189        1.2           5.4         112         14.0
                           4                  61        1.0          38.0          42         18.0

2A07831U     0.035842      3                  35        0.5           6.1          21         12.2
                           4                 155        1.6          57.0          24         18.0

2A07832L     0.056625      1                   5        0.3           1.0          11         11.0
                           2                  10        1.1           2.0          10          8.2
                           3                  21        1.7           1.7          13         14.5
                           4                  68        0.9          49.0          19         19.0

2A07832U     0.056625      3                  18        1.2           1.2          12         15.0
                           4                  13        0.4           2.8          13         18.0
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                                                     SAS

STRM_ID          WGT      SAMPLE           PTL11      NH416      TURVAL      CONIS      TMPSTR

2A07833L    0.167785      1                    6        1.0         1.0         17         9.0
                          2                   10        0.0         2.4         18         7.5
                          3                   12        0.9         1.7         23        17.0
                          4                   18        0.8         6.6         30        17.8

2A07833U    0.167785      3                   14        0.4         0.4         22        12.0
                          4                   13        0.3         1.4         30        10.5

2A07834L    0.222222      0                    4        0.3         0.7          6         7.0
                          1                    6        0.7         1.1          6         8.0
                          2                   15        1.0         2.9          8        11.5
                          3                   13        0.4         1.5          8        13.0
                          4                   10        0.2         1.8         11        17.0

2A07834U    0.222222      4                   10        0.2         3.2         12        13.0

2A07835L    0.093721      1                    4        0.6         0.4         11        11.1
                          2                    7        0.7         0.6         11        12.4
                          3                   11        0.1         1.4         14        18.2
                          4                   12        0.9         2.8         12        20.0

2A07835U    0.093721      4                   10        0.6         3.0         14        19.0

2A07881L    0.074963      1                   18        0.4         3.5         72        14.0
                          2                   27        0.9         9.6         70        11.3
                          3                   39        1.3         8.0         92        19.0
                          4                   62        0.9        14.0        149        22.0

2A07881U    0.074963      3                   53        1.5         4.8         62        18.1
                          4                   57        1.6         3.9         54        20.0

2A07882L    0.450450      1                    4        0.6         0.3         10         5.8
                          2                    8        0.8         1.4         10         8.5
                          3                   11        0.5         0.4         13        12.2
                          4                   17        0.3         0.6         19        16.0

2A07882U    0.450450      4                   16        0.2         1.6         10        13.3

2A07891L       -          1                    5        0.7         0.1         10         9.5
                          2                   11        3.1         0.3         11         8.7
                          3                   12        0.9         0.1         11        12.5
                          4                   11        0.1         0.1         17        16.0

2A07892L       -          1                    8        0.6         0.5          9         8.0
                          2                   11        0.6         0.4          9         8.0
                          3                   12        0.9         1.3          9        15.4
                          4                   21        0.4         2.7         12        18.0
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                                                SAS
STRM_ID          WGT      SAMPLE          PTL11     NH416        TURVAL      CONIS       TMPSTR
2A07893L         -        0                   4       1.1           0.3          9          6.5
                          1                   5       1.1           0.3         10         11.0
                          2                   8       1.2           0.5         10          9.5
                          3                  11       0.3           1.7         10         12.1
                          4                   7       2.2           0.8         14         13.0
2A07894L         -        1                   5       0.8           0.3          9          8.0
                          2                  47       1.0           0.8         11         10.9
                          3                  12       0.3           1.5         10         12.6
                          4                  12       0.1           2.5         10         16.0
2A07895L         -        1                   4       0.2           0.8         11          4.0
                          2                   7       0.8           1.1         11          4.0
                          3                  11       0.7           1.0         12         13.9
                          4                   8       0.9           1.5         16         16.0
2A07895U         -        3                  11       0.5           1.1         12         14.8
2A07896L         -        1                   2       0.3           0.2          5          8.0
                          2                  44       0.6           0.2          8         10.0
                          3                  10       0.1           0.6          8         12.1
                          4                   8       0.4           1.2          9         15.0
2A08801L    0.591716      0                   6       0.2           1.0        115         10.0
                          1                   7       0.4           2.0          4         14.5
                          2                  43       0.3           9.1         92         14.5
                          3                  12       0.7           2.1        144         19.0
                          4                  24       0.8          20.0        150         20.0
2A08801U    0.591716      4                  11       0.6           1.4        135         19.0
2A08802L    0.456621      1                   3       1.1           1.6          4          9.8
                          2                   5       0.9           3.3          9         10.0
                          3                   9       0.8           2.3         12         14.3
                          4                   6       0.4           2.9          8         16.0
2A08802U    0.456621      4                  20       0.5           5.4         13         17.5
2A08803L    0.393701      1                   5       0.6           2.4          7          9.5
                          2                  10       0.5           4.9         20         14.0
                          3                  10       0.4           6.7         20         17.0
                          4                  14       1.5           9.5          1         17.0
2A08803U    0.393701      4                  10       1.1           4.8         18         17.0
2A08804L    1.010101      1                   9       1.2           0.6          8          9.9
                          2                  12       1.0           0.9          8          9.0
                          3                  10       0.7           2.3         10         14.2
                          4                  12       0.3           1.5         10         17.5
2A08804U    1.010101      4                  10       0.4           2.2         10         16.5
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                                                  SAS
STRM_ID          WGT      SAMPLE           PTL11      NH416       TURVAL      CONIS       TMPSTR

2A08805L    0.302115      1                   13        0.2          2.2         11         11.0
                          2                    8        0.6          2.5         16         15.5
                          3                   14        0.6          5.3         15         18.0
                          4                   17        0.5          4.8         19         18.0

2A08805U    0.302115      4                    6        0.6          5.9         18         16.0

2A08806L    1.666667      1                   26        2.0          2.0         20         10.5
                          2                   22        0.8          7.2         20         17.7
                          3                   49        2.9         12.5         23         15.0
                          4                   37        1.9         11.0         19         16.0

2A08806U    1.666667      4                   21        0.4          4.8         16         16.5

2A08808L    0.311526      1                   11        0.2          2.2         29          9.0
                          2                    4        0.4          1.7         31         13.7
                          3                    9        0.2          5.5         39         14.0
                          4                   16        0.2         15.9         63         21.0

2A08808U    0.311526      4                   22        0.1         10.8         20         18.0

2A08809L    0.510204      0                    4        0.3          1.0         15          6.9
                          1                    6        0.4          2.3         22         11.3
                          2E                  70        0.5         40.0         11         14.0
                          3                   13        0.8          5.9         11         18.0
                          4                   21        1.3          9.5         15         20.0

2A08809U    0.510204      4                   11        0.2          6.3          9         19.0

2A08810L    0.531915      1                    5        0.5          1.6         11         10.5
                          2                   12        0.2          2.9         18         11.2
                          3                   14        1.1          2.5         20         16.9
                          4                   24        2.1          7.1         19         14.0

2A08810U    0.531915      4                    7        0.5          0.8         18         14.0

2A08811L    0.775194      0                    4        0.2          1.4         23         10.7
                          1                    6        0.4          1.3         27         16.0
                          2                   15        0.1          7.3         20         16.5
                          3                   12        0.6          2.7         22         18.9
                          4                    9        0.5          2.0          4         19.0

2A08811U    0.775194      4                   10        0.3          3.5         13         18.0

2A08391L       -          1                    3        0.6          0.5          9          8.5
                          2                    7        0.4          0.8          7          6.2
                          3                   10        0.3          0.8         10         13.9
                          4                    9        0.4          1.4          9         19.0

2A08391U       -          3                   20        1.2          1.9         11         14.0
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                                       SAS
STRM_ID             WGT    SAMPLE      PTL11    NH416    TURVAL    CONIS    TMPSTR
2A08901L       0.133511    1              19      1.7       2.3       11      13.0
                           2              49      1.6      12.4       12      11.9
                           3              23      0.7       6.2       15      20.5
                           4              25      1.1      10.0       24      21.5
2A08901U       0.133511    3              16      0.0       2.3        9      14.0
                           4              10      0.2       4.5        8      15.0
2A08902L       0.124844    0               3      0.2       0.9        8       5.5
                           1               5      0.9       1.6        8       9.2
                           2E             18      0.4       9.5        9      11.5
                           3              12      0.3       2.8       10      15.0
                           4               9      0.5       5.2       15      20.0
2A08902U       0.124844    4              14      0.5       7.0        9      18.0
2A08903L       0.440529    1               8      0.9       1.0       15       9.5
                           2              16      1.2       1.6       12      11.2
                           3              17      1.0       4.3       17      16.0
                           4              18      2.8       3.8       20      18.0
2A08903U       0.440529    3              16      1.2       4.6       20      16.0
                           4              20      3.2       4.5       20      17.0
2A08904L       0.199203    0               8      0.1       5.9       18      10.1
                           1               9      0.2       3.8       18      12.0
                           2E             11      9.5    1550.0       22      14.1
                           3              14      0.9       6.5       22      17.9
                           4              27      1.4      20.0       22      19.0
2A08904U       0.199203    3              12      0.5       4.0       15      15.9
                           4              16      0.1       4.0       19      17.0
2A08905L       0.507614    1               4      1.0       0.5       10      12.0
                           2               9      0.9       1.0        8       8.0
                           3              10      0.8       0.7       10      16.5
                           4               8      0.2       1.1       15      23.0
2A08905U       0.507614    3              10      0.4       0.5        8      16.0
                           4               6      0.2       1.4       14      23.5
2A08906L       0.196850    0              16      1.1       5.4       11       8.0
                           1              23      2.2      11.6       11      15.7
                           2E              4       16    1000.0       17      14.0
                           3              44      3.3      22.0       12      15.2
                           4              40      0.9      25.0        7      17.5
2A08906U       0.196850    4              88      4.9      55.0       12      17.0
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                                            SAS
STRM_ID         WGT      SAMPLE       PH_CLO     PH_OPN     PHSTVL     DICVAL     ALKA11

2A07701L   0.120627      1              6.83       6.89       7.03       1.25       90.0
                         2              6.99       6.88       7.08       1.26       84.5
                         3              7.06       7.06       7.12       1.26       93.3
                         4              7.33       7.32       7.27       1.80      147.0

2A07701U   0.120627      3              6.57       6.59       6.70       0.63       38.0
                         4              6.73       6.75       6.61       0.88       55.0

2A07702L   0.236967      0              8.72       8.51       8.64      12.97     1174.0
                         1              8.66       8.57       8.69      12.40     1137.5
                         2E             8.22       8.09       8.22      11.32      967.0
                         3              8.38       8.34       8.27      15.86     1300.0
                         4              8.21       8.20       8.20      17.15     1542.0

2A07702U   0.236967      4              6.97       6.95       6.95       5.84      458.0

2A07703L   0.255102      1              6.77       6.62       6.94       2.00      147.0
                         2              6.90       6.74       6.93       1.98      145.5
                         3              7.01       6.94       6.95       2.06      143.0
                         4              6.92       6.90       7.00       2.44      181.0

2A07703U   0.255102      3              6.94       6.72       6.94       1.55       97.9
                         4              6.87       6.84       6.96       1.87      132.0

2A07801L   0.423729      1              8.69       8.47       8.51       4.68      450.0
                         2              8.33       7.73       8.21       4.33      384.0
                         3              8.16       7.84       8.19       4.04      370.0
                         4              8.83       8.82       8.81       9.03      886.0

2A07801U   0.423729      3              8.50       8.22       8.38       3.95      364.0
                         4              8.51       8.51       8.51       7.71      729.0

2A07802L   0.136426      1              7.16       6.93       7.44       2.61      219.5
                         2              7.25       7.11       7.24       2.55      211.0
                         3              7.44       7.12       7.44       2.76      228.0
                         4              7.64       7.53       7.67       2.99      278.0

2A07802U   0.136426      4              7.25       7.20       7.35       3.27      281.0

2A07803L   0.505051      1              8.51       8.39       8.50      18.57     1719.5
                         2              8.07       7.83       8.05      17.51     1483.0
                         3              8.18       8.09       8.11      22.48     1929.0
                         4              8.26       8.25       8.29      31.80     2896.0

2A07803U   0.505051      3              8.09       7.99       8.02      25.75     2201.0
                         4              8.00       8.03       8.06      33.08     3019.0

2A07805L   0.729927      1              6.78       6.66       7.12       1.11      106.0
                         2              6.90       6.68       6.99       1.16       85.5
                         3              7.03       6.81       7.03       1.40      105.0
                         4              7.15       7.12       7.11       2.35      189.0
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                                            SAS
STRM_ID           WGT      SAMPLE      PH_CLO      PH_OPN      PHSTVL      DICVAL      ALKA11
2A07805U     0.729927      4             6.93        6.89        6.93        1.60       111.0
2A07806L     0.178571      0             6.18        5.89        6.90        1.20       116.0
                           1             6.97        6.86        7.06        1.25       118.0
                           2             6.97        7.07        7.06        1.25        99.4
                           3             7.08        6.93        6.97        1.36        95.7
                           4             6.93        6.94        6.93        1.56       133.0
2A07806U     0.178571      4             6.69        6.49        6.70        1.01        83.0
2A07807L     0.066313      0             6.32        6.14        7.20        1.89       158.0
                           1             7.11        6.83        7.35        2.02       177.0
                           2             7.15        6.90        7.36        1.94       159.0
                           3             7.32        7.23        7.31        2.23       189.0
                           4             7.25        7.18        7.35        2.53       228.0
2A07807U     0.066313      4             6.93        6.88        7.11        1.88       172.0
2A07808L     0.038212      1             7.15        6.83        7.17        1.96       162.0
                           2             6.87        6.60        7.20        2.02       173.0
                           3             7.17        7.19        7.23        1.55       127.0
                           4             7.35        7.32        7.37        2.36       213.0
2A07808U     0.038212      4             7.16        7.16        7.13        2.53       202.0
2A07810L     0.036563      1             6.61        6.51        6.88        0.89        68.5
                           2             6.70        6.57        6.88        0.96        60.9
                           3             6.97        6.75        7.07        0.92        68.6
                           4             7.33        7.27        7.32        1.27       113.0
2A07810U     0.036563      4             6.61        6.57        6.63        0.95        64.9
2A07811L     0.208768      1             6.28        6.28        6.26        0.35        13.4
                           2             6.39        6.36        6.37        0.43        17.5
                           3             6.40        6.40        6.55        0.45        17.6
                           4             6.50        6.61        6.47        0.59        37.0
2A07811U     0.208768      4             6.24        6.28        6.24        0.53        23.6
2A07812L     0.341297      1             6.80        6.52        7.01        1.25        99.7
                           2             6.94        6.73        7.09        1.31       100.3
                           3             7.01        6.81        7.14        1.36       108.0
                           4             7.12        7.11        7.09        1.97       153.0
2A07812U     0.341297      4             6.83        6.79        6.80        1.32        85.4
2A07813L     0.104275      0             7.20        6.44        7.75        3.91       358.0
                           1             7.59        7.16        7.72        4.31       363.0
                           2             7.98        7.78        8.07        4.09       357.0
                           3             7.97        7.84        7.83        4.56       395.0
                           4             7.52        7.45        7.54        4.99       448.0
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                                              SAS
STRM_ID           WGT      SAMPLE        PH_CLO        PH_OPN        PHSTVL        DICVAL        ALKA11
2A07813U     0.104275      3               7.41          7.20          7.43          3.08         254.0
                           4               7.10          6.89          7.10          2.98         293.0

2A07814L     0.072516      0                -             -            7.73          3.72         322.0
                           1               7.78          7.21          7.91          4.31         373.0
                           2               7.53          7.31          7.67          3.57         297.0
                           3               7.61          7.53          7.51          4.08         352.0
                           4               7.55          7.43          7.67          4.88         444.0

2A07814U     0.072516      3               7.43          7.29          7.39          2.86         229.0
                           4               7.54          7.35          7.63          4.17         368.0

2A07815L     0.059952      1               6.91          6.70          6.98          1.19          95.5
                           2               6.65          6.53          7.04          1.21          94.1
                           3               6.75          6.75          6.86          0.94          70.3
                           4               6.91          6.89          6.91          1.38         103.0

2A07815U     0.059952      4               6.91          6.85          6.93          1.11          84.8

2A07816L     0.084602      1               6.54          6.39          6.72          0.74          46.4
                           2               6.57          6.54          6.81          0.78          64.9
                           3               6.78          6.74          6.89          0.78          58.2
                           4               6.91          6.82          6.92          1.03          72.1

2A07816U     0.084602      4               6.55          6.49          6.49          0.48          31.7

2A07817L     0.096618      1               6.61          6.53          6.59          0.69          36.0
                           2               6.58          6.45          6.65          0.58          27.5
                           3               6.86          6.41          6.64          0.53          27.6
                           4               6.59          6.59          6.58          0.64          40.0

2A07817U     0.096618      4               6.17          6.09          6.06          0.27          12.0

2A07818L     0.990099      1               6.71          6.45          6.91          1.06          81.2
                           2               7.01          6.75          7.10          1.13          86.3
                           3               7.02          6.79          7.08          1.16          92.4
                           4               7.12          7.06          7.18          1.39         115.0

2A07818U     0.990099      3               7.10          6.80          7.08          1.09          97.2
                           4               7.02          6.96          7.06          1.37         113.0

2A07819L     0.027739      1               7.36          7.12          7.34          2.97         244.0
                           2               6.98          6.75          7.47          3.02         251.0
                           3E              7.02          7.04          7.13          2.58         201.0
                           4               7.43          7.42          7.45          3.30         294.0

2A07819U     0.027739      4               7.31          7.21          7.31          4.59         393.0
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                                        SAS
STRM_ID          WGT     SAMPLE     PH_CLO     PH_OPN     PHSTVL     DICVAL     ALKA11

2A07820L    0.081566     0            7.14       7.33       6.96       1.09      108.0
                         1            6.74       6.65       7.07       1.13       70.1
                         2            6.90       6.79       6.91       1.00       75.9
                         3            6.84       6.65       6.93       1.24       80.6
                         4            6.89       6.79       6.94       1.14      102.0

2A07820U    0.081566     3            6.73       6.52       6.83       0.95       55.8
                         4            6.72       6.72       6.70       0.85       67.0

2A07821L    0.393701     1            6.83       6.65       7.06       1.75      127.0
                         2            6.82       6.68       7.13       1.69      137.5
                         3            6.99       6.94       7.06       1.47      115.0
                         4            7.20       7.20       7.19       1.85      158.0

2A07821U    0.393701     4            7.18       7.14       7.16       1.93      158.0

2A07822L    0.151976     1            6.86       6.80       7.10       2.21      149.0
                         2            7.30       7.18       7.30       1.99      158.0
                         3            7.28       7.07       7.34       2.13      169.0
                         4            7.44       7.39       7.44       2.83      241.0

2A07822U    0.151976     4            7.27       7.19       7.30       2.80      237.0

2A07823L    0.132275     1            6.89       6.73       7.00       1.45       91.4
                         2            7.07       6.95       6.98       1.50      110.0
                         3            7.16       7.15       7.26       1.35      106.0
                         4            7.39       7.34       7.38       3.18      271.0

2A07823U    0.132275     3            6.98       6.98       7.23       1.33       99.7
                         4            7.44       7.37       7.45       4.82      408.0

2A07824L    0.080775     1            6.45       6.26       6.67       0.77       45.2
                         2            6.54       6.50       6.69       0.77       52.1
                         3            6.48       6.53       6.81       0.73       50.2
                         4            6.95       6.94       6.86       0.94       72.0

2A07824U    0.080775     4            6.53       6.53       6.56       0.72       53.0

2A07825L    0.043995     0            6.97       7.12       6.72       0.88       80.0
                         1            6.59       6.50       6.88       1.01       58.6
                         2            6.79       6.67       6.82       0.84       52.9
                         3            6.82       6.76       6.93       0.88       60.6
                         4            6.60       6.57       6.66       0.89       76.0

2A07825U    0.043995     3            6.55       6.51       6.63       0.86       40.3
                         4            6.33       6.32       6.52       0.75       51.0

2A07826L    0.245098     1            6.93       6.79       7.10       4.63      357.0
                         2            6.90       6.73       7.05       5.00      359.0
                         3            6.97       7.00       7.09       4.79      327.0
                         4            7.04       7.03       7.06       5.44      412.0
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                                                 SAS
STRM_ID           WGT       SAMPLE        PH_CLO      PH_OPN      PHSTVL      DICVAL      ALKA11

2A07826U     0.245098       3               6.77        6.80        6.92        4.79       298.0
                            4               6.33        6.36        6.42        2.83       221.0

2A07827L     0.252525       1               7.29        7.11        7.37        3.43       279.0
                            2               7.28        7.24        7.26        2.70       220.0
                            3               7.08        7.01        7.19        2.88       205.0
                            4               7.27        7.27        7.16        4.07       318.0

2A07827U     0.252525       4               6.71        6.75        6.69        1.27        77.0

2A07828L     0.135870       0               6.67        6.47        6.65        0.81        44.0
                            1               6.79        6.70        6.86        0.86        47.6
                            2               6.70        6.70        6.82        0.69        43.0
                            3               6.85        6.84        6.72        1.32        54.1
                            4               6.81        6.75        6.87        1.98       155.0

2A07828U     0.135870       3               6.52        6.56        6.58        0.66        31.9
                            4               6.51        6.34        6.38        0.69        40.5

2A07829L     0.118203       1               6.52        6.43        6.88        0.95        66.9
                            2               6.55        6.46        6.88        0.92        65.3
                            3               6.78        6.74        6.83        0.79        62.1
                            4               6.88        6.85        6.83        1.09        82.5

2A07829U     0.118203       3               6.68        6.66        6.78        0.92        63.7
                            4               6.98        6.30        6.91        1.17        89.6

2A07830L     0.184843       0                  -        6.86        7.10        2.41       189.0
                            1               6.82        6.74        7.09        2.80       197.0
                            2               6.23        6.30        6.84        2.82       251.0
                            3               6.99        6.89        7.02        2.62       203.5
                            4               6.94        6.94        7.03        3.84        95.0

2A07830U     0.184843       4               6.66        6.72        6.82        1.34       257.0

2A07831L     0.035842       0                  -        7.13        7.28        3.87       327.0
                            1               7.02        6.86        7.24        4.38       320.0
                            2E              7.00        7.03        7.14        3.69       274.0
                            3               7.22        7.16        7.22        4.52       382.0
                            4               7.13        7.09        7.29        4.10       338.0

2A07831U     0.035842       3               7.21        7.20        7.32        2.23       207.0
                            4               7.30        7.09        7.41        2.73       251.0

2A07832L     0.056625       1               6.94        6.79        6.99        1.18        88.7
                            2               6.84        6.76        6.90        1.27        81.2
                            3               6.91        6.86        6.94        1.34        92.7
                            4               6.93        6.86        6.99        1.46       116.0

2A07832U     0.056625       3               6.94        6.96        7.00        1.30       110.0
                            4               7.06        6.93        7.06        1.46       118.0
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                                          SAS

STRM_ID          WGT        SAMPLE       PH_CLO     PH_OPN     PHSTVL     DICVAL     ALKA11

2A07833L    0.167785        1              7.17       7.00       7.54       2.41      211.5
                            2              7.22       7.05       7.37       2.55      201.0
                            3              7.65       7.62       7.44       2.52      223.0
                            4              7.34       7.32       7.38       3.65      314.0

2A07833U    0.167785        3              6.80       6.81       6.90       3.12      202.0
                            4              6.71       6.65       6.80       3.63      232.0

2A07834L    0.222222        0              6.58       6.49       6.71       0.74       44.0
                            1              6.61       6.46       6.77       0.85       49.6
                            2              6.60       6.64       6.73       0.60       37.2
                            3              6.71       6.67       6.83       0.69       42.9
                            4              6.80       6.83       6.75       0.99       66.0

2A07834U    0.222222        4              6.62       6.54       6.59       0.92       50.0

2A07835L    0.093721        1              6.82       6.72       6.98       1.33       97.7
                            2              6.76       6.74       7.11       1.33       93.7
                            3              6.81       6.78       7.01       1.25       97.4
                            4              6.92       6.84       7.00       1.95      147.0

2A07835U    0.093721        4              6.83       6.80       6.95       1.56      113.0

2A07881L    0.074963        1              8.19       7.98       8.17       6.10      538.0
                            2              8.32       8.28       8.21       5.78      513.0
                            3              8.25       8.15       8.22       6.64      587.0
                            4              8.24       8.21       8.26      10.90      973.0

2A07881U    0.074963        3              7.98       7.72       7.97       4.86      429.0
                            4              7.69       7.66       7.72       8.77      758.0

2A07882L    0.450450        1              6.81       6.65       7.01       1.41      105.5
                            2              7.00       6.89       7.00       1.17       96.1
                            3              7.04       7.00       7.09       1.44      118.0
                            4              7.11       7.11       7.08       2.05      160.0

2A07882U    0.450450        4              6.93       6.85       6.94       0.99       83.0

2A07891L       -            1              6.52       6.55       6.59       0.56       33.2
                            2              6.63       6.60       6.68       0.64       36.9
                            3              6.59       6.59       6.70       0.71       40.9
                            4              6.64       6.69       6.68       0.95       65.4

2A07892L       -            1              6.57       6.34       6.77       0.84       59.7
                            2              6.62       6.58       6.87       0.87       58.8
                            3              6.63       6.69       6.92       0.98       66.4
                            4              6.80       6.75       6.80       1.05       81.8
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                                                    SAS
STRM_ID             WGT      SAMPLE       PH_CLO       PH_OPN       PHSTVL       DICVAL       ALKA11

2A07893L        -             0            6.99         6.63         6.90         1.17         82.0
                              1            6.92         6.72         6.94         1.23         89.9
                              2            6.87         6.87         6.94         1.19         82.4
                              3            6.99         6.97         6.84         1.27         87.6
                              4            6.88         6.86         6.80         1.44        111.0

2A07894L        -             1            6.78         6.67         6.90         1.09         81.5
                              2            6.95         6.86         6.94         1.03         66.3
                              3            6.89         6.86         6.96         1.05         81.0
                              4            6.94         7.02         6.96         1.46        108.0

2A07895L        -             1            6.86         6.71         7.12         1.85        137.0
                              2            6.82         6.65         7.11         1.74        126.0
                              3            6.85         6.93         7.24         1.76        139.0
                              4            7.23         7.10         7.22         2.29        181.0

2A07895U        -             3            6.82         6.83         7.11         1.50        113.0

2A07896L        -             1            6.63         6.62         6.81         0.74         51.7
                              2            6.74         6.68         6.78         0.64         45.4
                              3            6.82         6.78         6.73         0.67         44.2
                              4            6.98         7.02         6.87         0.99         67.1

2A08801L       0.591716       0            7.88         7.27         8.03        19.61       1662.0
                              1            7.98         7.90         8.03        18.38       1604.0
                              2            7.72         7.58         7.73        13.85       1092.0
                              3            8.11         8.12         8.03        22.34       1797.0
                              4            7.93         7.88         7.89        20.19       1750.0

2A08801U       0.591716       4            7.72         7.67         7.67        19.20       1650.0

2A08802L       0.456621       1            6.50         6.47         6.58         1.76         92.0
                              2            6.54         6.42         6.58         1.69         85.0
                              3            6.59         6.51         6.60         1.77         86.3
                              4            6.53         6.51         6.60         1.82         93.5

2A08802U       0.456621       4            6.82         6.82         6.88         1.71        112.0

2A08803L       0.393701       1            6.81         6.59         7.07         2.31        136.2
                              2            6.94         6.79         7.09         2.48        194.0
                              3            6.49         6.39         7.13         2.65        183.0
                              4            7.01         6.98         7.05         3.02        231.0

2A08803U       0.393701       4            6.97         6.97         6.93         3.59        268.0

2A08804L       1.010101       1            6.73         6.62         6.73         0.88         58.8
                              2            6.72         6.75         6.84         0.86         53.8
                              3            6.82         6.82         6.88         0.92         63.2
                              4            6.85         6.86         6.79         1.09         75.5

2A08804U       1.010101       4            6.79         6.77         6.77         0.97         62.9
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                                                    SAS

STRM_ID           WGT        SAMPLE        PH_CLO       PH_OPN       PHSTVL       DICVAL      ALKA11

2A08805L     0.302115        1               6.68         6.51         6.88         1.73       124.0
                             2               6.94         6.96         6.95         1.57       117.5
                             3               6.33         6.30         7.00         1.71       113.0
                             4               6.92         6.91         6.94         2.10       151.0

2A08805U     0.302115        4               6.18         6.19         6.23         2.04        61.6

2A08806L     1.666667        1               6.76         6.80         6.86         2.42       161.0
                             2               6.80         6.81         6.88         2.28       175.0
                             3               6.78         6.81         6.88         2.54       157.0
                             4               6.77         6.81         6.78         2.95       192.0

2A08806U     1.666667        4               6.78         6.80         6.76         2.35       154.0

2A08808L     0.311526        1               6.92         6.67         7.18         2.57       177.5
                             2               7.25         7.18         7.21         2.70       226.0
                             3               6.72         6.62         7.24         2.78       205.0
                             4               7.26         7.21         7.31         3.86       318.0

2A08808U     0.311526        4               6.80         6.74         6.82         2.03       139.0

2A08809L     0.510204        0               6.32         6.78         6.83         1.20        84.0
                             1               6.57         6.33         6.95         1.26        90.4
                             2E              6.78         6.75         6.86         1.25        75.1
                             3               7.06         6.97         6.99         1.41        90.9
                             4               6.78         6.72         6.95         1.21        97.0

2A08809U     0.510204        4               6.77         6.69         6.88         1.06        87.0

2A08810L     0.531915        1               6.94         6.89         7.19         1.71       134.0
                             2               6.86         6.76         7.11         1.57       133.0
                             3               6.58         6.48         7.22         1.89       147.0
                             4               7.10         7.08         7.17         2.39       183.5

2A08810U     0.531915        4               6.83         6.77         6.90         2.69       182.0

2A08811L     0.775194        0               7.14         6.87         7.01         1.45       112.5
                             1               6.94         6.64         7.13         1.49       118.0
                             2               6.98         6.91         7.01         1.58       112.0
                             3               7.08         7.01         7.32         1.78       134.0
                             4               7.13         6.97         7.08         1.98       179.5

2A08811U     0.775194        4               6.89         6.82         6.85         1.72       135.0

2A08891L         -           1               6.50         6.44         6.73         0.69        44.1
                             2               6.49         6.42         6.67         0.66        39.6
                             3               6.24         6.19         6.70         0.65        39.8
                             4               6.64         6.67         6.67         0.96        64.0

2A08891U         -           3               6.14         6.13         6.67         1.14        51.2
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                                                    SAS
STRM_ID           WGT      SAMPLE        PH_CLO        PH_OPN        PHSTVL        DICVAL       ALKA11
2A08901L      0.133511     1               6.95          6.79          7.29          1.66        129.0
                           2               7.04          6.96          6.97          1.57        107.5
                           3               7.11          7.08          7.25          1.55        125.0
                           4               7.18          7.11          7.14          1.97        161.0

2A08901U      0.133511     3               6.64          6.65          6.75          0.97         55.9
                           4               6.71          6.67          6.71          1.15         65.1

2A08902L      0.124844     0               6.77          6.72          6.85          0.96         62.0
                           1               6.79          6.67          6.86          0.98         68.5
                           2E              6.67          6.67          6.68          0.80         40.8
                           3               6.92          6.85          6.97          0.86         58.2
                           4               6.96          6.91          6.95          1.15         83.1

2A08902U      0.124844     4               6.92          6.80          6.91          1.26         96.3

2A08903L      0.440529     1               6.91          6.93          7.06          1.53        112.0
                           2               6.97          6.85          7.08          1.58        116.0
                           3               6.99          6.97          7.04          1.57        105.0
                           4               7.12          7.14          7.05          1.83        140.0

2A08903U      0.440529     3               6.95          6.95          7.09          1.38         98.8
                           4               7.05          7.08          7.01          1.90        139.0

2A08904L      0.199203     0               7.01          6.76          7.10          2.32        178.0
                           1               7.06          6.96          7.25          2.26        183.0
                           2E              6.76          6.78          6.80          2.13        132.5
                           3               7.20          7.20          7.23          2.57        190.0
                           4               6.94          6.80          6.83          2.60        191.0

2A08904U      0.199203     3               6.86          6.86          6.89          2.65        166.0
                           4               6.87          6.79          6.85          2.63        191.0

2A08905L      0.507614     1               6.79          6.58          6.83          1.07         71.0
                           2               6.70          6.57          6.79          1.11         71.7
                           3               6.80          6.83          6.88          1.16         76.0
                           4               7.18          7.09          7.19          1.09         97.2

2A08905U      0.507614     3               6.91          6.93          7.03          1.02         66.7
                           4               7.10          7.06          7.11          0.96         86.3

2A08906L      0.196850     0               6.63          6.63          6.46          1.42         69.0
                           1               6.52          6.48          6.64          1.26         70.4
                           2E              6.25          6.28          6.32          1.40         52.2
                           3               6.46          6.43          6.53          1.82         74.9
                           4               6.27          6.28          6.26          1.20         50.0

2A08906U      0.196850     4               6.23          6.27          6.31          1.37         47.0
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                                              SAS
STRM_ID          WGT       SAMPLE       PHEQ11       PHAC11       PHAL11       DICE11       ALKA11
2A07701L     0.120627       1            7.34         7.10         7.05         0.90         90.0
                            2            7.12         6.90         6.86         1.11         84.5
                            3            7.41         6.87         6.85         1.04         93.3
                            4            7.37         6.95         6.94         1.65        147.0
2A07701U     0.120627       3            7.05         6.43         6.40         0.44         38.0
                            4            7.00         6.46         6.49         0.59         55.0
2A07702L     0.236967       0            8.57         8.37         8.25        13.90       1174.0
                            1            8.27         8.36         8.36        12.50       1137.5
                            2E           8.38         7.73         7.75        10.70        967.0
                            3            8.43         7.83         7.87        15.10       1300.0
                            4            8.58         7.92         7.93        17.20       1542.0
2A07702U     0.236967       4            7.94         7.17         7.22         5.64        458.0
2A07703L     0.255102       1            7.40         7.07         7.15         1.50        147.0
                            2            7.45         6.86         6.91         1.68        145.5
                            3            7.40         6.86         6.91         1.35        143.0
                            4            7.47         6.90         6.87         1.84        181.0
2A07703U     0.255102       3            7.29         6.93         6.90         1.07         97.9
                            4            7.25         6.68         6.68         1.52        132.0
2A07801L     0.423729       1            8.36         7.65         7.64         5.10        450.0
                            2            7.79         7.52         7.49         4.40        384.0
                            3            7.81         7.57         7.53         3.99        370.0
                            4            8.20         8.44         8.43         9.52        886.0
2A07801U     0.423729       3            7.83         7.42         7.43         4.01        364.0
                            4            8.23         8.02         7.96         7.55        729.0
2A07802L     0.136426       1            7.61         7.17         7.20         2.33        219.5
                            2            7.63         6.77         6.80         2.28        211.0
                            3            7.60         7.02         7.05         2.61        228.0
                            4            7.70         7.13         7.15         2.65        278.0
2A07802U     0.136426       4            7.68         7.13         7.15         3.07        281.0
2A07803L     0.505051       1            8.61         8.29         8.27        18.60       1719.5
                            2            8.49         7.94         7.89        17.60       1483.0
                            3            8.65         7.61         7.75        23.20       1929.0
                            4            8.63         7.90         7.93        33.80       2896.0
2A07803U     0.505051       3            8.65         7.65         7.74        24.60       2201.0
                            4            8.60         7.97         7.99        30.40       3019.0
2A07805L     0.729927       1            7.37         6.96         6.95         0.98        106.0
                            2            7.13         6.58         6.62         1.03         85.5
                            3            7.32         6.81         6.78         0.94        105.0
                            4            7.39         6.95         6.96         2.19        189.0
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                                          SAS
STRM_ID            WGT      SAMPLE      PHEQ11      PHAC11      PHAL11      DICE11      ALKA11

2A07805U      0.729927      4             7.32        6.81        6.81        1.25       111.0

2A07806L      0.178571      0             7.21        6.81        6.81        1.39       116.0
                            1             7.23        6.87        6.93        1.04       118.0
                            2             7.23        6.45        6.36        0.40        99.4
                            3             7.12        6.80        6.75        0.85        95.7
                            4             7.32        6.95        6.93        1.26       133.0

2A07806U      0.178571      4             7.22        6.77        6.73        0.77        83.0

2A07807L      0.066313      0             7.43        6.99        6.95        1.61       158.0
                            1             7.46        7.20        7.17        1.99       177.0
                            2             7.58        6.85        6.79        1.76       159.0
                            3             7.60        6.78        6.77        1.76       189.0
                            4             7.62        6.92        6.87        2.45       228.0

2A07807U      0.066313      4             7.55        6.86        6.90        1.50       172.0

2A07808L      0.038212      1             7.46        7.28        7.33        1.85       162.0
                            2             7.47        6.81        6.83        1.83       173.0
                            3             7.44        6.55        6.63        1.37       127.0
                            4             7.57        6.91        6.91        2.39       213.0

2A07808U      0.038212      4             7.53        7.07        7.04        2.31       202.0

2A07810L      0.036563      1             6.96        6.72        6.78        0.69        68.5
                            2             7.11        6.74        6.64        0.75        60.9
                            3             7.27        6.53        6.48        0.89        68.6
                            4             7.27        6.73        6.76        1.25       113.0

2A07810U      0.036563      4             7.02        6.38        6.40        0.78        64.9

2A07811L      0.208768      1             6.43        6.09        6.11        0.28        13.4
                            2             6.86        6.22        6.25        0.32        17.5
                            3             6.86        6.22        6.23        0.35        17.6
                            4             6.67        6.35        6.31        0.31        37.0

2A07811U      0.208768      4             6.54        6.18        6.15        0.23        23.6

2A07812L      0.341297      1             7.59        6.83        6.91        1.11        99.7
                            2             7.15        6.77        6.76        1.09       100.3
                            3             7.20        6.69        6.74        1.14       108.0
                            4             7.33        7.06        7.01        1.78       153.0

2A07812U      0.341297      4             6.98        6.72        6.77        0.87        85.4

2A07813L      0.104275      0             7.84        7.40        7.49        4.34       358.0
                            1             7.69        7.38        7.32        3.59       363.0
                            2             7.82        7.19        7.11        4.41       357.0
                            3             7.84        7.34        7.37        4.58       395.0
                            4             7.93        7.38        7.41        4.86       448.0
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                                              SAS
STRM_ID          WGT     SAMPLE      PHEQ11      PHAC11      PHAL11      DICE11      ALKA11

2A07813U    0.104275     3             7.77        7.19        7.23        2.73       254.0
                         4             7.63        6.85        6.86        2.88       293.0

2A07814L    0.072516     0             7.84        7.44        7.45        3.49       322.0
                         1             7.76        7.63        7.63        4.16       373.0
                         2             7.70        6.99        6.94        3.16       297.0
                         3             7.80        6.99        6.99        3.68       352.0
                         4             7.96        7.06        7.01        4.71       444.0

2A07814U    0.072516     3             7.57        7.00        7.03        2.53       229.0
                         4             7.88        7.18        7.22        4.12       368.0

2A07815L    0.059952     1             7.27        6.96        7.03        0.97        95.5
                         2             7.32        6.85        6.82        1.08        94.1
                         3             7.10        6.41        6.56        0.74        70.3
                         4             7.24        6.74        6.73        0.96       103.0

2A07815U    0.059952     4             7.14        6.57        6.58        0.77        84.8

2A07816L    0.084602     1             7.08        6.71        6.65        0.52        46.4
                         2             6.84        6.55        6.55        0.65        64.9
                         3             6.97        6.39        6.40        0.63        58.2
                         4             6.97        6.76        6.71        0.77        72.1

2A07816U    0.084602     4             6.44        6.39        6.34        0.30        31.7

2A07817L    0.096618     1             7.01        6.79        6.71        0.53        36.0
                         2             6.90        6.51        6.37        0.49        27.5
                         3             6.76        6.40        6.39        0.34        27.6
                         4             6.84        6.46        6.46        0.47        40.0

2A07817U    0.096618     4             6.29        5.95        5.94        0.23        12.0

2A07818L    0.990099     1             7.10        6.92        6.89        0.86        81.2
                         2             7.10        6.63        6.66        0.85        86.3
                         3             7.18        6.46        6.46        0.82        92.4
                         4             7.26        6.73        6.70        1.05       115.0

2A07818U    0.990099     3             7.12        6.50        6.52        0.72        97.2
                         4             7.30        6.73        6.68        1.22       113.0

2A07819L    0.027739     1             7.60        7.44        7.43        2.72       244.0
                         2             7.64        7.17        7.16        2.67       251.0
                         3E            7.50        6.65        6.74        1.89       201.0
                         4             7.73        6.91        6.92        3.35       294.0

2A07819U    0.027739     4             7.81        7.05        7.05        4.26       393.0
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                                         SAS

STRM_ID           WGT     SAMPLE     PHEQ11     PHAC11     PHAL11     DICE11     ALKA11

2A07820L     0.081566     0            7.24       6.80       6.81       1.39      108.0
                          1            7.06       6.80       6.75       0.86       70.1
                          2            7.19       6.63       6.67       0.89       75.9
                          3            7.20       6.83       6.72       0.81       80.6
                          4            7.31       6.71       6.69       1.03      102.0

2A07820U     0.081566     3            6.98       6.69       6.66       0.52       55.8
                          4            7.09       6.64       6.69       0.67       67.0

2A07821L     0.393701     1            7.33       6.96       6.90       1.13      127.0
                          2            7.31       6.83       6.82       1.49      137.5
                          3            7.28       7.02       7.08       1.05      115.0
                          4            7.35       6.90       6.91       1.51      158.0

2A07821U     0.393701     4            7.34       7.03       6.95       1.65      158.0

2A07822L     0.151976     1            7.35       6.88       6.84       1.84      149.0
                          2            7.57       6.81       6.80       1.68      158.0
                          3            7.45       6.95       6.92       1.95      169.0
                          4            7.62       7.00       7.00       2.62      241.0

2A07822U     0.151976     4            7.50       6.87       6.88       2.64      237.0

2A07823L     0.132275     1            7.22       6.86       6.83       1.24       91.4
                          2            7.30       6.85       6.90       1.17      110.0
                          3            7.34       6.96       6.96       1.29      106.0
                          4            7.63       7.19       7.19       2.69      271.0

2A07823U     0.132275     3            7.35       6.98       6.92       1.24       99.7
                          4            7.87       7.27       7.28       4.43      408.0

2A07824L     0.080775     1            7.02       6.73       6.69       0.47       45.2
                          2            6.66       6.79       6.61       0.61       52.1
                          3            7.10       6.76       6.77       0.55       50.2
                          4            6.95       6.82       6.78       0.61       72.0

2A07824U     0.080775     4            6.74       6.70       6.65       0.35       53.0

2A07825L     0.043995     0            7.08       6.73       6.67       1.20       80.0
                          1            7.07       6.64       6.62       0.76       58.6
                          2            7.01       6.64       6.60       0.69       52.9
                          3            7.19       6.79       6.75       0.59       60.6
                          4            7.23       6.67       6.67       0.66       76.0

2A07825U     0.043995     3            6.92       6.61       6.51       0.42       40.3
                          4            7.00       6.44       6.42       0.61       51.0

2A07826L     0.245098     1            7.41       7.23       7.20       2.80      357.0
                          2            7.79       6.97       7.02       4.09      359.0
                          3            7.30       7.21       7.18       3.67      327.0
                          4            7.92       6.92       6.93       4.56      412.0
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                                          SAS

STRM_ID          WGT    SAMPLE       PHEQ11      PHAC11      PHAL11       DICE11     ALKA11

2A07826U    0.245098    3              7.64        6.89        6.91         3.17      298.0
                        4              7.02        6.17        6.13         2.57      221.0

2A07827L    0.252525    1              7.59        7.31        7.28         2.99      279.0
                        2              7.45        7.21        7.16         2.32      220.0
                        3              7.53        7.05        7.01         2.27      205.0
                        4              7.75        7.07        7.04         3.49      318.0

2A07827U    0.252525    4              7.12        6.67        6.65         0.77       77.0

2A07828L    0.135870    0              7.00        6.52        6.50         1.18       44.0
                        1              7.01        6.62        6.64         0.58       47.6
                        2              7.08        6.56        6.56         0.60       43.0
                        3              7.32        6.71        6.75         0.57       54.1
                        4              7.22        6.77        6.82         1.59      155.0

2A07828U    0.135870    3              7.08        6.45        6.45         0.36       31.9
                        4              6.87        6.26        6.25         0.43       40.5

2A07829L    0.118203    1              7.19        6.77        6.71         0.73       66.9
                        2              7.06        6.48        6.45         0.80       65.3
                        3              6.97        6.52        6.53         0.65       62.1
                        4              7.15        6.68        6.73         0.89       82.5

2A07829U    0.118203    3              7.10        6.68        6.72         0.65       63.7
                        4              7.18        6.69        6.72         0.98       89.6

2A07830L    0.184843    0              7.41        7.24        7.14         1.84      189.0
                        1              7.62        7.02        7.06         2.25      197.0
                        2              7.65        6.34        6.44         2.28      251.0
                        3              7.70        6.58        6.59         2.42      203.5
                        4              7.34        6.74        6.74         0.84       95.0

2A07830U    0.184843    4              7.76        6.66        6.62         2.83      257.0

2A07831L    0.035842    0              7.52        7.22        7.24         3.01      327.0
                        1              7.75        7.27        7.20         3.93      320.0
                        2E             7.77        6.82        6.85         2.60      274.0
                        3              7.93        6.86        6.87         4.33      382.0
                        4              7.80        6.95        6.97         2.77      338.0

2A07831U    0.035842    3              7.90        6.72        6.65         1.99      207.0
                        4              7.72        6.79        6.79         2.66      251.0

2A07832L    0.056625    1              7.02        6.88        6.97         0.87       88.7
                        2              7.29        6.80        6.84         0.95       81.2
                        3              7.40        6.39        6.37         1.11       92.7
                        4              7.29        6.66        6.68         1.33      116.0

2A07832U    0.056625    3              7.22        6.56        6.72         1.06      110.0
                        4              7.31        6.80        6.80         1.25      118.0
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                                              SAS
STRM_ID            WGT      SAMPLE      PHEQ11     PHAC11     PHAL11     DICE11     ALKA11
2A07833L      0.167785      1             7.65       7.34       7.42       2.30      211.5
                            2             7.53       7.08       7.12       2.32      201.0
                            3             7.60       7.09       7.03       2.51      223.0
                            4             7.73       7.16       7.16       3.52      314.0

2A07833U      0.167785      3             7.56       6.77       6.69       2.29      202.0
                            4             7.58       6.89       6.91       2.63      232.0

2A07834L      0.222222      0             7.06       6.65       6.58       0.60       44.0
                            1             6.87       6.64       6.58       0.67       49.6
                            2             7.06       6.42       6.38       0.31       37.2
                            3             7.23       6.40       6.45       0.45       42.9
                            4             7.02       6.57       6.54       0.63       66.0

2A07834U      0.222222      4             6.90       6.38       6.38       0.37       50.0

2A07835L      0.093721      1             7.31       7.06       7.01       1.04       97.7
                            2             7.34       6.90       6.86       1.39       93.7
                            3             7.16       6.92       6.91       0.93       97.4
                            4             7.34       6.90       6.90       1.66      147.0

2A07835U      0.093721      4             7.26       6.88       6.87       1.24      113.0

2A07881L      0.074963      1             8.08       7.43       7.48       6.31      538.0
                            2             8.04       7.19       7.23       5.68      513.0
                            3             8.02       7.35       7.32       7.31      587.0
                            4             8.27       7.82       7.78      10.50      973.0

2A07881U      0.074963      3             7.95       7.13       7.04       5.35      429.0
                            4             8.13       7.35       7.38       8.25      758.0

2A07882L      0.450450      1             7.33       6.98       6.99       1.07      105.5
                            2             7.30       6.94       6.94       1.03       96.1
                            3             7.28       6.63       6.68       1.12      118.0
                            4             7.39       6.80       6.80       1.70      160.0

2A07882U      0.450450      4             6.94       6.55       6.53       0.79       83.0

2A07891L          -         1             6.74       6.37       6.39       0.40       33.2
                            2             7.06       6.19       6.24       0.43       36.9
                            3             6.96       6.42       6.40       0.57       40.9
                            4             7.17       6.37       6.35       0.66       65.4

2A07892L          -         1             7.15       6.80       6.79       0.66       59.7
                            2             7.00       6.55       6.53       0.65       58.8
                            3             7.02       6.50       6.50       0.80       66.4
                            4             7.06       6.71       6.69       0.82       81.8
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                                                 SAS

STRM_ID          WGT   SAMPLE   PHEQ11      PHAC11      PHAL11      DICE11      ALKA11

2A07893L           -   0          7.18        6.68        6.74        1.46        82.0
                       1          7.18        6.94        6.89        0.96        89.9
                       2          7.23        6.73        6.82        0.94        82.4
                       3          7.27        6.86        6.88        0.91        87.6
                       4          7.27        6.94        6.89        1.13       111.0

2A07894L           -   1          7.23        6.95        6.93        0.83        81.5
                       2          7.07        6.79        6.75        0.99        66.3
                       3          7.21        6.86        6.85        0.80        81.0
                       4          7.24        6.87        6.85        1.15       108.0

2A07895L           -   1          7.47        7.25        7.20        1.71       137.0
                       2          7.34        7.16        7.11        1.50       126.0
                       3          7.29        7.14        7.10        1.34       139.0
                       4          7.40        7.03        7.04        1.87       181.0

2A07895U           -   3          7.35        7.02        7.06        1.23       113.0

2A07896L           -   1          7.12        6.68        6.69        0.51        51.7
                       2          6.87        6.73        6.72        0.75        45.4
                       3          6.81        6.71        6.61        0.51        44.2
                       4          7.06        6.65        6.68        0.66        67.1

2A08801L    0.591716   0          8.16        8.16        8.16       19.40      1662.0
                       1          8.49        7.96        8.06       17.74      1604.0
                       2          8.36        7.59        7.63       11.60      1092.0
                       3          8.53        7.92        7.92       18.00      1797.0
                       4          8.59        7.96        7.87       20.70      1750.0

2A08801U    0.591716   4          8.62        7.78        7.78       18.80      1650.0

2A08802L    0.456621   1          7.22        6.87        6.95        0.93        92.0
                       2          7.16        6.68        6.79        0.99        85.0
                       3          7.19        6.67        6.74        0.82        86.3
                       4          7.22        6.59        6.58        0.95        93.5

2A08802U    0.456621   4          7.26        6.75        6.80        1.12       112.0

2A08803L    0.393701   1          7.49        7.76        6.76        1.59       136.2
                       2          7.41        7.09        7.09        2.21       194.0
                       3          7.49        7.18        7.24        1.71       183.0
                       4          7.55        7.06        7.06        2.51       231.0

2A08803U    0.393701   4          7.67        6.91        6.90        2.89       268.0

2A08804L    1.010101   1          6.89        6.75        6.67        0.67        58.8
                       2          6.91        6.59        6.55        0.63        53.8
                       3          7.00        6.46        6.49        0.63        63.2
                       4          7.10        6.57        6.59        0.74        75.5

2A08804U    1.010101   4          6.99        6.58        6.58        0.68        62.9
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                                        SAS
STRM_ID           WGT     SAMPLE      PHEQ11      PHAC11      PHAL11      DICE11      ALKA11

2A08805L     0.302115     1             7.19        6.80        6.82        0.99       124.0
                          2             7.28        6.83        6.81        1.42       117.5
                          3             7.32        6.96        6.88        1.06       113.0
                          4             7.37        6.71        6.70        1.74       151.0

2A08805U     0.302115     4             6.83        6.26        6.23        0.77        61.6

2A08306L     1.666667     1             7.13        6.55        6.61        1.60       161.0
                          2             7.38        6.82        6.87        1.65       175.0
                          3             7.43        6.71        6.67        1.55       157.0
                          4             7.55        6.65        6.63        2.11       192.0

2A08806U     1.666667     4             7.46        6.76        6.79        1.77       154.0

2A08308L     0.311526     1             7.43        7.02        6.91        1.83       177.5
                          2             7.54        7.29        7.26        2.33       226.0
                          3             7.56        7.26        7.24        2.09       205.0
                          4             7.69        7.15        7.14        3.71       318.0

2A08808U     0.311526     4             7.35        6.75        6.75        1.47       139.0

2A08809L     0.510204     0             7.14        6.68        6.76        1.11        84.0
                          1             7.04        6.72        6.82        0.91        90.4
                          2E            7.13        6.50        6.43        1.21        75.1
                          3             7.14        6.79        6.78        0.97        90.9
                          4             7.28        6.64        6.64        1.04        97.0

2A08809U     0.510204     4             7.11        6.59        6.59        0.91        87.0

2A08810L     0.531915     1             7.07        7.08        7.19        1.43       134.0
                          2             7.40        6.75        6.85        1.41       133.0
                          3             7.39        6.73        6.74        1.63       147.0
                          4             7.48        6.95        6.94        1.93       183.5

2A08810U     0.531915     4             7.42        7.03        7.00        1.90       182.0

2A08811L     0.775194     0             7.32        7.08        7.10        1.37       112.5
                          1             7.18        7.00        7.02        0.99       118.0
                          2             7.26        6.86        6.83        1.44       112.0
                          3             7.70        6.94        7.00        1.35       134.0
                          4             7.50        6.97        6.98        1.80       179.5

2A08811U     0.775194     4             7.51        6.75        6.75        1.39       135.0

2A08891L            -     1             7.20        6.67        6.76        0.46        44.1
                          2             6.94        6.57        6.59        0.51        39.6
                          3             7.13        6.40        6.41        0.56        39.8
                          4             6.76        6.56        6.61        0.68        64.0

2A08891U            -     3             7.37        6.42        6.45        0.75        51.2
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SAS

| STRM_ID | WGT | SAMPLE | PHEQ11 | PHAC11 | PHAL11 | DICE11 | ALKA11 |
|---|---|---|---|---|---|---|---|
| 2A08901L | 0.133511 | 1 | 7.50 | 7.07 | 7.06 | 1.35 | 129.0 |
| | | 2 | 7.17 | 6.78 | 6.74 | 1.34 | 107.5 |
| | | 3 | 7.53 | 6.90 | 6.92 | 1.36 | 125.0 |
| | | 4 | 7.50 | 7.05 | 7.00 | 1.72 | 161.0 |
| 2A08901U | 0.133511 | 3 | 7.08 | 6.72 | 6.61 | 0.71 | 55.9 |
| | | 4 | 6.94 | 6.79 | 6.70 | 0.78 | 65.1 |
| 2A08902L | 0.124844 | 0 | 7.19 | 6.87 | 6.86 | 0.73 | 62.0 |
| | | 1 | 7.09 | 6.82 | 6.79 | 0.82 | 68.5 |
| | | 2E | 6.78 | 6.57 | 6.46 | 0.40 | 40.8 |
| | | 3 | 7.19 | 6.60 | 6.63 | 0.58 | 58.2 |
| | | 4 | 7.13 | 6.79 | 6.75 | 0.76 | 83.1 |
| 2A08902U | 0.124844 | 4 | 7.06 | 6.67 | 6.67 | 0.84 | 96.3 |
| 2A08903L | 0.440529 | 1 | 7.25 | 6.52 | 6.49 | 1.04 | 112.0 |
| | | 2 | 7.22 | 6.78 | 6.78 | 1.34 | 116.0 |
| | | 3 | 7.38 | 6.89 | 6.84 | 1.06 | 105.0 |
| | | 4 | 7.42 | 6.78 | 6.76 | 1.57 | 140.0 |
| 2A08903U | 0.440529 | 3 | 7.39 | 6.92 | 6.87 | 0.91 | 98.8 |
| | | 4 | 7.44 | 6.70 | 6.65 | 1.56 | 139.0 |
| 2A08904L | 0.199203 | 0 | 7.41 | 7.25 | 7.24 | 2.16 | 178.0 |
| | | 1 | 7.50 | 7.02 | 7.04 | 1.80 | 183.0 |
| | | 2E | 7.21 | 6.18 | 6.21 | 1.46 | 132.5 |
| | | 3 | 7.46 | 6.85 | 6.77 | 1.65 | 190.0 |
| | | 4 | 7.56 | 6.74 | 6.77 | 1.90 | 191.0 |
| 2A08904U | 0.199203 | 3 | 7.37 | 6.80 | 6.74 | 1.72 | 166.0 |
| | | 4 | 7.59 | 6.74 | 6.75 | 1.90 | 191.0 |
| 2A08905L | 0.507614 | 1 | 7.13 | 6.85 | 6.90 | 0.77 | 71.0 |
| | | 2 | 7.26 | 6.63 | 6.64 | 0.92 | 71.7 |
| | | 3 | 7.17 | 6.76 | 6.69 | 0.72 | 76.0 |
| | | 4 | 7.28 | 6.83 | 6.83 | 1.03 | 97.2 |
| 2A08905U | 0.507614 | 3 | 7.07 | 6.81 | 6.79 | 0.73 | 66.7 |
| | | 4 | 7.25 | 6.78 | 6.78 | 0.98 | 86.3 |
| 2A08906L | 0.196850 | 0 | 6.97 | 7.01 | 7.04 | 0.91 | 69.0 |
| | | 1 | 7.20 | 6.48 | 6.52 | 0.71 | 70.4 |
| | | 2E | 6.80 | 5.70 | 5.75 | 0.66 | 52.2 |
| | | 3 | 6.95 | 6.31 | 6.32 | 0.85 | 74.9 |
| | | 4 | 7.01 | 6.30 | 6.30 | 0.67 | 50.0 |
| 2A08906U | 0.196850 | 4 | 6.93 | 6.12 | 6.12 | 0.59 | 47.0 |

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