



National Surface Water Survey:

National Stream Survey Phase I - Pilot Survey Field Operations Report



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A Contribution to the
National Acid Precitation Assessment Program



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

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Notice

The information in this document has been funded by the U.S. Environmental Protection Agency under contract no. 68-03-3249 to Lockheed Engineering and Management Services Company, Inc. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document.

The mention of corporate names, trade names, or commercial products in this report is for illustration purposes only and does not constitute endorsement or recommendation for use.

This document is one volume of a set which fully describes the National Stream Survey - Pilot and Phase I. The complete document set includes the major data report, quality assurance plan, analytical methods manual, field operations report, processing laboratory operations report, and quality assurance report. Similar sets are being produced for each Aquatic Effects Research Program component project. Colored covers, artwork, and the use of the project name in the document title serve to identify each companion document set.

The correct citation of this document is:

Knapp, C. M., C. L. Mayer, D. V. Peck, J. R. Baker, and G. J. Filbin. 1987. National Stream Survey, Phase I-Pilot Survey: Field Operations Report. EPA-600/8-87/019. U.S. Environmental Protection Agency, Las Vegas, Nevada.

Abstract

The National Stream Survey (NSS) is one of the programs within the National Surface Water Survey of the U.S. Environmental Protection Agency. The proposed research plan for Phase I of the NSS was evaluated during a pilot survey conducted in the spring and summer of 1985. A base of operations that included a mobile laboratory was established at Sylva, NC. Selected locations of 61 streams in the southern Blue Ridge region of the United States were sampled four times during a 57-day period. This report chronicles the activities required to plan and conduct the field operations of the NSS pilot survey.

Preparatory activities for the NSS pilot survey are described, including the personnel training program and site reconnaissance activities. The equipment and protocols (including quality assurance measures) used to collect water samples and field measurements of pH, conductivity, and dissolved oxygen are presented. Field laboratory activities are summarized, including a protocol for preparing a fraction for analysis of organically-complexed monomeric aluminum species. The fractionation procedure used was feasible, but alternative methodologies should be investigated. Certain protocols for collecting samples or for conducting field measurements were compared against possible alternatives. Filtering samples during collection was determined to be unfeasible. The use of a peristaltic pump to collect samples was found to be more suitable than collecting discrete grab samples. Measurements of pH could be conducted at streamside without concern for effects of CO₂ degassing. Experiments investigating the holding time of unpreserved water samples are presented in two appendices to this report. The results of these experiments indicate that sample holding times could be extended without compromising the accuracy or quality of the data.

The NSS pilot survey was completed on schedule and demonstrated that a large-scale synoptic survey of streams was logistically feasible. The NSS also confirmed that the basic research design, quality assurance plan, and data analysis plan of the NSS would provide the necessary information to meet the objectives of the NSS. Pertinent cost information and specific recommendations regarding various aspects of field operations are provided for those planning similar projects.

This report is submitted in partial fulfillment of contract 68-03-3249 by Lockheed Engineering and Management Services Company, Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from January 1985 to July 1985 and work was completed as of September 1986.

Contents

	<i>Page</i>
Notice	ii
Abstract	iii
Figures	vii
Tables	viii
Acknowledgements	x
 1. Introduction	 1
2. Planning and Preparation for Field Operations	3
Site Selection	3
Protocol Development	3
Procurement	6
Field Station Site Selection	6
Personnel Recruitment and Training	7
Field Sampler Training Program	7
Field Laboratory Personnel Training Program	7
Field Laboratory Modifications	8
Site Reconnaissance Activities	8
 3. Field Station Operations	 11
Field Station Organization	11
Field Station Communications	12
 4. Field Sampling Operations	 14
Sampling Equipment	14
Quality Assurance and Quality Control of Field Measurements	14
Daily Sampling Activities	15
Preparation for Sampling	15
Sampling and Field Measurements	15
pH Measurement	16
In Situ Conductivity Measurement	17
In Situ Dissolved Oxygen Measurement	17
Other Measurements	18
Post-sampling Activities	18

Contents (continued)

5. Field Laboratory Operations	20
Field Laboratory Personnel	20
Daily Field Laboratory Activities	20
Audit Samples	20
Preparation of the Field Laboratory	22
Receipt of Samples and Data Forms from Field Crews	22
Organization of Samples into a Batch	23
Transfer of Samples to Field Laboratory	23
Sample Analysis and Processing	23
Sample and Data Form Shipment	26
6. Evaluation of Equipment and Protocols	28
Field Laboratory Methods Evaluations	28
Field Laboratory Conductivity Measurements	28
Preparation of Organic Monomeric Aluminum Fraction	28
Field Equipment Evaluations	29
Field Methods Evaluations	29
In-line Filtration at Streamside	29
Sample Collection Method	29
Streamside pH Measurements	30
In Situ pH Measurement Method	30
Sample Holding Time	30
7. Summary of Field Operations	31
8. Observations and Recommendations	34
Field Safety	34
Planning Activities	34
Field Sampling Operations	34
Field Laboratory Operations	38
References	41
<i>Appendices</i>	
A. Syringe Sample Holding Time Study	42
B. Cubitainer Holding Time Study	52

Figures

<i>Number</i>	<i>Page</i>
1. Regions of the eastern United States selected for sampling during the National Stream Survey-Pilot Survey.	2
2. Map of National Stream Survey-Pilot Survey study area showing location of stream reaches selected for sampling.	5
3. Watershed characteristics form, National Stream Survey-Pilot Survey.	10
4. Flowchart of daily field station operations, National Stream Survey-Pilot Survey.	12
5. Daily field sampling activities, National Stream Survey-Pilot Survey.	16
6. Field data form, National Stream Survey-Pilot Survey.	19
7. Flowchart of daily field laboratory operations, National Stream Survey-Pilot Survey.	21
8. Field laboratory data form, National Stream Survey-Pilot Survey.	24
9. Flowchart of field sample processing and analyses conducted at field laboratory during National Stream Survey-Pilot Survey.	25
10. Shipping form, National Stream Survey-Pilot Survey.	27
A-1. Changes in pH and dissolved inorganic carbon over time in a sample initially having no dissolved carbon dioxide.	46
A-2. Changes in DIC and pH over a 12-hour period in a sample initially supersaturated with carbon dioxide.	47
A-3. Changes in DIC and pH over a 165-hour period in a sample initially supersaturated with carbon dioxide.	47
B-1. Mean values for pairs of measurements at 4 holding times for 10 lakes and streams.	55

Tables

<i>Number</i>	<i>Page</i>
1. Streams Sampled During the National Stream Survey-Pilot Survey	4
2. Summary of Field Sampler Training Program, National Stream Survey-Pilot Survey	7
3. Summary of Field Laboratory Training Program, National Stream Survey-Pilot Survey	8
4. Sampling Equipment Used During National Stream Survey-Pilot Survey	15
5. Sampling Activity Time Summary for Summer Sampling Period, National Stream Survey-Pilot Survey	31
6. Summary of Distance Traveled by Field Sampling Teams, National Stream Survey-Pilot Survey	32
7. Selected Cost Estimates, National Stream Survey-Pilot Survey	33
8. National Stream Survey-Pilot Survey Problems and Recommendations: Field Safety	35
9. National Stream Survey-Pilot Survey Problems and Recommendations: Site Reconnaissance and Access	35
10. National Stream Survey-Pilot Survey Problems and Recommendations: Field Sampling Activities and Equipment	36
11. National Stream Survey-Pilot Survey Problems and Recommendations: Field Laboratory Operations	39
A-1. Dissolved Inorganic Carbon and pH Measurements of a Sample Initially Having No Dissolved CO ₂	46
A-2. Dissolved Inorganic Carbon and pH Measurements Over Time on a Sample Initially Supersaturated with Dissolved Carbon Dioxide	46
A-3. Summary Statistics of pH and DIC Changes Over Time for Solutions of Different Levels of Dissolved Carbon Dioxide Stored at Different Temperatures	48
A-4. Summary of F-Tests Performed on Variances of Sample and QCCS Measurements for Solutions of Different Initial Dissolved Carbon Dioxide Concentrations	49

Tables (continued)

A-5. Comparisons of Variances for pH Measurements of Solutions Having Different Dissolved CO ₂ Concentrations Versus a Low Ionic Strength pH 7.00 Quality Control Check Sample	50
A-6. Summary Statistics for Each Time Interval From Samples Collected From Padden and Bagley Lakes	51
B-1. Locations of Lakes and Streams	53
B-2. Treatment Means and Overall Standard Error of 25 Chemical Parameters at Four Holding Times for Three Lakes and Seven Streams	62
B-3. Relative Difference Between the Means for Each Parameter for Holding Time Intervals of 12 to 24, 24 to 48, 48 to 84, and 12 to 84 hours.	63

Acknowledgements

S. L. Pierett was responsible for the overall administration of Lockheed-EMSCO logistical operations. K. Asbury (Lockheed-EMSCO) coordinated the procurement of equipment and supplies. K. J. Cabbie (Lockheed-EMSCO) selected the site for the field station and provided technical assistance during the early days of the field operation. J. Tuschall (Northrop Services, Inc., Research Triangle Park, NC) assisted with establishing contact with local cooperators during site reconnaissance activities. The assistance and support of N. Myers, S. Monroe, and T. Ashe (Southwest Technical College, Sylva, NC) are gratefully acknowledged.

Comments on earlier drafts of this report from the following individuals are gratefully acknowledged: K. N. Eshleman and P. Kaufmann (Northrop Services, Inc., Corvallis, OR); V. Sheppe, S. Drou  , and D. Hillman (Lockheed-EMSCO); and R. D. Schonbrod, (U.S. EPA, Las Vegas, NV). Special thanks are directed to P. Kellar (Radian Corporation, Research Triangle Park, NC), whose thorough review improved the quality of the manuscript. M. Faber (Lockheed-EMSCO) served as technical editor. Formal reviewers were P. Gehring (U.S. EPA, Westlake, OH), J. H. Gibson (Colorado State University), and T. Janecki (Martin Marietta Corporation, Columbia, MD).

F. Garner (Lockheed-EMSCO) provided statistical advice for the syringe holding time experiments. For Appendix B (holding time study of bulk water samples), E. A. Yfantis, M. J. Miah, F. C. Garner, and T. J. Permutt assisted with statistical analyses. J. Scanlan helped with computer programming.

L. Steele and S. Reppke (Computer Sciences Corp.) are gratefully acknowledged for their excellent support typing the various drafts of this report. B. Sheets, L. Gurzinski, R. Buell, S. Garcia and D. Hamby (Lockheed-EMSCO) prepared most of the figures presented in this report. Finally, acknowledgement is due to W. L. Kinney (U.S. EPA, Las Vegas, NV) who served as project officer for this survey.

Section 1

Introduction

The apparent acidification of surface waters in areas of the United States has recently been the subject of intensive debate. The influence of acidic deposition on surface water acidification has been the subject of numerous studies (e.g., see review by Altshuller and Linthurst, 1984). Attempts to extrapolate the results from localized studies to a regional or national scale have not been successful. Comparisons between localized studies are compromised by (1) differences in methodologies, (2) biased selection of study sites, (3) small or incomplete data bases, or both, or (4) lack of adequate quality assurance information.

In an effort to overcome these problems, the U.S. Environmental Protection Agency (EPA) has designed and implemented the National Surface Water Survey (NSWS) as part of the monitoring and assessment effort of the National Acid Precipitation Assessment Program. The NSWS is a three-phase program to provide regional-scale assessments of the present chemical and biological status of lakes and streams and to select representative sites for long-term monitoring of aquatic resources.

The NSWS has two major components, the National Lake Survey (NLS) and the National Stream Survey (NSS). The NSS will investigate lotic systems in regions of the eastern United States considered to be at risk from acidic deposition. Phase I of the NSS will be a synoptic survey in some of these regions to assess the present chemical status of streams.

In preparation for Phase I of the NSS, the U.S. EPA and cooperating scientists con-

ducted a pilot survey during the spring and summer of 1985. The National Stream Survey-Pilot Survey (NSS-PS) was conducted in the southern Blue Ridge area of Tennessee, North Carolina, South Carolina, and Georgia (Figure 1). The study had the following objectives:

1. Evaluate the proposed NSS-Phase I protocols and equipment that will be used to collect, process, and analyze stream water samples.
2. Evaluate the proposed NSS-Phase I logistics plan, including site access, safety, and field operations.
3. Evaluate the proposed NSS-Phase I data quality objectives and quality assurance plan.
4. Provide suitable data to evaluate the proposed NSS-Phase I sampling design and data analysis plan.
5. Train personnel who will be involved in NSS-Phase I activities.

This report documents and evaluates the pilot survey logistical planning activities, field sampling methods, and field laboratory operations. Reports on two special experiments related to sample holding times that were conducted during the pilot survey are appended to this report. Analytical methods used in the pilot survey are described by Hillman et al. (1987). The quality assurance plan is documented in Drou   et al. (1986). The research design, analytical results, data interpretation, and study conclusions are presented in Messer et al. (1986).

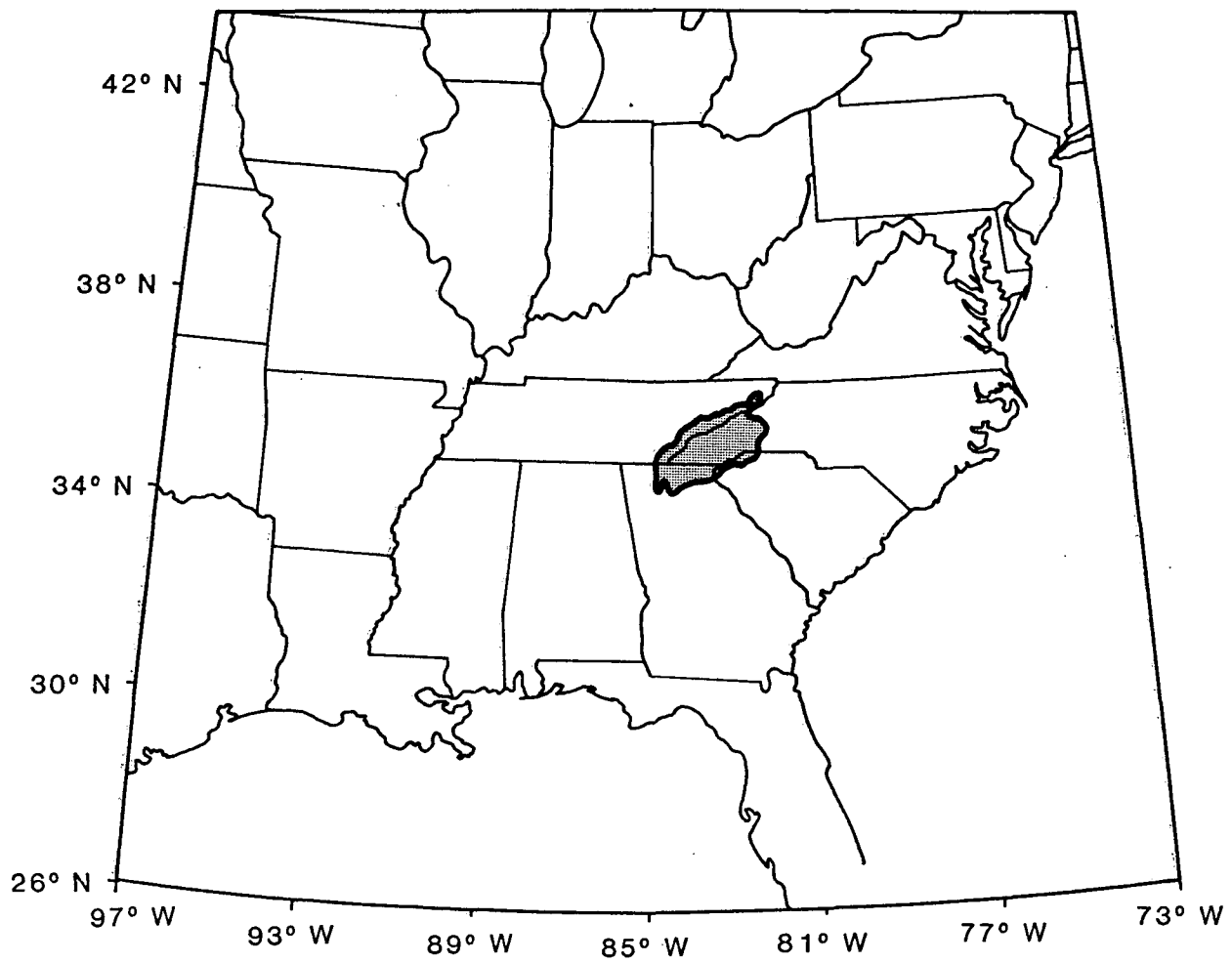


Figure 1. Regions of the eastern United States selected for sampling during the National Stream Survey-Pilot Survey (from Messer et al., 1986).

Section 2

Planning and Preparation for Field Operations

The Environmental Monitoring Systems Laboratory of the EPA in Las Vegas, Nevada, was responsible for planning and conducting the pilot survey field operation. Lockheed Engineering and Management Services Company, Inc. (Lockheed-EMSCO) provided logistics support and field personnel. Other groups and agencies also participated in planning and implementing the pilot survey. These groups are described further by Messer et al. (1986).

The major planning activities were the selection and reconnaissance of sampling sites, procurement of equipment, development of sampling and analytical protocols, selection of a location for base of operations, and the training of field personnel. These activities are described more fully in this section.

Site Selection

The research design for the pilot survey used a stream "reach" as the basic statistical sampling unit (Messer et al., 1986). A reach was operationally defined as the length of a stream that lies between corresponding upstream and downstream points of confluence (or "nodes") with other streams, or to the headwater when no upstream node was present. For the pilot survey, 54 such reaches were selected by using procedures described by Messer et al. (1986). These reaches, termed "second stage" (Messer et al., 1986) or "regular" reaches, were selected as a statistically unbiased sample without consideration of accessibility or availability of historical water quality data. In addition to the regular reaches, seven additional reaches were included for sampling. These additional reaches, termed "special interest" reaches, were study sites for other monitoring or research programs; thus considerable data on water qual-

ity were available. All stream reaches sampled during the pilot survey are identified, along with their NSS site identification code, in Table 1. The location of each of these reaches is shown in Figure 2.

Protocol Development

Field protocols for collecting water samples from streams and for measuring chemical parameters both in situ and at streamside were developed in early January 1985. These protocols were based on the proposed research plan and on discussions with other researchers. Protocols were adapted from a recommended methodology to meet the requirements of the NSS. Methods were modified for specific equipment or instrumentation, and appropriate quality assurance and quality control procedures were incorporated into each protocol. Procedures to collect water from midchannel by using a portable peristaltic pump, to measure pH at streamside, and to determine dissolved oxygen content and conductivity in situ were developed and were documented in a draft field operations manual that was used during the pilot survey.

Additional field protocols were developed to determine stream stage height and cross-sectional profile and to classify riparian characteristics in the vicinity of the sample site. These methods were not documented in manuals but were incorporated into the sampling personnel training program. Field protocols were modified or were otherwise evaluated during the pilot survey. These tests are summarized in Section 6.

The physical and chemical parameters measured in water samples collected during the pilot survey were the same as those

Table 1. Streams Sampled During the National Stream Survey-Pilot Survey

NSS-PS ^a ID	Stream Name	State	County	Downstream Site	
				Latitude	Longitude
2A07701	Sugar Cove Branch of North River	TN	Monroe	35°19'21"	084°06'01"
2A07702	Childers Creek	TN	Polk	35°11'30"	084°29'30"
2A07703	Halls Creek	TN	Polk	35°05'45"	084°21'80"
2A07801	Gulf Fork of Big Creek	TN	Cocke	35°53'45"	083°05'15"
2A07802	Puncheon Fork	NC	Madison	35°54'30"	082°34'45"
2A07803	N.N.T. to Ellejoy ^b	TN	Blount	35°47'00"	083°48'00"
2A07805	Cosby Creek	TN	Cocke	35°48'00"	083°14'15"
2A07806	Roaring Fork of Meadow Fork	NC	Madison	35°48'30"	082°53'45"
2A07807	North Fork of Dillingham Creek	NC	Bancombe	35°46'30"	082°27'30"
2A07808	Armstrong Creek	NC	McDowell	35°48'30"	082°02'20"
2A07810	Little River	TN	Sevier	35°40'15"	083°40'30"
2A07811	False Gap Prong	TN	Sevier	35°41'59"	083°23'24"
2A07812	Correll Branch	NC	Haywood	35°40'15"	083°05'00"
2A07813	Little Sandymush Creek	NC	Madison	35°42'10"	082°45'38"
2A07814	Reems Creek	NC	Buncombe	35°42'06"	082°35'12"
2A07815	Curtis Creek	NC	McDowell	35°38'30"	082°09'30"
2A07816	Eagle Creek	NC	Swain	35°29'54"	083°45'50"
2A07817	Forney Creek	NC	Swain	35°31'40"	083°33'20"
2A07818	Bunches Creek	NC	Swain	35°33'38"	083°14'48"
2A07819	Crooked Creek	NC	McDowell	35°36'30"	082°06'50"
2A07820	East Fork Pigeon River	NC	Haywood	35°27'10"	082°50'50"
2A07821	Grassy Creek	NC	Henderson	35°27'53"	082°17'05"
2A07822	Sweetwater Creek	NC	Graham	35°19'39"	083°48'02"
2A07823	Brush Creek	NC	Swain	35°19'07"	083°30'59"
2A07824	Middle Prong of West Fork	NC	Haywood	35°22'21"	082°56'18"
2A07825	South Fork of Mills River	NC	Transylvania	35°20'45"	082°39'50"
2A07826	Henderson Creek	NC	Henderson	35°22'43"	082°23'02"
2A07827	Welch Mill Creek	NC	Cherokee	35°11'08"	083°53'37"
2A07828	Whiteoak Creek	NC	Macon	35°13'56"	083°37'09"
2A07829	Cathey's Creek	NC	Transylvania	35°12'42"	082°47'09"
2A07830	Mud Creek	NC	Henderson	35°15'17"	082°30'04"
2A07831	North Picolet River	NC	Polk	35°12'50"	082°13'15"
2A07832	Tusquitee Creek	NC	Clay	35°04'13"	083°48'59"
2A07833	Allison Creek	NC	Macon	35°07'12"	083°29'34"
2A07834	Brush Creek	NC	Macon	35°06'50"	083°15'28"
2A07835	Middle Saluda River	SC	Greenville	35°07'46"	082°32'17"
2A07881	Walnut Creek	NC	Madison	35°48'57"	082°44'15"
2A07882	Little Branch Creek	NC	Madison	35°27'04"	083°03'39"
2A07891 ^c	Cosby Creek	TN	Cocke	35°44'58"	083°12'05"
2A07892 ^c	Twentymile Creek	NC	Swain	35°28'17"	083°52'16"
2A07893 ^c	Jarrett Creek	NC	Macon	35°09'07"	083°36'29"
2A07894 ^c	Shope Fork	NC	Macon	35°03'48"	083°26'09"
2A07895 ^c	Moses Creek	NC	Jackson	35°19'30"	083°06'21"
2A07896 ^c	Pinnical Branch	NC	Macon	35°03'28"	083°27'58"
2A08801	N.N.T.	GA	Murray	34°57'42"	084°44'12"
2A08802	Dunn Mill Creek	GA	Fannin	34°56'36"	084°26'28"
2A08803	Owenby Creek	GA	Fannin	34°58'15"	084°08'45"
2A08804	Bear Creek	GA	Gilmer	34°49'28"	084°33'57"
2A08805	Weaver Creek	GA	Fannin	34°52'20"	084°17'56"
2A08806	N.N.T. to Kintuestia Creek	GA	Union	34°53'28"	084°01'24"
2A08808	Whitepath Creek	GA	Gilmer	34°44'15"	084°26'00"
2A08809	Tickanetley Creek	GA	Gilmer	34°37'50"	084°16'50"
2A08810	Bryant Creek	GA	Lumpkin	34°36'36"	083°59'55"
2A08811	Hinton Creek	GA	Pickens	34°29'09"	084°25'16"
2A08891 ^c	Chester Creek	GA	Fannin	34°38'26"	084°10'05"
2A08901	Little Persimmon Creek	GA	Rabun	34°54'18"	083°30'08"
2A09902	West Fork of Chattooga River	GA	Rabun	34°54'21"	083°11'32"
2A09903	Nottely River	GA	Union	34°49'26"	083°54'30"
2A09904	She Creek	GA	Rabun	34°50'06"	083°20'39"
2A09905	Chattahoochee Creek	GA	White	34°42'32"	083°44'30"
2A09906	Deep Creek	GA	Hebersham	34°40'37"	083°27'19"

^a National Stream Survey-Pilot Survey site identification code.^b No-name tributary.^c Special interest reach.

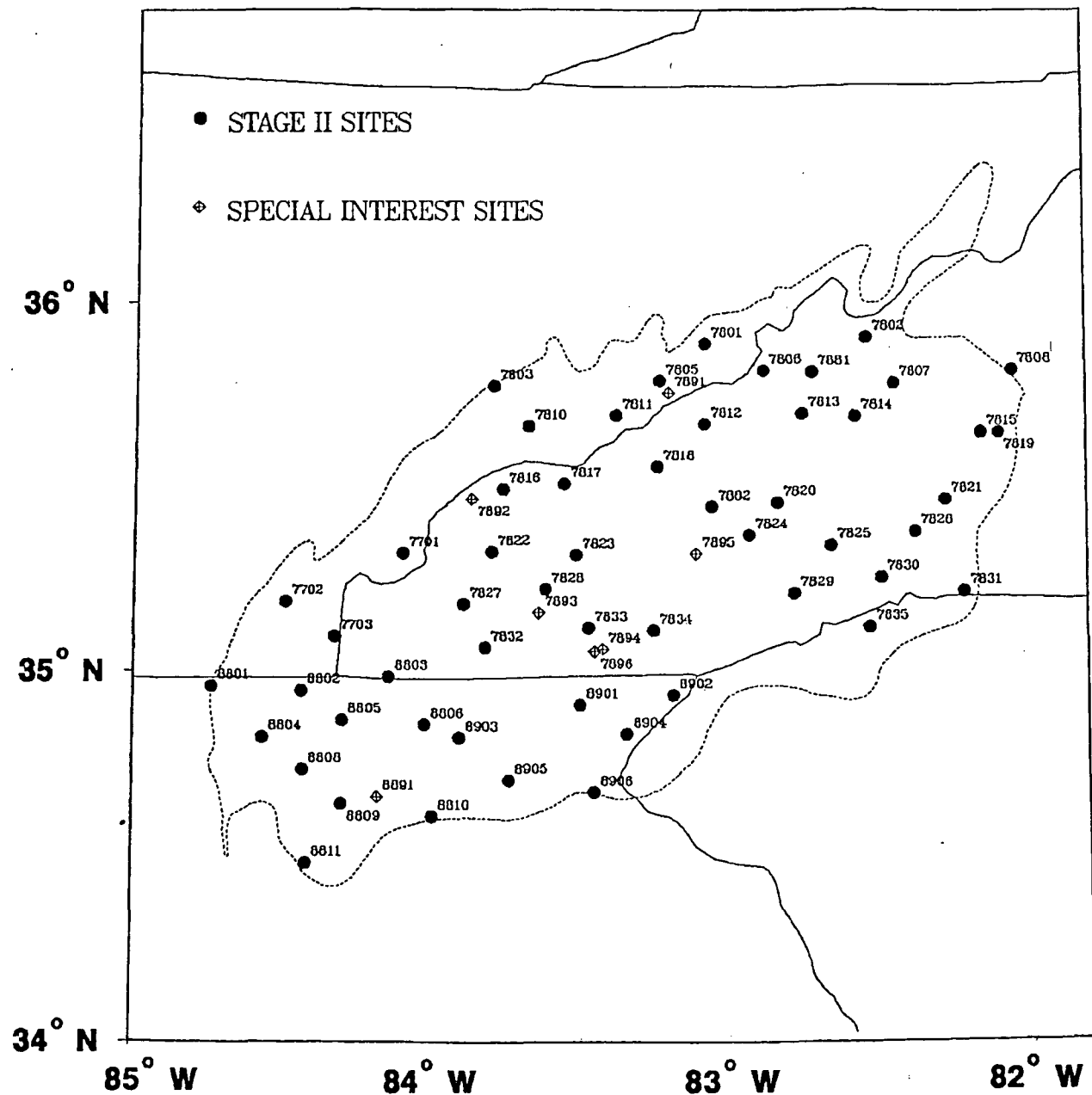


Figure 2. Map of National Stream Survey-Pilot Survey study area showing location of stream reaches selected for sampling (from Messer et al., 1986). (Numbers are the last four digits of the site identification code from Table 1).

measured during Phase I of the Eastern Lake Survey (Linthurst et al., 1986). Analytical methodologies for these parameters also remained the same. One additional parameter, organic monomeric aluminum, was measured during the pilot survey. A measurement of conductivity at the field laboratory was also implemented late into the pilot survey.

The determination of organic monomeric aluminum was added to provide a more accurate estimate of toxic forms of dissolved aluminum. Total dissolved aluminum concentrations are not always indicative of the potential toxicity to fishes. Only certain species, particularly monomeric forms, are believed to be toxic (Driscoll et al., 1980; Baker and Schofield, 1982). In the NSWS, water samples are analyzed for their total extractable aluminum content. This extractable aluminum fraction contains dissolved monomeric species of aluminum and thus provides a crude estimate of the potential toxicity. The toxicity of monomeric aluminum species can be mitigated by the presence of organic ligands (e.g., dissolved organic acids). Organic monomeric aluminum represents a nontoxic component of the extractable aluminum fraction. The concentration of toxic monomeric aluminum species could then be estimated as the difference between total extractable and organic monomeric aluminum concentrations in a water sample.

There are several different methods for determining the various forms of dissolved aluminum in natural waters. The procedure for preparing an organic monomeric aluminum fraction developed by Driscoll (1984) was selected for evaluation during the pilot survey. This methodology did not require expensive or complex equipment. It could be carried out in a small space and could be done in a short time. Both of these attributes made this methodology suitable for use in a field laboratory. The organic monomeric aluminum fraction was prepared by using the same extraction process as was used for total extractable aluminum, and this allowed for a more direct estimation of inorganic monomeric aluminum concentrations.

The measurement of conductivity of samples at the field laboratory would provide a precise estimate of conductivity within 16 hours of collection. This measurement would

serve as an additional check on overall data quality and sample stability. A protocol for this measurement was developed and evaluated during the pilot survey.

Procurement

The equipment and other supplies required to perform the required field and field laboratory protocols were procured between December 1984 and February 1985 by following U.S. government-approved purchasing procedures. Experience had indicated that demands for certain pieces of equipment or supplies (e.g., membrane filters) could deplete stockpiles on a nationwide basis. The field laboratory trailer and much of its instrumentation and equipment were already available because they had been used during Phase I of the Eastern Lake Survey, and only consumable supplies and spare parts had to be obtained. The trailer is described in Morris et al. (1986), and the specific equipment and supplies used in the field laboratory are outlined in Hillman et al. (1986, 1987 in press).

Field Station Site Selection

The site selected for the pilot survey field station had to meet numerous requirements. Primary concerns were a reliable supply of good quality water delivered at moderate pressure (50 psi), an adequate calibration room facility, and on-site storage facilities for supplies and backup equipment. The location had to be served by a courier service that offered morning and afternoon service for delivery and pickup and that could deliver samples overnight to other locations. Efficient field operations also dictated that the field station and field laboratory be centrally located within the study area.

Advance travel throughout the study area was necessary to select a site for the field station which would accommodate needs for housing, a field operations facility, and a communications center. Each potential field station was evaluated by utilizing a site assessment sheet developed for this purpose.

After inspection of four proposed sites, Southwest Technical College in Sylva, NC, was selected as the field station for the pilot

survey. The field laboratory, calibration room, and equipment storage facility were located there. Housing and the field station communications center were located in Cullowhee, NC, approximately five miles from the field laboratory.

Personnel Recruitment and Training

Field sampling and field laboratory personnel were recruited between December 1984 and late January 1985. All pilot survey field personnel had previous experience as field samplers or field laboratory analysts from Phase I of the Eastern Lake Survey. All persons involved with the pilot survey field operation received extensive training specific to the survey. The training programs, which were held in Las Vegas, Nevada, are summarized below. Additional details are documented in an unpublished memorandum report available from the Acid Deposition Department, Lockheed-EMSCO, Las Vegas, Nevada.

Field Sampler Training Program

The field sampler training program (Table 2) was designed to ensure that all samplers would use precisely the same procedures to collect stream samples and to collect and record data. The program also served to familiarize personnel with the duties and responsibilities of the site coordinator. It was planned that all pilot survey field samplers would assume site coordinator positions for NSS-Phase I operations in 1986.

The 5-day field sampler training course, which was held from February 19 to 23, 1985, covered the basic concepts and protocols of the pilot survey. The training program provided a detailed introduction to locating and establishing a sample site, collecting water samples, conducting streamside and in situ measurements, recording data, and maintaining equipment. Safety training included wilderness survival, map reading, and proper operation of four-wheel drive vehicles. All samplers were certified in first aid and cardiopulmonary resuscitation.

Additional training was conducted at the field station before actual sampling activities

commenced. This training addressed basic measurements of hydrological parameters in streams and included practice with the field equipment and protocols. During the course of field operations, each field sampler assumed the duties of site coordinator for a short time.

Table 2. Summary of Field Sampler Training Program, National Stream Survey-Pilot Survey

-
-
1. Employee Orientation
 2. Project Orientation and Overview
 3. Instrument Operation and Calibration
 - a) pH meter
 - b) conductivity meter
 - c) dissolved oxygen meter
 - d) peristaltic pump
 4. Overview of Field Sampling Operation
 5. Care and Packing of Sampling Equipment
 6. Site Reconnaissance
 - a) map training
 - b) development of stream dossiers
 - c) completion of reconnaissance forms
 - d) completion of watershed characteristics form
 7. Staff Gauge Placement
 8. Completion of Logbook, Calibration Form, Stream Data Form
 9. Field Safety
 - a) safety gear
 - b) survival
 - c) communications
 - d) four-wheel drive training
 10. Simulated Sampling Operation
-
-

Field Laboratory Personnel Training Program

The training program for field laboratory personnel (Table 3) was designed to ensure that personnel would analyze and process water samples in accordance with approved pilot survey analytical and quality assurance protocols. During the 5-day field laboratory training program held in Las Vegas, field laboratory personnel received training in all technical aspects of field laboratory operation. During field operations each person assumed

the duties of laboratory supervisor to gain familiarity with the duties and responsibilities of the position.

Table 3. Summary of Field Laboratory Training Program, National Stream Survey-Pilot Survey

-
1. Employee Orientation
 2. Project Orientation and Overview
 3. Review of Field Laboratory Operations
 - a) sample flow
 - b) lab organization
 - c) personnel responsibilities
 4. Laboratory Safety
 5. Review of Methods
 - a) filtration and sample preservation
 - b) dissolved inorganic carbon analysis
 - c) pH determination
 - d) turbidity determination
 - e) true color determination
 - f) aluminum extraction
 - g) organic monomeric aluminum extraction (ion exchange column)
 6. Review of Batch and Shipping Forms, Logbooks
 7. Communications
 8. Inventory Control
 9. Waste Handling and Disposal
 10. Data Tracking/QA Plan
 11. Simulation of Daily Operation
 12. Medical Surveillance
-

Laboratory personnel were also trained in laboratory safety and in the use of safety equipment. Each person was fitted for a half-mask respirator and underwent medical surveillance physicals before the survey. All laboratory personnel were certified in first aid and cardiopulmonary resuscitation. Because a hazardous chemical, methyl isobutyl ketone (MIBK), was used in some pilot survey field laboratory procedures, it was necessary to monitor laboratory personnel for the presence and concentration of MIBK in the bloodstream. At the end of the survey, all personnel received blood tests to determine the absence of or presence and concentration of MIBK. This testing was conducted within 24 hours of an

individual's last exposure to MIBK, because this compound does not have a long residence time in the body.

Field Laboratory Modifications

To improve field laboratory safety, the field laboratory trailer to be used for the pilot survey was modified, and additional equipment was installed. As a result of experience gained during the Eastern Lake Survey-Phase I, a safety audit checklist was developed and implemented for the pilot survey. In addition, a portable photoionization detector was tested in the field laboratory during the pilot survey. This device monitored the concentration of MIBK vapors in the laboratory and sounded an alarm when the concentration of MIBK inside the trailer exceeded 25 ppm. The use of this detector eliminated the requirement that all field laboratory personnel wear respirators whenever MIBK was being used.

Site Reconnaissance Activities

Prior to the initiation of field activities, basic information on each stream reach was obtained by telephone from persons who were familiar with the areas of specific stream reaches. Members of the Soil Conservation Service, U.S. Forest Service, U.S. Geological Survey, National Park Service, Tennessee Valley Authority, and the Cherokee Indian Tribe, as well as personnel from state highway patrols, county sheriff's departments, and other local law enforcement agencies were called. These people provided information on ease of access to the reach, information on driving and hiking times, and the names of landowners to be called for access permission.

The basic information and a USGS 1:24,000 scale map delineating the stream reach were used to compile a dossier on each stream reach. Appropriate county and state road maps and any necessary access permits were added to the dossier before field operations were initiated.

Each field sampling team was assigned to sample 20 or 21 stream reaches during the pilot survey. Two sampling sites were located on each reach, one near the upstream node, the other near the downstream node. Each team visited all assigned sites before sampling

activities commenced. When possible, a sampling team was accompanied on this first visit by a local person who was familiar with the stream reach. Access permission was acquired prior to the visit; at the sampling site, site information contained in the dossier was verified or corrected. During and after the site visit, a reconnaissance form was completed for the sampling site. This form was used to record access routes (roads or trails), driving and hiking times, required maps, and the names of people who had authority to grant permission to access the sampling site.

A watershed characteristics form (Figure 3) was completed during the site visit. This form identified important characteristics useful in interpreting the results of chemical analyses. Photographs were taken at each sampling site (upstream view, downstream view, and any unique views that could assist with site identification). To assure that photographs could be readily matched with the proper sites, a card was photographed containing the sampling date, stream name, site ID number,

sampling team, and frame numbers of all site photographs. The card was photographed before any site photographs were taken. After the site visit, the completed reconnaissance form, the watershed characteristics form, and the photographs were added to the dossier.

During the reconnaissance visit, hydrologic staff gauges were installed in secure locations at each site. Gauges were installed in an area of quiet water (i.e., no obstructions and no eddies) at the side of the main channel. At least 6" of the scale was placed below the surface, and the gauge was oriented parallel to the direction of flow. The initial reading of gauge height was marked at a secondary location on shore. This secondary reference allowed qualitative changes to be observed in the event a gauge was lost during the survey. The staff gauges were left in place throughout the survey. The cross-sectional area of the stream at each site was determined by measuring the depth at 10 to 20 points spaced equally along a transect across the stream.

**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		1:250,000 MAP NAME	VISUAL ESTIMATES: _____ units
FRAME ID	AZIMUTH LAP CARD		STREAM WIDTH: _____
____ ○	____ °	1:24,000 MAP NAME	STREAM DEPTH: _____
____ ○	____ °		GAGE HEIGHT: _____ ft ○
____ ○	____ °		

WATERSHED ACTIVITIES/DISTURBANCES				units
(Check all that apply)				
<input type="checkbox"/> Roadways:	<input type="checkbox"/> Paved	<input type="checkbox"/> Unpaved	<input type="checkbox"/> Grade	Distance from Stream: _____ ○
	<input type="checkbox"/> Bridged	<input type="checkbox"/> Culvert		Distance from Stream: _____ ○
<input type="checkbox"/> Dwellings:	<input type="checkbox"/> Single unit(s)	<input type="checkbox"/> Multiple unit(s)		Distance from Stream: _____ ○
<input type="checkbox"/> Agriculture:	<input type="checkbox"/> Cropland	<input type="checkbox"/> Pasture		Distance from Stream: _____ ○
	<input type="checkbox"/> Fenced	<input type="checkbox"/> Unfenced		Distance from Stream: _____ ○
<input type="checkbox"/> Industry:	Specify Type: _____			Distance from Stream: _____ ○
<input type="checkbox"/> Logging:				Distance from Stream: _____ ○
<input type="checkbox"/> Mining:	Specify Type: _____			Distance from Stream: _____ ○
<input type="checkbox"/> Quarries:				Distance from Stream: _____ ○
<input type="checkbox"/> Beaver dams:	<input type="checkbox"/> Above Site	<input type="checkbox"/> Below Site		Distance from Stream: _____ ○
<input type="checkbox"/> Livestock:	<input type="checkbox"/> Cattle	<input type="checkbox"/> Sheep		Distance from Stream: _____ ○
	<input type="checkbox"/> Horses	<input type="checkbox"/> Other _____		
<input type="checkbox"/> Other:	_____			Distance from Stream: _____ ○

BANK VEGETATION WITHIN 100 METERS OF STREAM BED (Check all that apply)					STREAM SUBSTRATE (Check all that apply)				
Type	Absent	Sparse	Moderate	Heavy	Type	Absent	Sparse	Moderate	Heavy
Deciduous Trees:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Boulders:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Coniferous Trees:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Cobble:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Shrubs:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Gravel:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Wetland Areas:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Sand:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Grasses:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Silt:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Rocky/Bare:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Aufwuchs:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

COMMENTS ☐ SEE REVERSE SIDE DATA QUALIFIERS

(X) = Others _____

FIELD CREW DATA	
CREW ID _____	SAMPLER 2 _____
SAMPLER 1 _____	CHECKED BY _____

Figure 3. Watershed characteristics form, National Stream Survey-Pilot Survey.

Section 3

Field Station Operations

Field operations for the pilot survey were conducted in spring (March 1 through April 30, 1985) and summer (June 26 through July 17, 1985).

Spring sampling, preceded by 2 weeks of preliminary site visits, began on March 17, 1985. Each stream reach was sampled bi-weekly near its downstream node. Each downstream site was sampled three times. During the third set of site visits, 23 regular stream reaches were also sampled near their upstream nodes. Eighteen reaches that were sampled during the first 3 days of field operations were sampled a fourth time at the end of the spring sampling period because of equipment problems and protocol changes.

During the summer sampling period, each regular reach was sampled once near its downstream and once near its upstream node on the same day. Each special interest reach was sampled once, near its downstream node.

A generalized flowchart of field sampling and processing operations is given in Figure 4. Each team sampled one to three streams per day, 5 consecutive days a week. Samples and field data forms were delivered to the field laboratory within 9 hours of sample collection. At the field laboratory, samples were analyzed, and aliquots were prepared and preserved within 18 hours of collection. Preserved aliquots were shipped via overnight courier to a contract analytical laboratory (New York State Department of Health Laboratory, Albany, NY) to ensure they would arrive within 48 hours after collection.

Field Station Organization

The field station in Sylva, NC, was staffed by a site coordinator, three two-

member sampling teams, and a laboratory crew of four persons.

The site coordinator was responsible for the overall operation of the field station. Duties of the coordinator included:

1. Functioning as the on-site contact for the NSS management team, the Las Vegas communications center, and Lockheed-EMSCO administrative personnel.
2. Establishing a local communications center and setting up the field laboratory trailer.
3. Developing daily sampling itineraries for sampling teams.
4. Serving as the liaison between field sampling and field laboratory personnel.
5. Receiving audit samples.
6. Organizing batches and assigning sample numbers.
7. Shipping processed sample aliquots to the contract analytical laboratory and shipping data forms to the pilot survey data management center, quality assurance personnel, and the NSW sample tracking office.
8. Filing a daily sampling and operations report with the Las Vegas communications center.
9. Serving as a reserve field sampler or laboratory analyst.

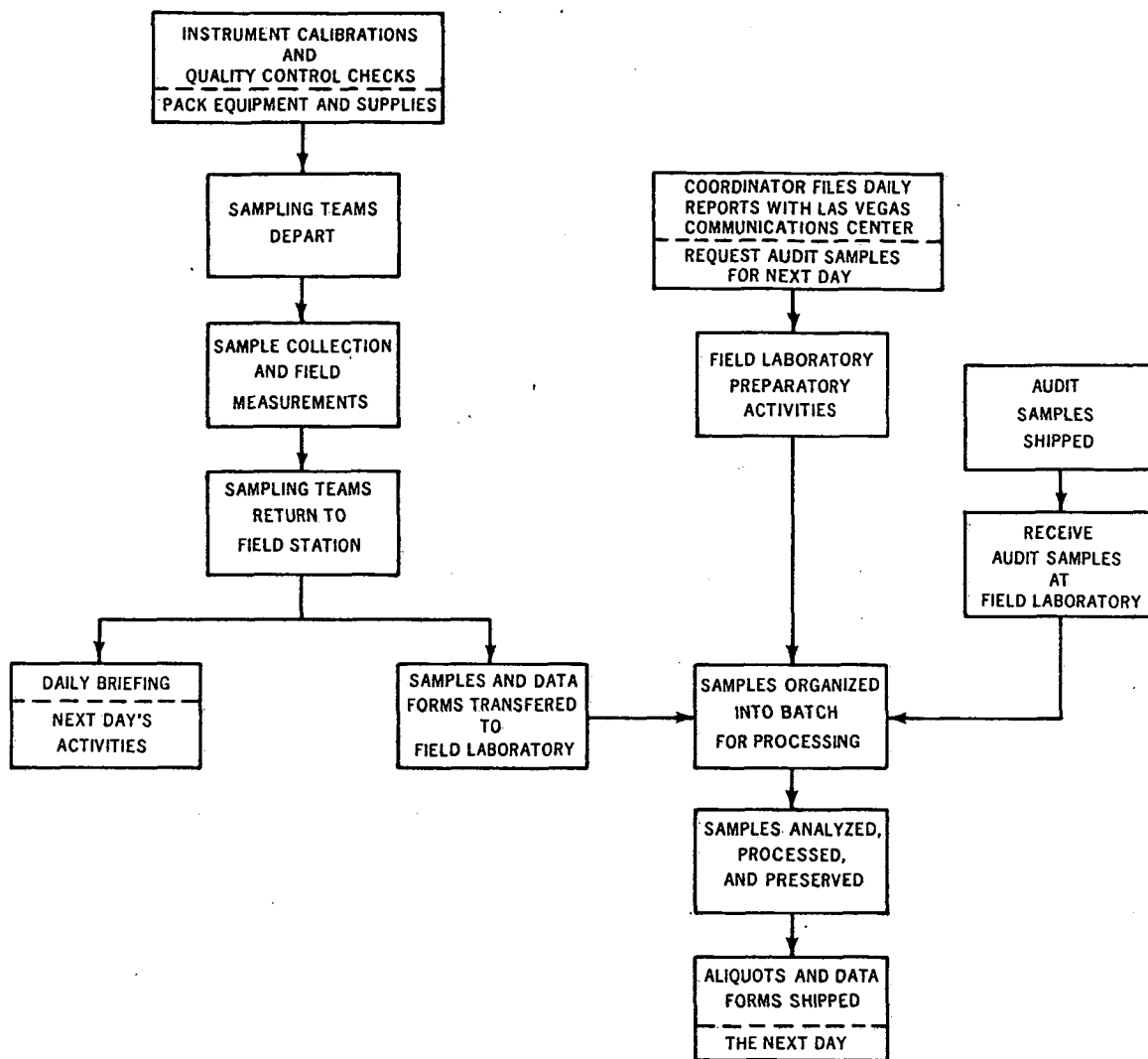


Figure 4. Flowchart of daily field station operations, National Stream Survey-Pilot Survey.

10. Maintaining field safety standards and initiating search and rescue procedures.

Duties of the field sampling and field laboratory personnel are described in Sections 4 and 5, respectively.

Field Station Communications

Daily communications was maintained by the site coordinator with the field sampling teams, the field laboratory, and the Las Vegas communications center. Communication with sampling teams in the field served to track

their progress, to resolve unexpected problems, and to ensure safety. The field laboratory was advised of the expected number of samples and of the expected arrival time of field crews. The Las Vegas communications center was informed daily about sampling activities, shipment of samples, and supply needs.

Each day the members of each sampling team (and all accompanying persons) completed a sampling itinerary form. The form included physical descriptions of each individual, clothing descriptions, names and telephone numbers of a person to call in the event of an emergency, a description of the planned

sampling schedule, and routes of travel. The completed form could be used by the coordinator to facilitate search and rescue operations; if necessary. Each team was required to telephone the local communications center or field laboratory by 4:30 p.m. (spring sampling period) or 6:00 p.m. (summer sampling period) to communicate their location and their expected arrival time at the field laboratory.

The coordinator called the Las Vegas communications center every day to report on the previous day's activities. A communications form completed by the coordinator was transcribed in Las Vegas over the telephone. Conference calls between the coordinator and members of the project management team were held weekly.

Section 4

Field Sampling Operations

Daily field sampling activities involved traveling to sampling sites, collecting samples and field data at each site, and delivering samples to the field laboratory. Four-wheel drive vehicles were used for transportation to most sampling sites. Sites inaccessible by vehicle were accessed by hiking, boat, or horseback. In addition to collecting water samples, the pH of the stream water was determined at streamside, and measurements of dissolved oxygen content and conductivity were measured in situ. The equipment, quality assurance measures, and field methodologies are described in this section.

Sampling Equipment

The equipment used by sampling teams at each stream site is listed in Table 4. A Cole-Palmer Masterflex 7533-30 portable peristaltic pump and a rechargeable battery were used in conjunction with 1/4-inch Tygon tubing (surgical grade) and a 6-foot bamboo boom to collect water from midchannel. Samples were collected in 4-liter Cubitainers, in 60-mL polypropylene syringes, and in 500-mL wide-mouth bottles constructed of amber high-density linear polyethylene.

A Beckman PHI-21 portable pH meter equipped with an Orion Ross model 81-56 combination electrode was used to measure pH. After the spring sampling period, the model 81-56 electrodes were replaced with Orion-Ross model 81-04 glass-bodied combination electrodes. For waters of low ionic strength, the 81-04 electrodes had improved response characteristics over the model 81-56 electrodes. Orion model 231 portable pH meters were available as backup instruments.

A Yellow Springs Instruments (YSI) model 33 S-C-T portable meter was used to measure conductivity in situ. YSI model 54 and model 57 portable oxygen meters were used to measure dissolved oxygen in situ. These two meters are nearly identical, and an equipment shortage necessitated the use of two models.

Quality Assurance and Quality Control of Field Measurements

Calibration procedures and quality control checks for the pilot survey were developed and documented in a quality assurance plan (Drou   et al., 1986). Instruments were calibrated daily at the field station. At each site before and after sample measurements, the calibration of pH and conductivity meters were checked by using standards of known concentration prepared daily. The dissolved oxygen meters were calibrated at each site before sample measurements.

The calibration of the instrument was checked by using an independent method at the field station before and after each day's use. All calibration information was recorded in a field logbook and on the field data forms.

To calibrate the pH meter, the previous day's calibration information was cancelled, and the meter was standardized with NBS-traceable pH 7.00 and pH 4.01 buffer solutions. The standardization values were checked with new aliquots of the buffer solutions. If the measured pH of each buffer solution was not within 0.02 pH units of the theoretical value, the instrument was restandardized. Next, a 1×10^{-4} N H_2SO_4 solution that had a theoretical

Table 4. Sampling Equipment Used During National Stream Survey-Pilot Survey

<p>I. SAMPLE COLLECTION</p> <p>Reconnaissance forms Maps Field logbook and forms Pump Battery and cables Stream data forms Watershed characteristics forms Field sample labels (tie-on/adhesive) Ziploc bags Portable coolers (w/gel packs) Pens/pencils/markers Deionized, H₂O (two 4-liter Cubitainers/field blank) 4-liter Cubitainers* (1/sample) 500-ml bottles* (1/sample) Tygon pump tubing* (10-20'/sample) Syringes/valves* (3/sample)</p>	<p>II. pH MEASUREMENT (cont.)</p> <p>4.00 buffer (2 bottles) QCCS solution (2 bottles) Wash bottle with deionized H₂O Electrode filling solution Instruction manual</p>
<p>II. pH MEASUREMENT</p> <p>pH meter/case Batteries 2 Electrodes (with BNC connectors) ATC probe Sample chamber Ringstand/clamp 250-ml beakers 7.00 buffer (2 bottles)</p>	<p>III. CONDUCTIVITY</p> <p>Meter/case Batteries Probe/storage bottle Calibration tables Deionized H₂O wash bottle 74 μS/cm QCCS (2 bottles) Instruction manual</p> <p>IV. DISSOLVED OXYGEN</p> <p>Meter/case Batteries Probe Calibration chamber Calibration tables Bucket Calculator Membrane kit Filling solution Instruction manual</p>

* Prepackaged in plastic bags for each site.

pH of 4.00 was used as a quality control check sample (QCCS). The QCCS was measured with each successfully standardized meter. If the measured pH of the QCCS was more than 0.10 unit different from 4.00, a new QCCS was prepared. If the measured pH of the new QCCS was not within control limits, the electrode or meter was replaced.

The factory calibration of each conductivity meter was checked by using KCl solutions. These solutions had specific conductances of 1413, 147, and 74 μ S/cm at 25 °C. Measurements of the 1413 and 147 μ S/cm QCCS solutions were required to be within 10 percent of the theoretical value. Readings of the 74 μ S/cm solution were allowed a range of ± 10 μ S/cm (13.5 percent). Meters or probes that did not produce acceptable QCCS measurements were replaced.

The dissolved oxygen meter was calibrated by using a chamber containing water-saturated air (air at 100 percent relative humidity). The calibration was checked in water that had been saturated with bubbled air. Readings were required to be within 0.5 mg/L O₂ of

each other, or the probe was serviced, and the unit was recalibrated.

Daily Sampling Activities

The daily routine of each sampling team (Figure 5) consisted of preparing for sampling, traveling to sites and collecting samples and field data, and post-sampling activities.

Preparation for Sampling

At the field station, each instrument was calibrated and checked. The sampling equipment and supplies necessary for the day's sampling schedule were obtained. A daily travel itinerary that listed the intended routes of travel, the sites to be visited, and a physical description of each member of the team was filed with the site coordinator.

Sampling and Field Measurements

Upon arrival at a stream site, the two samplers set up the equipment, checked the

calibration of each instrument, and collected all required samples and field measurements. The calibration of the pH meter was checked by using the pH 4.00 QCCS (see p. 14). The conductivity meter was checked by using the 74 $\mu\text{S}/\text{cm}$ QCCS (see above). At each site, the dissolved oxygen meter was recalibrated with water-saturated air. Sample collection, in situ measurements, and streamside measurements were conducted simultaneously but in such a way as to avoid affecting one another.

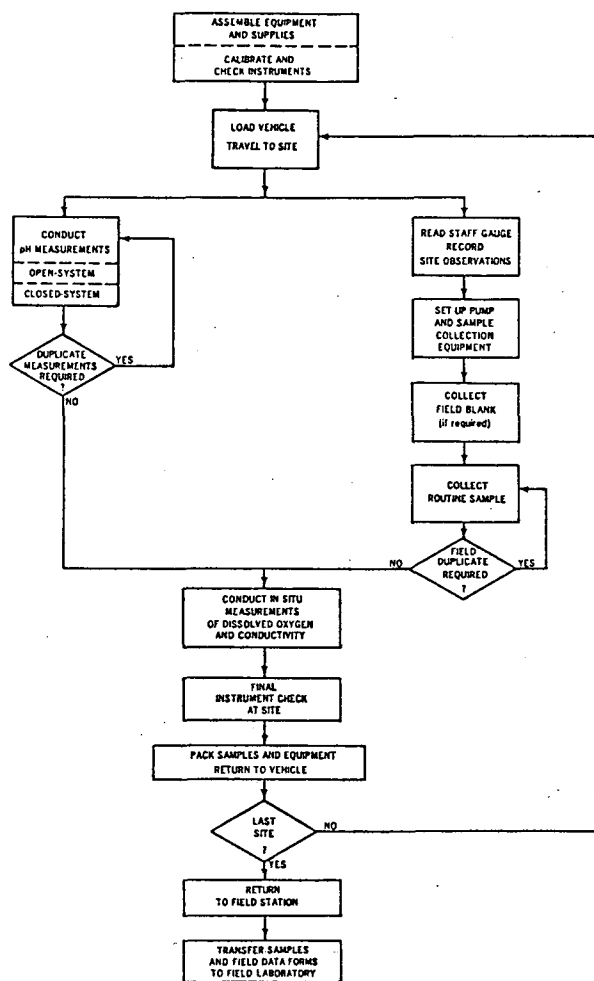


Figure 5. Daily field sampling activities, National Stream Survey-Pilot Survey.

Sample Collection--

Water samples were collected mid-channel in an area of flowing water that was not classified as a riffle. Water was pumped

to the bank by using the peristaltic pump and the Tygon tubing that was attached to the sampling boom with clamps. The end of the tubing was placed below the surface in mid-channel. This submerged tubing was located far enough above the bottom of the stream to avoid stirring up the sediments and introducing them into the sample. Water from each stream was collected sequentially in several containers. A routine sample consisted of one 4-L aliquot (collected in a 4-L Cubitainer), three 60-mL aliquots collected in syringes (one of which was used to measure pH at streamside), and one 500-mL aliquot for total suspended solids analysis (collected in a wide-mouth polyethylene bottle). All containers were rinsed three times with stream water before they were filled.

Each day, one of the three teams collected a field blank sample. The field blank sample was collected before any routine samples. To collect the field blank sample, deionized water (from two 4-L Cubitainers filled at the field laboratory) was pumped into a clean 4-L Cubitainer and into a 500-mL bottle. Syringes were not filled for the field blank sample.

Each day, one of the three teams also collected a field duplicate sample at one site. A field duplicate sample was collected by filling a second set of containers with stream water immediately after the routine sample was collected.

pH Measurement

At each site, pH was measured by two methods. One measurement was obtained from a sample aliquot collected in an open beaker. This sample was exposed to the atmosphere during collection and measurement and the measurement was operationally defined as an open-system determination. A second pH measurement was obtained from a sample aliquot collected in a syringe and measured in a sample chamber. The syringes were affixed directly to the end of the pump tubing to form an airtight seal. This sample was not exposed to the atmosphere during either collection or measurement, and the measurement was operationally defined as a closed-system determination. During the pilot survey, both methods were modified (see Section 6 for further discussion). The

procedures described below were in use at the end of the survey.

Open-system pH Measurement--

A 250-mL beaker was rinsed three times with stream water and then was filled with stream water by using the peristaltic pump. The electrode and the automatic temperature-compensating (ATC) probe were immersed in the sample, and the sample was swirled for 3 minutes. A fresh aliquot was collected, the electrode and the probe were immersed in the sample, and the measurement was taken. The sample was not swirled during the measurement process. The pH and temperature were recorded when the pH reading was stable (i.e., changed less than 0.01 pH unit over a 1-minute period).

For the field duplicate measurement, this process was repeated by using a third 250-mL aliquot of sample.

Closed-system pH Measurement--

A sample chamber, described in Hillman et al., (1986) was assembled at streamside. The ATC probe, immersed in a 250-mL beaker filled with stream water, was used to monitor the approximate water temperature inside the chamber during the pH measurement process. A 60-mL syringe was rinsed three times with stream water, was attached to the end of the pump tubing, and then was filled with stream water by using the peristaltic pump. The syringe was affixed to the sample chamber, and the electrode was inserted loosely into the chamber. The chamber and electrode were rinsed twice with 5- to 10-mL aliquots injected from the syringe. The chamber then was filled with sample injected from the syringe, and the electrode was inserted into the chamber to seal it. The initial pH and temperature readings were noted; a stopwatch was used to track elapsed time.

The pH, temperature, and elapsed-time values were recorded again when the pH reading was stable. A 5-mL aliquot (the approximate volume of the sealed chamber) from the syringe was slowly injected into the chamber, and when the pH reading was stable, values were recorded again.

A second 5-mL aliquot was slowly injected into the chamber, and the process was repeated. If the pH value for the second 5-mL aliquot was within 0.03 pH unit of the first 5-mL aliquot, the pH, temperature, and elapsed-time values were recorded as final readings for the sample. If they were not in agreement, a third 5-mL aliquot was injected and measured. Additional 5-mL aliquots were injected and measured until the stable pH readings of two successive aliquots agreed to within 0.03 pH unit. The pH, temperature, and elapsed time values of the last aliquot measured were recorded as final readings.

For the field duplicate measurement, this process was repeated by using a second syringe.

In Situ Conductivity Measurement

The conductivity probe was attached to a bamboo sampling boom and was immersed in the stream to a depth of at least 10 cm (mid-depth if the site depth was less than 10 cm) in an area of flowing water. The water temperature and conductivity readings were recorded when stable (i.e., the conductivity changed less than 5 $\mu\text{S}/\text{cm}$ over a 1-minute period). No field duplicate measurements of conductivity were made.

In Situ Dissolved Oxygen Measurement

The dissolved oxygen meter was calibrated by sealing the probe in a moist calibration chamber constructed of 6 inch by 1 inch flanged stainless steel plumbing pipe sealed with rubber stoppers at both ends. This chamber was immersed in the stream for 15 to 20 minutes to produce an atmosphere of water-saturated air inside the chamber. The meter and probe were calibrated by using a correction factor derived from the temperature of the chamber and the theoretical value of the partial pressure of oxygen at the elevation of the sample site.

The dissolved oxygen probe was attached to the sampling boom and immersed to a depth of at least 10 cm in an area of flowing water. The water temperature and dissolved oxygen values were recorded when

the dissolved oxygen reading was stable (i.e., changed less than 0.5 mg/L O over a 1-minute period). No field duplicate measurements of dissolved oxygen were made.

Other Measurements

All quality control and final field measurements were recorded in logbooks at streamside. Additional data recorded at streamside included stage height, cloud cover, instrument problems, QCCS results, date, time, team member identification, elevation of the site, and unique conditions which could affect water quality.

All data and observations were transcribed from field logbooks onto standardized field data forms (Figure 6). Copies of the watershed characteristics form (see Figure 3) were also carried on each site visit. Any significant change in the characteristics of a site was noted by completing a new form.

Post-sampling Activities

At each site, quality control checks were repeated on the pH and conductivity meters after measurements were made. Water samples were placed in portable soft insulated coolers that contained chemical refrigerant packs to maintain sample temperatures near 4 °C during transport to the vehicle. At the vehicle, samples were transferred to insulated coolers that contained six to eight chemical refrigerant packs. Equipment and supplies were packed for transport to the next site.

At the completion of sampling for the day, the teams returned to the field laboratory. The dissolved oxygen meter was checked by using an air-saturated water solution (see p. 15). The conductivity and dissolved oxygen probes were stored overnight in tap water, and the pH electrodes were stored in 3 M KCl. Water samples (Cubitainers, sealed syringes, and 500-mL bottles) were delivered to the coordinator to be organized into a batch for processing and analysis in the field laboratory.

Section 5

Field Laboratory Operations

The field laboratory trailer provided a facility to process dilute water samples in a controlled environment within a short time after collection. Measurements of physico-chemical parameters that had short holding times were conducted in the field laboratory. These measurements included closed-system determinations of pH and dissolved inorganic carbon (DIC), turbidity, and true color.

Each sample of stream water was prepared into several aliquots at the field laboratory for later, more detailed analyses at a contract analytical laboratory. These activities were conducted in an environment that minimized the potential for contamination.

Field Laboratory Personnel

The laboratory was staffed by a laboratory supervisor and three laboratory analysts. The laboratory supervisor was responsible for the daily operation, security, and safety of the laboratory. The laboratory supervisor also ensured that samples were analyzed and processed by approved methods and in accordance with the quality assurance plan. The supervisor performed pH and dissolved inorganic carbon (DIC) determinations on water samples and transcribed all analytical data collected in the laboratory onto a standardized data form. Additional duties included troubleshooting instrument malfunctions, maintaining equipment, and tracking the inventory of supplies and equipment.

The three laboratory analysts were jointly responsible for preparing reagents and standards for the sampling teams and for preparing preserved sample aliquots for shipment by the coordinator to the contract analytical laboratory. Analyst 1 prepared all aluminum

extractions. Analyst 2 was responsible for the preparation of aliquots requiring filtration. Analyst 3 conducted turbidity and true color determinations, prepared all aliquot labels and containers, prepared unfiltered aliquots, and preserved all aliquots. Each person in the laboratory rotated through all four positions to become familiar with all aspects of the laboratory operations.

Daily Field Laboratory Activities

The daily activities associated with the operation of the field laboratory (Figure 7) began with calibration and other preparation prior to the arrival of samples from field crews and concluded with packing samples and data forms for shipment the following day. Field laboratory analytical and sample processing methodologies used in the pilot survey are presented in Hillman et al. (1987). Quality assurance and quality control measures used in the laboratory during the pilot survey are described in Drou   et al. (1986).

Audit Samples

To monitor the performance of the field laboratory and contract analytical laboratory, natural water samples collected from lakes having a well-known chemical composition (termed audit samples) were prepared by Radian Corporation, Austin, Texas. Audit samples were shipped daily via overnight courier service to the field laboratory. The coordinator was responsible for receiving the audit samples and for storing them at 4  C until they were incorporated into a sample batch for processing and analysis. Details on the chemical composition and preparation of audit samples can be found in Drou   et al. (1986).

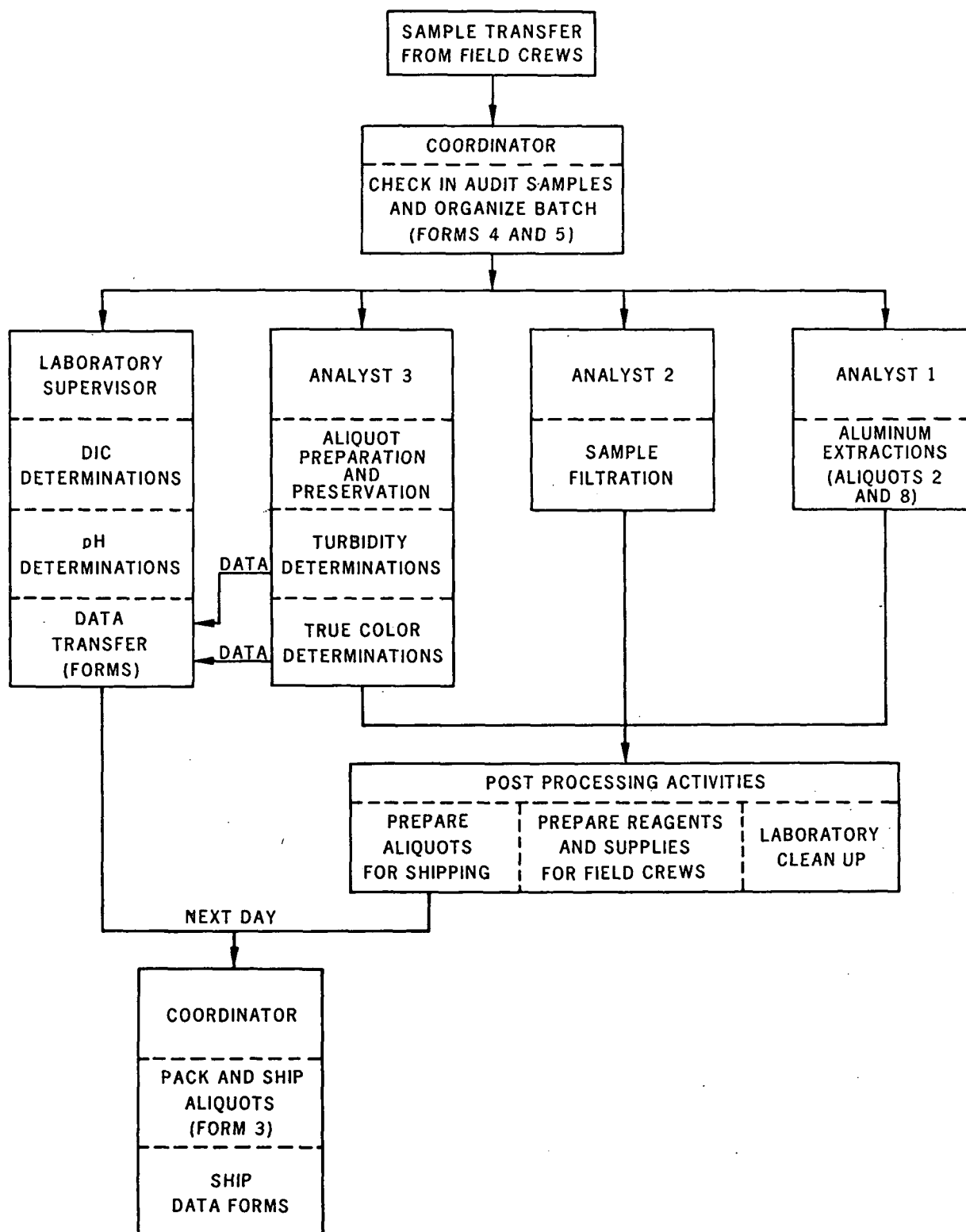


Figure 7. Flowchart of daily field laboratory operations, National Stream Survey-Pilot Survey.

Two types of audit samples ("field" audit samples and "laboratory" audit samples) were handled at the field laboratory. Field audit samples were sent to the field laboratory in 2-L wide-mouth amber polyethylene bottles. These audit samples were labeled, analyzed, and processed in the same manner as stream water samples. Laboratory audit samples were prepared and processed at Radian Corporation following the same protocols used in the field laboratory for natural water samples. Laboratory audit samples were shipped to the field laboratory in containers identical to the containers used to ship aliquots from the field laboratory to the contract laboratory. Laboratory audit samples received by the field laboratory were not processed but were relabeled and were incorporated into a sample batch.

Upon receipt of audit samples, the coordinator completed sample tracking forms which were later returned to Radian Corporation. Each audit sample was incorporated along with natural water samples into a batch for that day's processing (see p. 23). The assigned batch and sample identification numbers were recorded on the audit sample labels for each field audit sample and for each aliquot of a laboratory audit sample. The audit sample labels were then removed and were placed in a logbook. The batch and sample identification numbers were recorded on the field audit sample container. The various aliquot containers of a laboratory audit sample were relabeled with the appropriate sample aliquot labels. All audit samples were known to be audit samples at the field laboratory. However, they were indistinguishable from stream water samples when received at the contract laboratory.

Preparation of the Field Laboratory

The field laboratory staff began preparing for daily operation one to two hours prior to the arrival of samples from the field. Each day, prior to any sample processing or analyses, the field laboratory floor was mopped, and all counter surfaces were cleaned to minimize the potential of contamination from dust. All instrumentation in the field laboratory was left "on" or on "stand-by" at all times while the field laboratory was operational.

The field laboratory supervisor prepared calibration standards and QCCS solutions

(Hillman et al., 1987) for DIC analysis. The carbon analyzer was calibrated, and its operation checked with these solutions. The pH meter was standardized with pH 4.01 and 7.00 NBS-traceable buffers. The standardization was subsequently checked with fresh buffers and with a freshly prepared 1×10^{-4} N H_2SO_4 QCCS. The field laboratory supervisor collected syringe samples for closed-system determinations of pH and DIC from each field audit sample.

One analyst prepared reagents, equipment, and labels for use in the two aluminum extractions. Reagent dispensers were checked for accuracy of delivery. Ion exchange columns used to prepare the fraction of organic monomeric aluminum were adjusted to be within 0.5 pH unit of the expected sample pH values (Hillman et al., 1987) which ranged between 4.8 and 8.4 during the pilot survey. The peristaltic pump used in the procedure was calibrated to deliver 30 mL/min of sample through the column.

The second analyst assembled and organized all equipment and supplies required for the sample filtration and prepared a logbook to check off sample aliquots as they were prepared and preserved. The nephelometer was calibrated and was checked for proper operation; the color test kit was assembled; and the logbook for recording turbidity and true color data was prepared.

The third analyst prepared all necessary aliquot bottles and aliquot labels for the sample batch and also prepared materials necessary for aliquot preparation. Sample aliquot bottles and labels were prepared prior to the start of processing activities to minimize the possibilities of error in filling the bottles. To minimize the possibility of preserving an aliquot with the wrong acid, labels were color-coded with respect to the type of preservative required.

Receipt of Samples and Data Forms from Field Crews

Three types of water samples were received at the field laboratory from field sampling crews: routine samples, field duplicate samples, and field blank samples. The collection of these samples was described in Section 4.

All sample containers and field data forms collected during each day's sampling operation were transferred to the coordinator. The temperature of each cooler was checked and was recorded on the appropriate field data forms. All sample containers were inspected for leakage and possible contamination. Syringes were checked for the presence of air bubbles. All comments regarding samples were recorded on the appropriate field data forms.

Data forms were inspected for completeness and legibility by the coordinator. Sampling personnel were debriefed by the coordinator to discuss any problems encountered in the field.

Organization of Samples into a Batch

The coordinator organized stream water samples and audit samples into a batch for processing and analysis. A field batch was defined as all samples processed by the field laboratory on a given day. Field batches were sequentially assigned unique batch identification numbers, beginning with 2001 and concluding with 2057.

Each sample in the batch (routine, field duplicate, field blank, and audit) was then assigned, at random, a unique sample identification number. The batch and sample identification numbers were recorded on all field sample container labels (4-L Cubitainers, syringes, and 500-mL bottles). These numbers were also recorded on the labels of corresponding sample aliquots prepared from each Cubitainer sample.

After batch and sample identification numbers were recorded on field sample labels, the coordinator entered batch information, stream identification numbers, and sample codes from all samples on the field laboratory data form (Figure 8). The stream identification number and sample code for each sample were entered on the field laboratory data form on the line corresponding to its assigned sample identification number. In the case of an audit sample, no stream identification number was entered. The audit sample code was entered in the "sample code" column.

During the organization of a batch and until the batch was processed by the field

laboratory, all samples were held at 4 °C, either in the field laboratory refrigerator or in a cooler containing frozen chemical refrigerant packs. When the assignment of sample identification numbers was complete, the field laboratory coordinator informed the field laboratory supervisor.

While the samples were being organized into a batch, the field laboratory supervisor and analysts made preparations to process and analyze samples.

Transfer of Samples to Field Laboratory

Once the batch was organized and all field sample containers were properly labeled, one syringe from each field sample was placed in the laboratory refrigerator for DIC analysis. The other syringe from each field sample was placed on a shelf in the laboratory to warm to ambient temperature prior to pH determination. The field laboratory supervisor collected two syringes from each field audit sample and labeled them with batch and sample identification numbers. One audit sample syringe was placed in the refrigerator for DIC analysis, and the other was placed on the shelf with those syringes used for pH determinations.

Sample Analysis and Processing

The flow of samples through the field laboratory is diagrammed in Figure 9. The 500-mL aliquots of sample collected in the field were delivered to the Environmental Biology Laboratory at Southwest Technical College in Sylva, NC. This laboratory performed the determination of total suspended solids by using standard methodology (U.S. EPA, 1983; Hillman et al., 1987).

Eight separate aliquots were prepared from each Cubitainer sample (see Hillman et al., 1987). A 125-mL aliquot of filtered water from each Cubitainer was collected in an acid-washed glass beaker for aluminum extractions (for total extractable and organic monomeric aluminum). Details of the preparation of the organic monomeric aluminum fraction are presented in Section 6.

**NATIONAL SURFACE WATER SURVEY
BATCH / QC FIELD DATA
FORM 5**

DATE RECEIVED _____
BY DATA MGT. _____
ENTERED _____
RE-ENTERED _____

BATCH ID _____		LAB TO WHICH BATCH SENT _____		DATE SAMPLED _____			
NO. SAMPLES IN BATCH _____		DATE SHIPPED _____		AIR-BILL NO. _____			
STATION ID _____		CREW ID _____		FIELD LABORATORY SUPERVISOR _____			

SAMPLE ID	STREAM ID	SAMPLE CODE	DIC (mg/L) OCCS LIMITS		LABORATORY pH OCCS LIMITS		TURBIDITY (NTU) OCCS LIMITS		COLOR (APHA UNITS)	SPLIT CODES (E C N)
			UCL 2.2 LCL 1.8	UCL 4.1 LCL 3.9	UCL _____ LCL _____	UCL _____ LCL _____				
			VALUE OCCS	VALUE OCCS	VALUE OCCS	VALUE				
01										
02										
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COMMENTS:

WHITE ORNL COPY

YELLOW FIELD COPY

PINK EMSL TV COPY

Figure 8. Field laboratory data form, National Stream Survey-Pilot Survey.

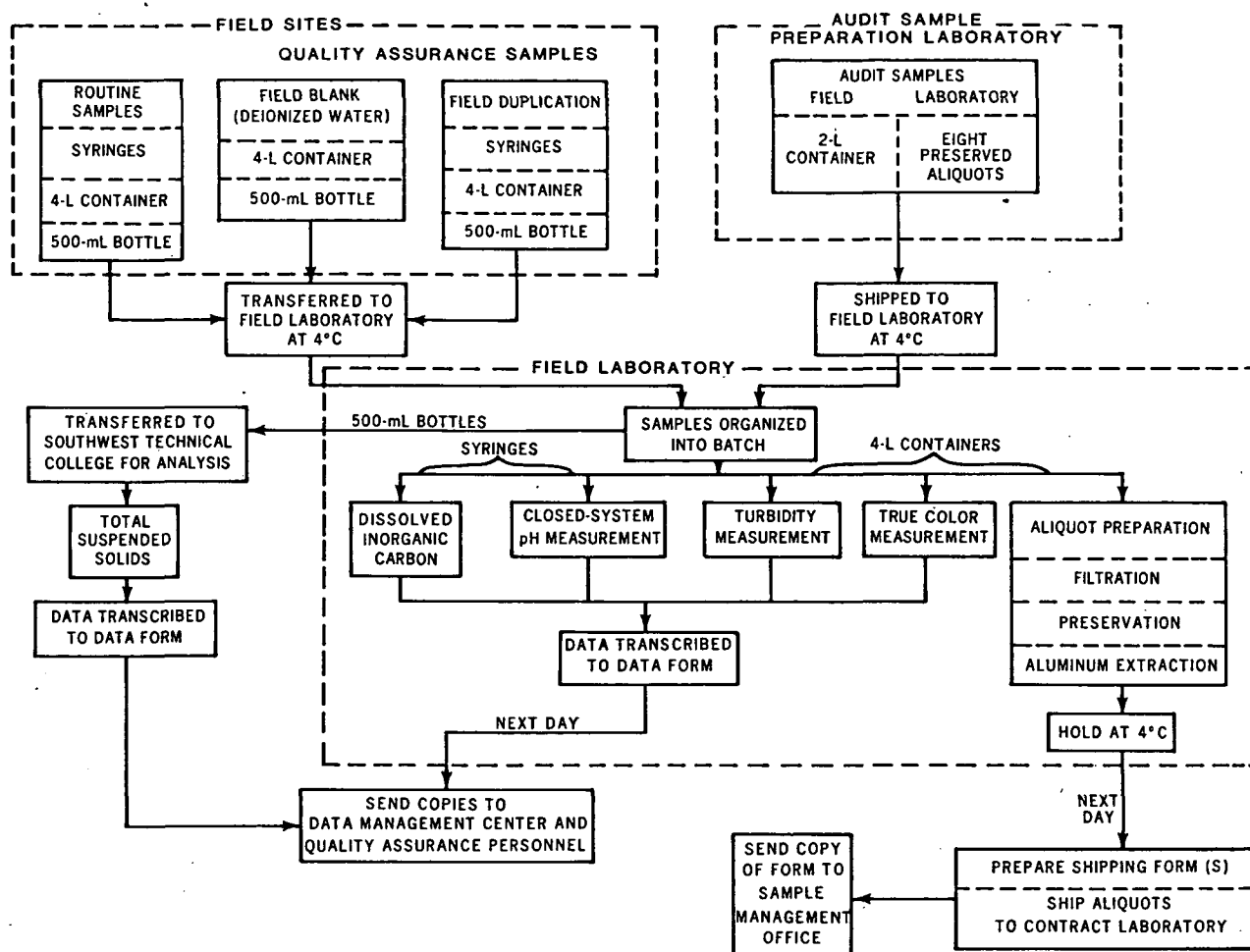


Figure 9. Flowchart of field sample processing and analyses conducted at field laboratory during National Stream Survey-Pilot Survey.

The remaining prepared aliquots were preserved with ultrapure acid if required (Hillman et al., 1987). All aliquots were refrigerated at approximately 4 °C. After aliquoting, samples in Cubitainers were allowed to warm to ambient temperature (18 to 25 °C) before turbidity and true color determinations were conducted.

While the samples were being aliquoted and preserved, the field laboratory supervisor analyzed the refrigerated syringe samples for DIC concentration. When these analyses were completed, the field laboratory supervisor performed pH determinations by using syringes that had warmed to ambient temperature.

One routine sample in each batch was selected at random as the "trailer duplicate." Two aliquots of this sample from each syringe were analyzed for DIC and pH. Two subsamples of the trailer duplicate sample from the Cubitainer were analyzed for turbidity and true color.

When sample processing operations were completed, preserved aliquots were prepared for shipping. Refrigerated aliquots were checked after 1 to 2 hours to ensure that container caps were tight. The cap of each aliquot bottle was taped to the bottle using electrician's tape wrapped clockwise around the seal. Each bottle was placed in a plastic

bag that was sealed with a twist tie. A set of six aliquots from each sample (not including the two aliquots for analysis of extractable aluminum fractions) was placed in a 1-gallon Ziploc bag. All aliquots were refrigerated at 4 °C. The aliquots for total and nonexchangeable extractable aluminum analyses (contained in 10-mL centrifuge tubes) were taped and then were bagged separately. The centrifuge tubes were then stored at approximately 4 °C in an insulated cooler with frozen chemical refrigerant packs.

When all analyses were completed, data for DIC, pH, turbidity, and true color were transcribed from laboratory logbooks onto the field laboratory data form (Figure 8). All of the glassware and the work area in the laboratory were cleaned and organized before the staff left the laboratory each night. A checklist was used to complete a safety inspection prior to departure.

Sample and Data Form Shipment

The morning after a batch was processed, the coordinator, with the assistance of an analyst, packed aliquot bottles and centrifuge tubes into containers for shipment to the contract analytical laboratory. The bagged sets of aliquot bottles and centrifuge tubes were placed in 30-quart insulated shipping coolers which were lined with frozen chemical refrigerant packs to maintain the temperature near 4 °C during shipment. The

centrifuge tubes were taped to the inside of the cooler. All aliquots from a single sample were shipped in the same cooler; each cooler held five to six sets of aliquots. Two frozen chemical refrigerant packs were placed on top of the samples, and styrofoam packing material was packed in the cooler to prevent aliquots from shifting during shipping.

A four-part shipping form for each cooler was prepared. The shipping form (Figure 10) identified the aliquots in the cooler. Two copies of this form were included in the cooler. One copy was sent from the field laboratory to the pilot survey sample management office (Viar and Company, Alexandria, VA), and one copy was retained in the field laboratory. One copy of the form received at the contract laboratory was sent to the sample management office to confirm the receipt of the aliquots. Aliquots were shipped from the field laboratory to the contract laboratory via overnight courier service, Monday through Friday.

The coordinator also prepared copies of field data forms, field laboratory data forms, and shipping forms for delivery to the data base manager at Oak Ridge National Laboratory (ORNL) and to quality assurance personnel at EMSL-LV. The coordinator also telephoned the Las Vegas communications center and provided a report on the day's sampling activities (including number and identification codes of streams visited, information on sample shipment, requests for supplies, problems encountered, and subsequent corrective actions).

NATIONAL SURFACE WATER SURVEY SAMPLE MANAGEMENT OFFICE P.O. BOX 818 ALEXANDRIA, VA 22314				NSWS FORM 3 SHIPPING		RECEIVED BY _____ IF INCOMPLETE IMMEDIATELY NOTIFY: SAMPLE MANAGEMENT OFFICE (703) 557-2490				
PAGE _____ OF _____										
FROM (STATION ID):	TO (LAB):	BATCH ID	DATE PROCESSED _____	DATE SHIPPED _____ AIR-BILL NO. _____	DATE RECEIVED _____					
SAMPLE ID	ALIQUOTS SHIPPED (FOR STATION USE ONLY)								SPLITS	SAMPLE CONDITION UPON LAB RECEIPT (FOR LAB USE ONLY)
	1	2	3	4	5	6	7	8		
01										
02										
03										
04										
05										
06										
07										
08										
09										
10										
11										
12										
13										
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28										
29										
30										
QUALIFIERS: ✓: ALIQUOT SHIPPED M: ALIQUOT MISSING DUE TO DESTROYED SAMPLE : :										
WHITE - FIELD COPY			PINK - LAB COPY			YELLOW - SMO COPY			GOLD - LAB COPY FOR RETURN TO SMO	

G.S.L.S. (702) 362-2100

Figure 10. Shipping form, National Stream Survey-Pilot Survey.

Section 6

Evaluation of Equipment and Protocols

The methods manual for the National Stream Survey (Hillman et al., 1987), describes all analytical methods used during the pilot survey in the contract analytical laboratory and the field laboratory. The contract analytical laboratory equipment and methods and the majority of the field mobile laboratory equipment and methods had been used successfully during Phase I of Eastern Lake Survey in 1984 (Linthurst et al., 1986).

A major objective of the pilot survey was to evaluate methods and equipment for collecting and processing stream water samples. Methods evaluated included all field procedures and two new field laboratory procedures that were not used in previous NSW studies. All field equipment and the equipment required for the two new laboratory methods were also tested. In addition, two holding time studies were conducted. Results of these studies were used to assess the chemical stability of water samples over time. The following sections describe the evaluations conducted during the pilot survey and present recommendations based upon evaluation results. The holding time studies are described in other documents that are appended to this report.

Field Laboratory Methods Evaluations

Field Laboratory Conductivity Measurements

The portable conductivity meter used during the pilot survey does not have a high resolution at the low conductivities ($<20 \mu\text{S}/\text{cm}$) observed at many stream sites. During the final days of the pilot survey, a YSI Model 32 laboratory conductivity meter and 3310

probe were used to evaluate the feasibility of conducting conductivity measurements on stream water samples in the field laboratory. Because the number of samples measured by using this procedure was small, the evaluation results must be interpreted cautiously. The few measurements that were made, however, indicated that accurate measurements of conductivity could be obtained in the field laboratory without adversely affecting other aspects of laboratory operations. Measuring conductivity at the field laboratory would provide an accurate measurement of conductivity on samples within 12 hours of their collection.

Preparation of Organic Monomeric Aluminum Fraction

The preparation of this fraction involved passing a filtered aliquot of sample through a cation-exchange column. After the ion-exchange process, the aliquot was subjected to the aluminum extraction protocol used in NSW projects (Hillman et al., 1987) to prepare a fraction for analysis of total extractable aluminum.

The ion exchange resin (Amberlite 125) was conditioned before use to bring the pH of the resin column within 0.5 pH unit of the expected sample pH. Columns were conditioned by adjusting a 1×10^{-5} N NaCl solution to the desired pH with HCl or NaOH. This adjusted solution was passed through the resin column, and the pH was measured on an aliquot of the collected eluant. This process was repeated until the desired pH of the resin column was achieved.

A 125-mL aliquot of sample was filtered into a 250-mL Pyrex beaker that had been washed with 5 percent HNO_3 and had been

rinsed with deionized water. The sample in the beaker was pumped through the ion-exchange column at a rate of 30 mL/min. The first 30 mL of sample collected from the column was discarded. The next 20 mL was collected, and its pH was measured. Three 5- to 10-mL portions of the sample were used to rinse a 50-mL polycarbonate centrifuge tube. The next 25.0 mL of sample was measured as accurately as possible (± 0.1 mL) into the centrifuge tube. The column was then flushed with the adjusted NaCl solution, an aliquot of the NaCl solution was collected, and its pH was measured. This measurement ensured that the column was conditioned properly for the next sample. The aluminum extraction procedure was then performed on the aliquot of sample.

Several aspects of the methodology merit attention by future workers. First, adjusting the pH of the NaCl solution was time-consuming, and the adjusted solution was not stable over time. Allowing the solution to equilibrate with the atmosphere overnight before adjusting the pH sometimes improved the stability of the solution pH. During the pilot survey, three or four different columns were prepared daily to cover the range of pH values. Second, a standard solution having a known concentration of organic monomeric aluminum was not available for use as an audit sample to check on the accuracy of the preparation procedure. Third, the methodology as used in the field laboratory was feasible; however, the additional equipment required crowded the work area in the laminar flow hood. It is suggested that other fractionation methods be investigated for possible implementation in future surveys.

Field Equipment Evaluations

The initial selection of field equipment for routine use in the pilot survey was based on the prior experience of field personnel and on recommendations from researchers. Under field conditions, the performance of this equipment was compared to the performance of several alternative instruments. Several pH, conductivity, and dissolved oxygen meters were evaluated on the basis of comparability in measurements, comparability with laboratory measurements, ease of use, portability, and overall durability. These evaluations confirmed that the equipment used during the survey was satisfactory in meeting the needs

of the NSS. Results of these comparisons are available as an unpublished memorandum report from the Acid Deposition Department, Lockheed-EMSCO, Las Vegas, Nevada.

Field Methods Evaluations

Field protocols developed for the pilot survey were based on analytical methods described in the NSS methods manual and upon recommendations of researchers and instrument manufacturers. Potential modifications of these methods were evaluated during field sampling operations. Some modifications were adopted immediately (e.g., pH). Other modifications (e.g., sample holding times) were evaluated experimentally for use in subsequent NSS or NSWs programs.

In-line Filtration at Streamside

The filtration of samples during the collection process was tested before the start of pilot survey field operations. Filtration in the field, if proven feasible, would minimize the potential deterioration of samples before their delivery to the field laboratory. A cartridge filtration unit that used disposable membrane filters (47 mm dia., 0.45- μ m pore size Gelman Metrical) was fitted into the Tygon pump tubing. The filtrator unit was tested on both the suction and the discharge sides of the peristaltic pump.

The evaluation was conducted over a 3-day period during which samples were collected from 16 streams. Difficulties in performing the operation were identified as (1) a high potential for sample contamination during filter replacement or as a result of filter rupture, (2) the increased time required at streamside to conduct filtration operations, (3) an increased load on the pump which required that the battery be recharged after only one site, and (4) an increased requirement for rinse water and other supplies. The consensus was that filtration of samples in the field using the equipment selected was not practical.

Sample Collection Method

During normal sampling operations, syringe samples were pumped from the

stream by using a portable peristaltic pump and Tygon tubing. This method was evaluated against the alternative of collecting samples directly from the stream into the sample container. The parameters of concern in syringe samples were pH and DIC concentration. Both of these parameters can be altered by direct contact with the atmosphere. A two-way analysis of variance indicated that there was no significant difference ($\alpha = 0.05$) between the collection methods on either pH or DIC measured at the field laboratory. After subjective evaluation of the methods, pumping was identified as the preferred method because samples can be collected in a consistent manner from streams of all sizes.

Streamside pH Measurements

Two methods of streamside pH measurement were used during the pilot survey. The closed-system method was designed to measure the pH of a sample that had not been allowed to come into contact with the atmosphere. The open-system method, which does allow atmospheric contact, is a more conventional approach. Both methods were used at each stream throughout the entire study.

An experiment was conducted to (1) evaluate the comparability of these two methods and (2) to compare the pH measurements of samples collected by using a pump with the pH measurement of samples collected directly from a stream. Three replicate samples of each treatment combination (method x collection device) were measured at each of three streams (12 samples per stream). The measurements were compared by using a two-way analysis of variance. No significant differences were detected ($\alpha = 0.05$); however, the open-system method required much less equipment and was simpler to conduct.

In Situ pH Measurement Method

Several devices were constructed and were tested in an effort to measure pH in situ. The two most promising of these were (1) a set of nested beakers with the pH electrode

and ATC probe suspended in the inner beaker and (2) a short section of PVC pipe with the electrode and ATC probe inserted through two openings near the center of the pipe. Measurements made with these devices were compared with both field pH measurements. A two-way analysis of variance revealed no significant differences among methods ($\alpha = 0.05$).

The results of this test indicate that the streamside methods used in the pilot survey yielded pH values that were comparable to in situ measurements. Streamside measurements proved to be more efficient because they require less equipment, are simpler to perform, and do not require that the field sampler enter the water.

Sample Holding Time

Current sample handling procedures used in all NSWIS programs involve processing and preserving raw samples at the field laboratory within a specified holding time (i.e., within 12 to 15 hours of sample collection). Future NSWIS projects may require longer intervals between sample collection and subsequent stabilization and preservation. Two separate studies were conducted to evaluate the effect of holding time on sample chemical composition. One study involved samples collected and stored in sealed syringes. The other involved samples collected and stored in 4-L Cubitainers.

The details and results of the two studies are presented in other documents that are appended to this report. The result of these studies indicated that syringes could be held for up to 7 days under conditions similar to those during the pilot survey without a significant change in either pH or dissolved inorganic carbon. Cubitainers could be held under conditions similar to those encountered during the pilot survey for as long as 84 hours before processing and preservation without a significant change in any of the chemical parameters measured.

Section 7

Summary of Field Operations

The pilot survey was completed on schedule on July 17, 1985. The down stream node of each of the 61 stream reaches was sampled four times during the survey. Upstream nodes of all reaches were sampled at least once (during the summer sampling period). Each of the three teams visited approximately 20 streams during a 2-week (10-day) sampling period. Fifty-seven days of operation (not including days off in the field) were required to complete the sampling.

A total of 759 samples (routine, field duplicate, field blank, and audit samples) were processed by the field laboratory in Sylva, NC, and were shipped (as 6,072 different aliquots) to the contract analytical laboratory. Only one shipment was delayed: the courier service did not deliver samples to the analytical laboratory on a Saturday.

The preliminary development of site dossiers and the reconnaissance of each sampling site were essential to the successful completion of the pilot survey. Problems associated with locating and gaining access to sampling sites were discovered and were resolved before actual sampling commenced. A great deal of time was saved, and the possibility of not obtaining samples from designated streams was minimized. The use of local cooperators expedited the reconnaissance process.

During spring sampling, which was conducted primarily at downstream sites, teams were in the field for an average of 8.8 hours per day. The average time consumed in a full day of sampling activities during the summer sampling period was 14 hours because upstream and downstream sites were sampled at all streams. The time spent on

each sampling activity performed during the summer survey is given in Table 5.

Table 5. Sampling Activity Time Summary for Summer Sampling Period, National Stream Survey-Pilot Survey

Activity	Time Summary (hours)	
	Range	Average
Calibration and preparation	0.5 - 3.0	1.5
First stream, upstream site		
Drive to access point	0.5 - 4.0	2.0
Hike to site	0.0 - 4.0	0.25
Sample	0.5 - 1.5	0.75
Hike from site	0.0 - 4.0	0.25
First stream, downstream site		
Drive to access point	0.25 - 1.0	0.5
Hike to site	0.0 - 4.0	0.25
Sample	0.5 - 1.5	0.75
Hike from site	0.0 - 4.0	0.25
Second stream, upstream site		
Drive to access point	0.5 - 3.0	1.5
Hike to site	0.0 - 0.5	0.25
Sample	0.5 - 1.5	0.75
Hike from site	0.0 - 0.5	0.25
Second stream, downstream site		
Drive to access point	0.25 - 1.0	0.5
Hike to site	0.0 - 0.5	0.25
Sample	0.5 - 1.5	0.75
Hike from site	0.0 - 0.5	0.25
Return to Field Station	0.0 - 4.0	2.0
Final calibration and cleanup	0.5 - 1.5	1.0
Total		14.00

Approximately 45,000 vehicle miles were traveled by the three field teams during field sampling activities. Additional miles by foot, boating, or horse back were required to access some sampling sites. The breakdown

of the total miles required by each field team to complete sampling activities is presented in Table 6.

Table 6. Summary of Distance Traveled by Field Sampling Teams, National Stream Survey-Pilot Survey

Mode of Travel	Daily Miles Traveled per Team		Total Miles Traveled
	Range	Average	
Automobile	60 - 400	270	~45,000
Boat	0 - 4	0.1	16
Horse	0 - 12	0.1	12
Foot	0 - 16	1.0	160

On occasions when long hikes were required to gain access to sampling points, one or two people assisted the field sampling team. The primary function of these additional personnel was to carry some of the sampling gear and samples. They were especially useful during the summer session when upstream and downstream samples were taken on the same trip.

The methods evaluations, equipment evaluations, and experiments conducted during the pilot survey provided information that will be used to modify the proposed research plan for NSS-Phase I operations. The pilot survey demonstrated that field operations could be conducted in such a manner that samples and field data from streams over a large geographic area could be collected and analyzed consistently and quickly.

Selected cost estimates for the pilot survey are presented in Table 7. These costs

reflect equipment and other supplies necessary to collect and process samples. These estimates are provided as an aid to planning studies of similar scope and purpose. Additional costs related to personnel support and to operating a field station are not included.

The cost to equip a team to conduct field sampling activities (visit 20 streams four times each) was between \$2,500 and \$3,000. This estimate includes purchasing the dissolved oxygen meters which for the pilot survey were borrowed rather than purchased. A set of sample containers (including Cubitainers, syringes, and aliquot bottles) cost about \$20 for each routine, field blank, or field duplicate sample collected.

The equipment and instrumentation in the field laboratory cost approximately \$40,000 (Morris et al., 1986). This estimate includes expendable supplies used in the laboratory during the pilot survey (approximately \$5,000). Because the field laboratory and its equipment had been purchased for Phase I of the Eastern Lake Survey, this cost was not part of the pilot survey budget. A field laboratory costs about \$20,000 to construct (Morris et al., 1986).

Containers for preparing eight preserved aliquots from each sample cost about \$13 per sample. All containers used during the survey were subjected to a rigorous cleaning procedure (Hillman et al., 1987) that cost about \$30 per sample (including field and laboratory containers). Preserved aliquots were shipped via overnight courier service to the contract analytical laboratory at a cost of about \$100 per container (6 to 8 sets of aliquots). Overnight service was necessary to assure that aliquots would arrive at the analytical laboratory within 48 hours of collection to meet sample holding times.

Table 7. Selected Cost Estimates^a, National Stream Survey-Pilot Survey

	<u>Cost (dollars)</u>
Field Sampling	
Vehicle Rental	1,000 per team (monthly)
Field Equipment:	
pH meter and electrode	600 per team
Conductivity meter and probe	540 per team
Dissolved oxygen meter and probe	900 per team
Staff gauges	40 per team
Peristaltic pumps and batteries	500 per team
Sampling Containers:	
4-L Cubitainers	3 per sample
60-mL syringes	15 per sample
500-mL bottles	2 per sample
Field Laboratory and Analytical Support:	
Instrumentation, equipment, and supplies	40,000 ^b
Aliquot containers	13 per sample
Bottle cleaning	30 per sample
Shipping cost (overnight courier service)	100 per container (6-8 samples)

^a Based on estimates provided by personnel responsible for procurement or quality assurance.

^b Field laboratory and its instrumentation was available from the Eastern Lake Survey. Necessary supplies for the pilot survey were approximately \$5,000.

Section 8

Observations and Recommendations

This section summarizes the problems experienced during the pilot survey and provides associated recommendations in tabular form. The information is presented in four categories: field safety, planning activities, field sampling operations, and field laboratory operations.

Field Safety

Table 8 summarizes problems associated with field safety. The daily itinerary form, which provided the field station with a record of the proposed routes of travel and estimated time in the field, was very useful. Portable radios would have improved communications in some areas where telephones were not convenient. Many field samplers complained of fatigue from driving the same roads day after day. A possible solution is to rotate samplers among teams such that a team would always contain one member who is familiar with the assigned sampling sites and their access.

Planning Activities

Preliminary site reconnaissance, as stated previously, was necessary to facilitate pilot survey field operations and to ensure that the objectives of the survey were achieved. Specific recommendations are listed in Table 9. In addition, future NSS projects should emphasize (during training) consistent guidelines for selecting a sampling location at a given stream site.

Field Sampling Operations

Recommendations concerning field sampling operations are listed in Table 10.

Recommendations related to data quality issues are also summarized in the following sections.

Field samplers should receive detailed training in basic hydrology, including the use and placement of staff gauges. Sampling containers and disposable collection equipment should be prepackaged into kits for each site to ensure that supplies are not forgotten and to reduce potential contamination during sample collection. The feasibility of reusing the pump tubing should be investigated with respect to potential contamination. Reusing tubing after rinsing with deionized water or sample water before collection would be much less expensive and would save space and weight during field excursions.

Protocols for measuring pH in the field during the pilot survey were designed to provide pH measurements that were equivalent in accuracy and precision to field laboratory measurements. It should be stressed that care of the pH meter and of the electrodes in the field is critical to the success of the protocol. The etching procedure recommended by the manufacturer should be used to clean the ceramic junction of the electrode, if required. The method involves removing the filling solution from the electrode and refilling it with deionized water; this is followed by immersing and stirring the electrode in a 50 percent (weight/volume) solution of sodium hydroxide for 3 minutes. The electrode is then drained, is rinsed twice with a 3 N KCl solution, is rinsed in pH 7.00 buffer for 2 minutes, and is refilled with 3 N KCl. This procedure improved the response and stabilization time of the electrode.

Measurement values of in situ conductivity may have been affected because, for the

Table 8. National Stream Survey-Pilot Survey Problems and Recommendations: Field Safety

Problem	Solutions Employed	Recommendations
Vehicle identification.	None used.	Use vehicle identification placard to identify a vehicle as being used for the NSS in remote locations.
Lack of radio communication.	Daily itinerary filed by all teams. Teams required to call-in at pre-determined times.	Investigate cellular or mobile radio units for all sampling vehicles.
Failure to meet call-in protocol.	Emphasized importance of call-in to team members. Added 1/2 hour delay from time of required call-in to initiation of search and rescue.	Require call-in according to protocol. Require daily itinerary. Emphasize call-in during training. Set flexible time for call-in for teams traveling to remote stream site.
Lack of safety protocol specifically relevant to storm episodes.	None used.	Develop safety protocol for teams isolated during storm events.
Lack of adequate shelter during storm events.	Standard supply included: One space blanket per person. One raincoat per person. One pair of sturdy, water repellent shoes per person.	Supply the following gear to each person: Space blanket. Rain coat. Rain pants. Sturdy, water repellent shoes. Sleeping bag. Supply the following gear to each team: Lightweight tent. Shelter half or rain fly to protect sampling gear.
Driver's fatigue.	Switched driving duties among team members. Driver education during training.	Discuss fatigue in driver training course. Have long-haul truck driver teach methods of reducing fatigue. Shorten driving duties. Provide driver with mechanical drowsiness detector. Switch driving duties.

Table 9. National Stream Survey-Pilot Survey Problems and Recommendations: Site Reconnaissance and Access

Problem	Solutions Employed	Recommendations
Inadequate maps (1:24,000 and 1:250,000 scale maps were often 30 years old).	Provided several map sources.	Provide as many map types as possible, including: USGS Topo maps. State transportation maps. County road maps. USFS road maps. Fishing and hunting maps. Provide the most recent maps of each type available.
Inadequate sample site selection criteria.	Training addressed generalities of site selection.	Use USGS or Fish and Wildlife service personnel to train sampling personnel and to emphasize site selection during training. Visit several stream sites and identify good and poor sample locations.
Site access.	Permission was acquired to gain access to a site. If permission could not be acquired, a new site was selected.	Use local cooperators at all sites to assist in gaining access permission. During training, stress friendliness to land owners and willingness to communicate about the need for access.

Table 10. National Stream Survey-Pilot Survey Problems and Recommendations: Field Sampling Activities and Equipment

Problem	Solutions Employed	Recommendations
Unclear objectives for stream stage measurement.	Developed protocol for collection of minimal information.	Clarify objectives of hydrologic data collection. Design data collection methods to fit needs.
Poor stream gauge placement.	Attempted to place staff at neutral location so staff could be read accurately at all stage heights.	Emphasize staff placement in training. Visit several streams with an experienced hydrologist to locate good placements and illustrate poor placement.
Loss of stream gauges due to vandalism and high flows.	Established secondary reference marks on permanent features for future re-establishment of staff base height.	Establish all sites with a secondary reference on first visit.
Excessive battery discharge in cold weather and during in-line filtration experiments.	Recharged battery daily. Carried spare batteries. Batteries were kept as warm as possible in transit.	Carry extra, fully charged batteries. Do not filter samples at streamside. Use thin-walled pump tubing through pump head (may require reuse of pump tubing).
Tripped pump circuit breaker in cold weather and in-line filtration experiments.	Waited for circuit breaker to cool and reset. Purged tubing for short period before taking sample.	Heavier duty pump needed for hard pumping. Thin-walled Tygon tubing would be useful, at least through pump head. May require reuse of a short section of pump tubing. Do not filter samples at streamside.
Faulty or loose battery cable connections.	Inspect and tightened terminals periodically. Removed faulty terminals. Carried replacement cables.	Carry replacement cables. Solder terminals onto wire. Provide replacement banana plugs.
Higher than expected consumption of surgical grade Tygon tubing, syringe, Cubitainers, syringe valves, and 500-mL aliquot bottles.	Inventory was checked weekly, supplies were ordered well in advance of need. Reduced length of tubing used for blank samples. Cleaned and reused 500-mL aliquot bottles for suspended solids.	Estimate number of samples prior to entering field. Order sufficient supplies for all samples well in advance of start-up date for sampling. Supply 10 percent minimum overage for unexpected consumption related to special samples and contaminated or damaged containers and supplies.
Incomplete sample collection supplies taken into field by teams.	Pre-made kits were assembled by teams in advance of demand (allowed advance warning of short supplies). Developed daily checklist of supplies.	Prepare kits for at least one week of sampling in advance of need. Maintain inventory weekly. Use daily checklist before departing for field sites.
Special experiments and studies required large amount of supplies.	None.	Plan special studies well in advance and allow for advance supply of materials. Allow 10 percent minimum overage for waste in all experiments.
Failure of 5 out of 9 portable pH meters in field.	Returned faulty meters as failures occurred. Provided alternative field pH meter for times when adequate numbers of primary meters were not available. Carried meters in carrying cases or vest to minimize shock.	Maintain a complement of two functional meters per team. Protect meters from shock in transport and use by carrying them in cases carried near sampler's chest.

(continued)

Table 10. (continued)

Problem	Solutions Employed	Recommendations
Battery failure and lack of replacement batteries for pH meters.	Back-up lithium batteries were provided as quickly as they could be supplied. Kept one full set of replacement batteries for all meters.	Supply at least one functional set of backup batteries with each meter. Maintain a store of one additional set of batteries for each meter at a central location.
Bubbles in coils of pH electrode.	Tapped electrode to remove bubbles. Carried electrodes in vertical position. Twirled electrodes by cable prior to reading at each site.	Twirl electrode by cable before reading at each site. Carry electrode in padded case and upright position.
Slow pH electrode response.	Replaced epoxy bodied electrodes with glass-bodied electrode. Etched glass-bodied electrodes periodically with NaOH.	Use glass bodied electrode. Etch glass-bodied electrodes as necessary with NaOH.
pH electrode breakage.	Carried electrodes in upright position in carrying case or vest pocket. Back-up electrodes were carried by each team and also kept at the field station.	At least 2 back-up electrodes should be available for each team in the field.
Slow pH electrode response for stream samples and apparent hysteresis following QCCS measurement.	Refined protocol to allow longer electrode equilibration time in pH measurement. Attempted to develop low ionic strength, circumneutral QCCS for pH.	Adopt modified protocol: Conditioning soak followed by successive aliquots measured to stability within and among aliquots. Continue to use pH 4.01 H ₂ SO ₄ QCCS.
Thermal inequality between pH chamber and ATC bath.	Attempted to design chamber that allowed ATC to fit in chamber with electrode. Sheltered ATC bath and pH chamber from direct sunlight.	Conduct open pH measurement only. Continue to develop chamber design to compensate for temperature change in small sample.
Poor comparability between field and lab pH measurements.	Modified field protocol to: Improve calibration. Provide stringent criteria for stability of a reading. Closely mimic field lab protocol. Eliminate dependence on auto-lock feature of portable pH meter.	Utilize field procedures which simulate field lab protocol (Hillman et al. 1987). Do not use auto-lock features of pH meters designed to automatically determine stability of pH measurements.
Stream conductivity below calibration and QCCS range.	Tested low conductivity (14.7 μ S/cm) QCCS in field.	Continue to use 74 μ S/cm QCCS at each site. Use a 14.7 μ S/cm QCCS as a low range QC check at calibration room daily.
Poor conductivity probe position while calibrating and sampling.	Adjusted cord length to keep probe off bottom of calibration bottle, but submerged in standard while calibrating. Required probe to be positioned under surface and in line with current while sampling.	Set up probes to facilitate calibration in 250-mL bottles. Standardize subsurface and in situ position of probe for sampling.

(continued)

Table 10. (continued)

Problem	Solutions Employed	Recommendations
Poor resolution of field meter at low end of conductivity scale.	Switched to meter with multiple range capabilities for summer sampling.	Lower range of meter used in summer worked well, should evaluate low range instrument under field conditions. Measure conductivity at field laboratory.
Lack of expertise in maintenance of dissolved oxygen meters.	Replaced membrane every other week. Developed expertise with maintenance procedures.	Include maintenance procedures in training program. Practice probe maintenance several times in lab environment before attempting it in the field.
Unclear qualitative data recorded on watershed characteristics form.	Attempted to train all teams to record data in a consistent manner.	Give numerical guidelines for all qualitative data: e.g., sparse = 5 individuals visible, or sparse = 5 percent of total. Emphasize during training. Clarify purpose of this
Some pertinent information was not requested on field data forms.	None.	Add time, gauge height, and flow velocity at arrival and at departure on field data form. Add percentage canopy cover to watershed characteristic form. Add space to identify duplicate, blank, and other special samples on field data form. Add box for "special samples taken," "not sampled," and boxes to clarify tracking of experiments, episode samples, duplicates, and blanks.
Illegible forms, difficult key punching.	Interacted with data management personnel frequently to clarify problems.	Use standard units for stream width, depth (don't mix feet and meters). Use standard qualifier to denote when a QCCS check failed. Use leading or trailing zeros to fill all data blocks in a field. Standardize shape of numbers and letters used on forms. Add hundredths digit to gauge height entry blank. Clarify "+" in dissolved oxygen block. Replace "Replicate Number" with "Site Visit Number" on Form 4. Train field personnel on data entry considerations. Train field personnel on proper use of comments and data qualifiers.
Repetitious data required on various forms.	None.	Redesign forms to eliminate repetitious information.

range of conductivities encountered (generally $<50 \mu\text{S/cm}$), the meter was not easily read. The meter that was most reliable under field conditions had a poorer resolution at conductivities less than $40 \mu\text{S/cm}$. Meters having greater resolution that were tested were not suitable for use under field conditions. A low-conductivity QCCS should be used in the field (e.g., $5 \times 10^{-4} \text{ N KCl}$ solution having a specific conductance of $14.7 \mu\text{S/cm}$ at 25°C), and conductivity should be measured in the

field laboratory to provide an accurate measurement of this parameter within a short time after sample collection.

Field Laboratory Operations

Problems and recommendations regarding field laboratory operations are summarized in Table 11. Dust in the laboratory was a problem at the beginning of the pilot survey,

Table 11. National Stream Survey-Pilot Survey Problems and Recommendations: Field Laboratory Operations

Problem	Solutions Employed	Recommendations
Feed water to the laboratory was of poor quality, affected performance of the reverse osmosis system.	Changed carbon prefilters every other day.	Install sediment filter in front of carbon pre-filter to remove large particulate material.
Laminar flow hood not functioning efficiently.	None.	Inspect blower unit for proper wiring and installation.
Dust in laboratory.	Moved laboratory away from heavy traffic area.	Locate the laboratory away from areas of traffic and dust, or locate the laboratory indoors in a controlled environment (e.g., warehouse).
Condensation coming into lab via A/C units.	Units operated during processing only when necessary.	Investigate use of replaceable filters on units, or locate laboratory indoors in controlled environment. Provide outside drain for condensation.
Laminar flow hood crowded with reagents and glassware used for filtration, aluminum extractions.	Prepared aliquots of organic monomeric aluminum first. Analyst 2 assisted with preparing aluminum extraction extracts after filtration was completed.	Conduct all filtering first, then use entire work area for aluminum extractions. Investigate alternative methods for preparing or analyzing dissolved aluminum fractions.
Preparation time for organic monomeric aluminum aliquot excessively long.	Processed samples through column in order of decreasing pH. Analyst 2 assisted in preparation and extractions.	Establish pH criteria for preparing organic monomeric aluminum aliquots.
Lack of audit sample or QCCS having known concentration of organic monomeric aluminum.	None.	Develop and test appropriate standard solution. Investigate alternative methodologies.
50-mL centrifuge tubes often leaked during MIBK extraction procedure.	Tubes were inspected during rinsing and again before shaking.	Use only 50-mL Corning tubes with orange screw-top sealing caps.
Teflon O-ring in MIBK aliquots dissolved into solution.	Use of sealing O-rings was	Use different type of container or obtain O-ring of solvent-resistant material.
Turbidity readings fluctuated because of presence of different size particles.	First reading on nephelometer was recorded.	Standardize protocol for turbidity measurement.
Lack of a QCCS <2 NTU.	5 NTU standard was diluted 1:3 to make a 1.25 NTU (Laboratory prepared solution yielded acceptable readings for 3-4 days.)	Use fresh standard that is certified.
Lack of acceptable QCCS for total suspended solids.	Diatomaceous earth suspension used was not adequate.	Acceptable standard must be developed.
Testing of pH after preservation required large numbers of pipette tips.	Nonheparinized glass capillary tubes used to test pH.	Continue to use capillary tubes.
Aliquots sometimes preserved with wrong acid.	Labels color-coded as to type of acid required.	Continue to use colored labels.

but the problem was corrected by relocating the laboratory trailer a short distance from its original location.

The supply of reagent grade water in the field laboratory was barely adequate. The daily requirements of three sampling teams for reagent grade water plus the daily requirements of the laboratory were barely satisfied with the existing reverse osmosis system that produced about 4-L per hour. The quality of the field water to the laboratory was also poor; this required that carbon prefilter cartridges be changed every 48 hours. During the pilot survey, a fibrous prefilter cartridge system was installed in front of the carbon prefilter cart-

ridge to filter the field water before it entered the reverse osmosis system. This filter extended the life of the purification cartridges. If future NSS operations require that a field laboratory support more than three sampling teams or if daily sample loads per laboratory are increased, the present water system would not be sufficient.

Audit samples or other QC samples should be developed for the organic monomeric aluminum fraction and for total suspended solids analysis if these parameters are to be measured in future NSS operations. Alternate methodologies for fractionating dissolved aluminum species should be evaluated.

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Appendix A

Syringe Sample Holding Time Study

by

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Introduction

In the various programs within the National Surface Water Survey (NSWS), water samples are analyzed for pH and dissolved inorganic carbon (DIC) in such a way that the sample is not exposed to the atmosphere during collection or analysis. These "closed-system" measurements are required because changes in the dissolved CO₂ concentration can significantly change these parameters in samples from dilute waters having little or no buffering capacity. Samples are collected in syringes, sealed, and analyzed at a field laboratory within 12 to 18 hours of collection. Proposed changes in the logistical plans for future NSWS activities (e.g., accessing lakes or streams from the ground rather than by helicopter) will require longer holding times for syringe samples before closed-system measurements can be made. This study investigated whether longer holding times would significantly alter the pH or DIC of dilute water samples stored in sealed syringes.

Three factors were initially considered to be significant in affecting pH or DIC in a syringe sample: biological activity, chemical activity, and permeation of CO₂ across the wall of the syringe. Biological and chemical activity are assumed to be negligible because of the holding conditions employed. Samples are stored in the dark at 4 °C until analysis. Thus the permeation of CO₂ is the important con-

sideration in how long syringe samples will provide an accurate representation of in situ conditions of pH and DIC. This study was composed of four experiments designed to investigate the stability of syringe samples at different concentrations of dissolved CO₂, different holding temperatures, and different levels of biological activity.

Analytical Methodologies and Reagents

Dissolved Inorganic Carbon Determinations

A Xertex Dohrmann DC-80 total carbon analyzer equipped with a Horiba DIR-2000 infrared detector was used. The unit was equipped with a 1-mL sample loop. The analysis involved converting all of the DIC in a sample aliquot into CO₂ with 5 percent H₃PO₄, and carrying the CO₂ into the infrared detector with nitrogen gas.

Deionized water meeting ASTM Type I specifications (ASTM 1984) was used to prepare all reagents and standards. A 1,000 mg/L C calibration stock standard was prepared by dissolving 8.825 g of over-dried, primary standard grade Na₂CO₃ in deionized water and by diluting to 1.000 liter. A quality control stock standard of 1,000 mg/L C was prepared independently of the calibration stock solution. A

10.00 mg/L C calibration standard was prepared by diluting 5.00 mL of the calibration stock to 500.00 mL with deionized water.

Quality control check samples (QCCS) of 2.00 and 20.00 mg/L C were prepared by diluting 1.00 mL and 10.00 mL of the quality control stock solution to 500.00 mL, respectively. Each of these solutions was transferred to Omnifit borosilicate glass reagent bottles having three one-way valves. These bottles were vented to the atmosphere through tubes of CO₂ absorbent (Mallcosorb) and water absorbent (Aquasorb). The head-space of each reagent bottle was purged with reagent grade, CO₂-free nitrogen gas (N₂) for 30 minutes. The DIC standards were maintained in these bottles under a CO₂ free atmosphere until analysis. The stock solutions were purged with N₂ before preparing any DIC standards.

pH Determinations

An Orion model 611 bench meter equipped with an Orion Ross glass combination pH electrode (model 81-02) was used to determine the pH of all samples. Closed-system measurements of pH were accomplished by using a custom-made sample chamber described in Hillman et al. (1986).

The meter was calibrated each day by using commercially available NBS-traceable buffer solutions (pH 7.00 and pH 4.00). A quality control check sample having a theoretical pH of 4.00 was prepared by diluting 1.00 mL of a 0.100 N H₂SO₄ solution to 1.000 L with deionized water. A pH 7.00 quality control standard was prepared by diluting 0.27 mL of a 1,000 mg/L C solution to 1.000 L and by sparging with 300 ppm CO₂ gas in air for 30 minutes.

Analytical Protocols

All samples to be measured were collected and stored in 60-mL polypropylene syringes (Becton-Dickinson) and were sealed with Dynatech Mininert syringe valves.

The DIC concentration of a standard or sample was determined by injecting a 5-mL aliquot into the sample loop. The instrument was calibrated with the 10.00 mg/L C standard. The linearity of the calibration was

checked with the 2.00 and 20.00 mg/L C quality control check samples and with a blank sample of deionized water. The calibration was checked after at least every eight sample measurements with the quality control check samples. The sample loop was rinsed between sample injections with 10 mL of deionized water.

The pH meter and electrode were calibrated and checked initially by using solutions contained in beakers. The pH 7.00 QCCS was prepared fresh each day. The pH 4.00 QCCS was prepared biweekly and was stored refrigerated when not in use. All syringe samples were allowed to equilibrate with room temperature before analysis. The sample chamber was rinsed with deionized water. A syringe containing sample was affixed to the chamber. The chamber was then filled with sample and was drained twice. The chamber was again filled with sample, and the electrode was inserted loosely into the top of the chamber. An additional 5-mL was injected to eliminate air bubbles. The chamber was sealed with the electrode, and an initial pH and temperature reading was noted. The pH of the aliquot in the chamber was considered stable when the reading changed less than 0.02 pH units over a 1-minute period. After the initial pH reading had become stable, a 5-mL aliquot was injected, and the pH was determined. The pH reading of this aliquot was recorded when stable. Additional 5-mL aliquots were injected and measured until the stable pH readings of two successive aliquots were within 0.03 pH units of each other. The reading of the last aliquot to be measured was recorded as the final pH reading for that syringe sample. The meter was checked after every four to five samples with the pH 4.00 quality control check sample. At least one measurement of the pH 7.00 quality control check sample was made each day.

Experiment 1

This experiment tested whether the pH and DIC of a sample initially devoid of dissolved CO₂ would change over time upon exposure to the atmosphere.

A synthetic sample was prepared by diluting 1.00 mL of a 1,000 mg/L C solution to 1 L. This solution was transferred to a

reagent bottle and sparged with N_2 for 30 minutes. Initial measurements of DIC and pH (time = 0) were made on this solution by collecting syringe samples directly from the reagent bottle. The solution was transferred to an open beaker and was covered with a watch glass. Aliquots were collected from this beaker into syringes, and measurements were made at 22, 47.4, 119.1, and 168 hours after the initial measurements.

Experiment 2

This experiment tested whether the pH and DIC of a sample initially supersaturated with dissolved CO_2 would change over time upon exposure to the atmosphere.

A synthetic sample was prepared by diluting 1.00 mL of a 1,000 mg/L C solution to 1 L. This solution was transferred to a reagent bottle and was sparged with 300 ppm CO_2 in air for 30 minutes. Initial measurements of DIC and pH were made on syringe samples collected directly from the bottle. The remaining solution was transferred to a beaker and was covered with a watch glass.

Syringe samples from the beaker were collected and analyzed at 24.2, 43.9, 118.3, and 165 hours after initial measurements were made.

Experiment 3

This experiment investigated the temporal stability of pH and DIC in synthetic samples representing different levels of initial dissolved CO_2 concentrations. The effect of temperature on temporal stability of these samples was also evaluated by holding syringe samples at two different temperatures: refrigerated (4-11 °C) and room temperature (21-26 °C).

A solution was prepared by diluting 10.00 mL of a 1,000 mg/L C solution to 10 L. This solution was sparged with N_2 gas for 45 minutes. This solution had no dissolved CO_2 initially ($pCO_2 = 0$ atm). Syringe samples were collected from this solution, and initial pH and DIC measurements were made (time = 0). Sixty-four additional syringes were filled with this sample (32 for pH, 32 for DIC measurements). These were identified as "Level 0" samples.

The remaining solution was sparged (with stirring) with 300 ppm CO_2 for 45 minutes. This solution initially had a dissolved CO_2 concentration in equilibrium with the atmosphere ($pCO_2 = 0.0003$ atm). Initial measurements of DIC and pH were made on this solution (time = 0). Sixty-four additional syringes were filled with this sample and were identified as "Level 1" samples.

The remaining solution was sparged (with stirring) with 3,000 ppm CO_2 gas for 45 minutes. This solution was equilibrated with 10 times the atmospheric concentration of CO_2 ($pCO_2 = 0.0030$ atm). Initial measurements of pH and DIC were made (time = 0). Sixty-four additional syringes were filled with this sample and were identified as "Level 10" samples. Finally, the remaining solution was sparged with 30,020 ppm CO_2 gas for 45 minutes. This solution was equilibrated with 100 times the atmospheric concentration of CO_2 ($pCO_2 = 0.0300$ atm). Initial measurements of DIC and pH were made (time = 0), and sixty-four additional syringes were filled with sample. These were identified as "Level 100" samples.

For each parameter (pH and DIC), there were 32 syringes from each CO_2 concentration level. Sixteen syringes for each parameter from each group were held at room temperature (21-26 °C). The remaining sixteen syringes for each parameter were refrigerated (4-11 °C) depending on the treatment level.

Four syringes from each level and temperature group were analyzed for pH and DIC at four times after initial measurements were made at time = 0. The exact times varied with the treatment level but ranged between 24 and 192 hours after time = 0. Instruments were recalibrated on each day of analyses. At least three measurements of QC check samples were made at each time samples were analyzed. These quality control solutions were prepared fresh each day, except for the pH 4.00 QCCS. In many cases, two aliquots from a syringe were measured for pH and DIC.

Experiment 4

This experiment investigated the stability of pH and DIC in samples of natural lake water held in sealed syringes. These samples represented waters similar to those under

study in the NSWS in terms of chemical complexity and biological activity.

Water was collected from Padden Lake and Bagley Lake, Washington. Samples were collected from below the surface and were stored in 4-L Cubitainers with no headspace and were shipped to the laboratory. The containers were kept sealed and at 4 °C until use. For each lake, 52 syringes (26 for pH, 26 for DIC) were filled and sealed. Twelve syringes from each lake were initially analyzed for either pH or DIC. Twenty syringes from each lake were held at 8 °C, and twenty syringes were held at room temperature (21-26 °C). Two syringes from each lake were analyzed for either pH or DIC at 13.0, 87.3, 108.9, and 170 hours after initial measurements were made. Two syringes were labelled for each sample. Measurements of pH and DIC were made on each syringe, and the process provided duplicate measurements for each parameter.

Data Analysis

Data collected for Experiments 1 and 2 were not analyzed statistically. Data from Experiments 3, 4, and 5 were evaluated for temporal changes in dissolved CO₂ concentration by using the following approach.

Because samples from each time group in a given experiment were analyzed on different days, any variation or differences observed can result from temporal changes in a chemical parameter over time or from day-to-day differences in the operation of an instrument. These two sources of variation are confounded, and comparing measurements of samples among days by ANOVA or similar analyses will not distinguish between the two sources of variation.

A simplified approach was used for the experiments conducted in this study. In a given experiment, the means of measurements made at each time interval were considered as observations drawn from a population having a grand mean estimated by \bar{X} and a variance about this mean estimated by $s^2(x)$. Holding time in itself is not considered as a classification factor. The means from each time group should be normally distributed according to the Central Limit Theorem.

The means of the measurements of QC check samples made at each time were treated in a similar manner, having a grand mean \bar{Y} and variance about this mean $s^2(y)$. The variance of the QC measurements provides an estimate of the day-to-day variation in the operation of the instrument, because they are standards of known concentration prepared fresh each day with negligible error which is due to preparation. The variance of the sample measurements provides an estimate of the variation which is due not only to instrument differences but also to changes in the chemical composition of the sample over time. If the dissolved CO₂ concentration of a sample changes over time, the measurement of DIC or pH will be farther away from the grand mean of the population, and the estimate of s^2 will be larger.

The two variances (samples and QC) were compared with an F-test. The null hypothesis was that $s^2(\text{sample}) \leq s^2(\text{QCCS})$. This was a one-tailed test with the alternate hypothesis being $s^2(\text{sample}) > s^2(\text{QCCS})$. Rejection of the null hypothesis ($P = 0.05$) would suggest that changes in dissolved CO₂ concentration in the samples over time contributed more variation than day-to-day differences in the operation of the instrument.

Results and Discussion

Experiment 1

The results from Experiment 1 are presented in Table A-1 and Figure A-1. The pH of the sample decreased substantially over the first 22 hours, while the DIC concentration nearly doubled during the same period of time. Between 22 hours and 168.9 hours, the pH fluctuated up and down between 7.2 and 7.7, while the DIC concentration slowly increased throughout the same period.

These results indicate the sample equilibrated with the atmosphere with respect to dissolved CO₂ within about 24 hours. Fluctuations observed after 24 hours may have resulted from changes in atmospheric CO₂ levels or from day-to-day differences in instrument operation. This experiment demonstrates the necessity of protecting samples low in dissolved CO₂ concentration from atmospheric exposure.

INITIAL $P_{CO_2} = 0$

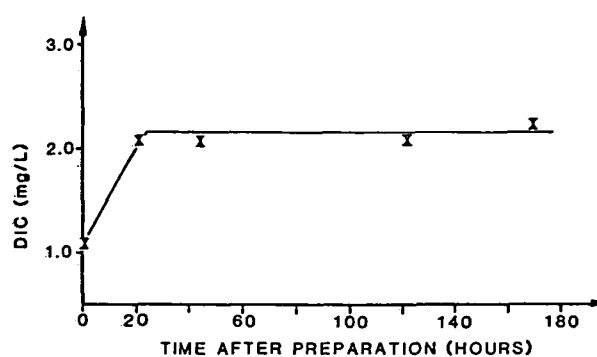
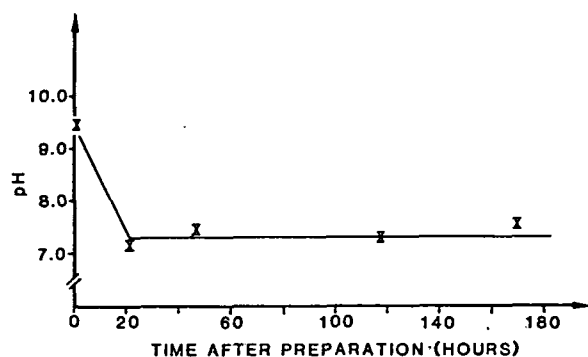


Figure A-1. Changes in pH and dissolved inorganic carbon over time in a sample initially having no dissolved carbon dioxide.

Table A-1. Dissolved Inorganic Carbon and pH Measurements of a Sample Initially Having No Dissolved CO_2

Time After Preparation (hours)	pH (n=1)	DIC (mg/L)		
		Mean	SD	n
0	9.47	1.109	0.025	2
0.33	—	1.113	0.001	2
22.0	7.23	2.110	0.011	2
47.4	7.44	2.154	0.016	2
119.1	7.22	2.167	0.002	2
168.9	7.68	2.249	0.010	4

over the first 2 hours and then decreased more sharply until 12 hours, after which the measurements appeared to stabilize.

Table A-2. Dissolved Inorganic Carbon and pH Measurements Over Time on a Sample Initially Supersaturated with Dissolved Carbon Dioxide

Time After Preparation (hours)	pH			DIC (mg/L)		
	Mean	SD	n	Mean	SD	n
0.0	5.66	0.02	2	12.94	0.160	2
0.25	5.67	0.01	2	12.41	0.020	2
1.0	5.70	0.02	2	11.58	0.130	2
2.1	5.74	0.01	2	10.60	0.150	2
4.1	5.94	0.01	2	7.80	0.052	2
5.5	6.04	0.01	2	6.55	0.150	2
8.6	6.56	0.01	2	3.29	0.011	2
12.0	7.13	0.01	2	2.29	0.011	2
24.2	6.86	0.08	2	2.53	0.008	2
43.9	9.01	0.13	2	2.40	0.018	2
118.3	7.18	0.06	3	2.17	0.016	3
165.0	7.31	0.01	2	2.18	0.016	2

Experiment 2

The results of Experiment 2 are summarized in Table A-2. One sample was analyzed during a 12-hour period (Figure A-2), while the second sample was analyzed during a 165-hour period (Figure A-3). The results of both sets of measurements are combined in Table A-2. The initial measurements of the 165-hour sample are not presented, but they were very near those values obtained from the 12-hour sample. The values for pH increased from 5.66 to 7.13 over the first 12 hours and were fairly stable after that time. A mean pH of 9.01 was measured on the sample at 43.9 hours. This value is an outlier, but no explanation for the discrepancy could be found, as measurements of quality control samples at the same time indicated the meter and electrode were operating properly. The DIC concentration of the sample decreased slowly

The results of this experiment demonstrate that samples high in dissolved CO_2 concentration should also be protected from atmospheric exposure prior to analysis.

Experiment 3

Summary statistics for each of the four levels of dissolved CO_2 concentrations are presented in Table A-3. For the Level "0" solution, mean pH decreased 0.1 pH unit over

EXPERIMENT TWO-PART ONE

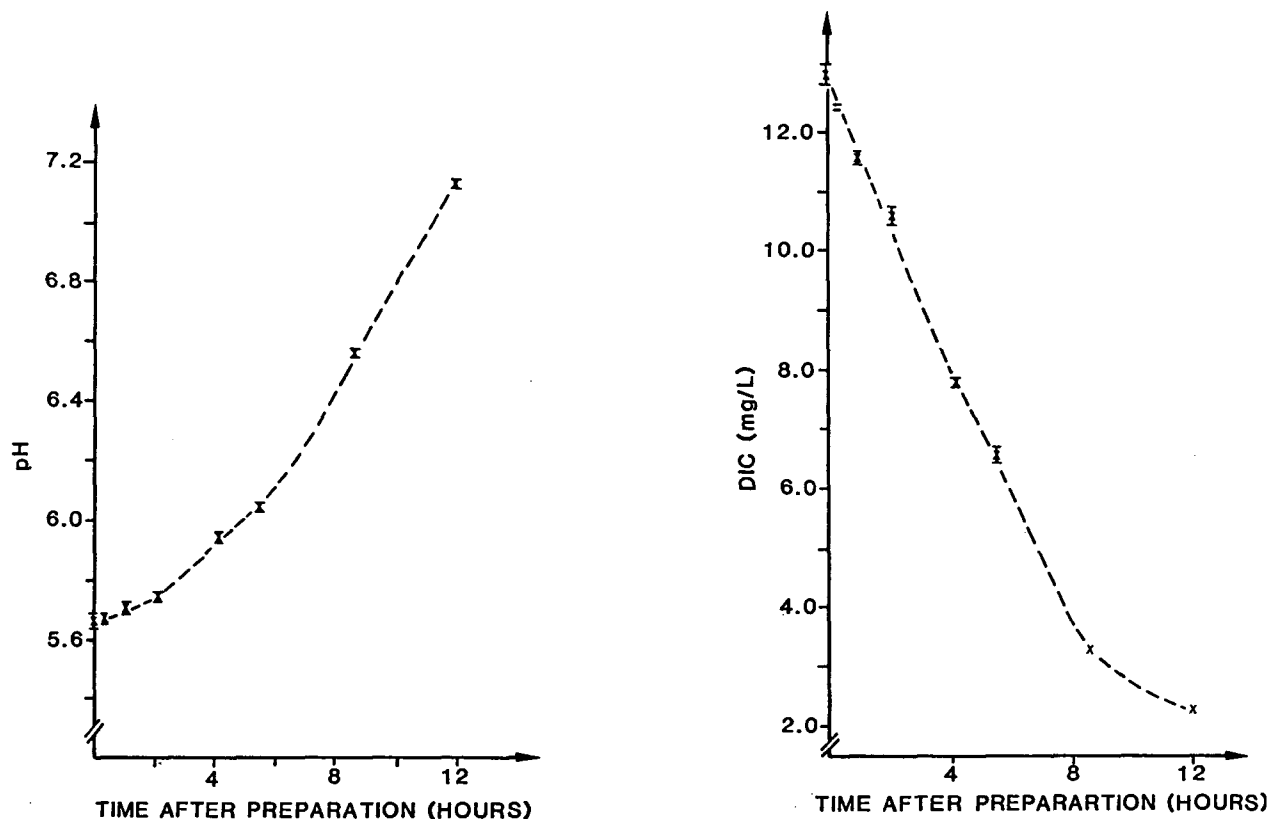


Figure A-2. Changes in DIC and pH over a 12-hour period in a sample initially supersaturated with carbon dioxide. (Means with standard deviations are presented).

EXPERIMENT TWO - PART TWO

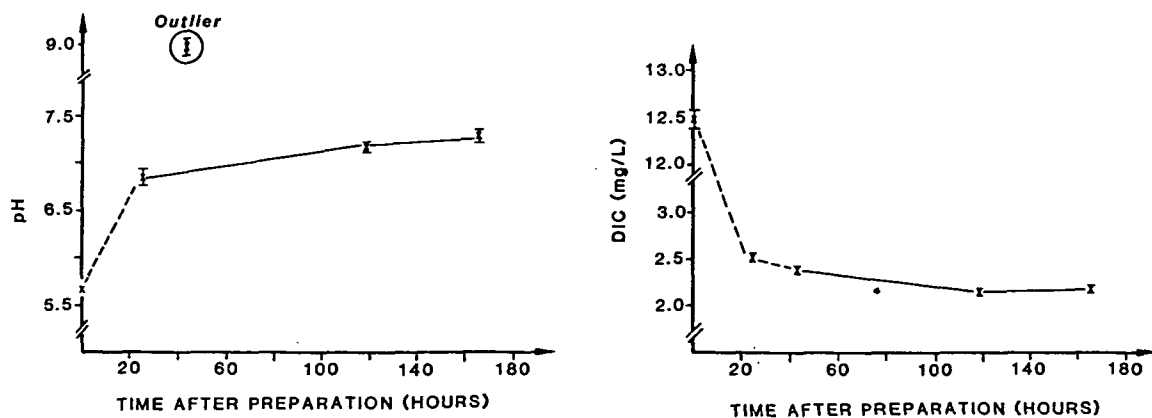


Figure A-3. Changes in DIC and pH over a 165-hour period in a sample initially supersaturated with carbon dioxide. (Means with standard deviations are presented).

Table A-3. Summary Statistics of pH and DIC Changes Over Time for Solutions of Different Levels of Dissolved Carbon Dioxide Stored at Different Temperatures (values are presented as means \pm SD, with sample sizes in parentheses.)

Time After Preparation (hours)	Refrigerated				Room Temperature			
	pH		DIC (mg/L)		pH		DIC (mg/L)	
LEVEL "0" SOLUTION								
0.0	9.46 ±0.07	(3)	1.538 ±0.023	(3)	9.46 ±0.07	(3)	1.538 ±0.023	(3)
24.5	9.40 ±0.04	(7)	1.535 ±0.033	(8)	9.39 ±0.03	(8)	1.533 ±0.029	(8)
96.8	9.37 ±0.02	(6)	1.479 ±0.015	(7)	9.22 ±0.02	(7)	1.525 ±0.034	(8)
119.8	9.32 ±0.09	(8)	1.487 ±0.040	(8)	9.09 ±0.07	(8)	1.596 ±0.017	(8)
191.2	9.36 ±0.02	(8)	1.514 ±0.036	(7)	8.78 ±0.03	(8)	1.757 ±0.023	(8)
LEVEL "1" SOLUTION								
0.0	7.52 ±0.01	(3)	2.134 ±0.003	(3)	7.52 ±0.01	(3)	2.134 ±0.003	(3)
18.3	7.48 ±0.06	(8)	2.091 ±0.056	(7)	7.44 ±0.07	(8)	2.137 ±0.025	(8)
91.4	7.41 ±0.13	(8)	2.142 ±0.006	(7)	7.21 ±0.05	(8)	2.283 ±0.024	(8)
113.8	7.45 ±0.09	(8)	2.110 ±0.066	(8)	7.15 ±0.04	(8)	2.276 ±0.051	(8)
161.0	7.52 ±0.08	(8)	2.078 ±0.037	(8)	7.10 ±0.05	(8)	2.286 ±0.036	(7)
LEVEL "10" SOLUTION								
0.0	6.70 ±0.01	(3)	2.840 ±0.038	(3)	6.70 ±0.01	(3)	2.840 ±0.038	(3)
24.0	6.75 ±0.01	(7)	2.919 ±0.020	(7)	6.73 ±0.03	(8)	2.928 ±0.059	(8)
47.6	6.74 ±0.02	(8)	3.067 ±0.085	(8)	6.74 ±0.04	(8)	3.067 ±0.086	(8)
144.3	6.72 ±0.01	(8)	2.800 ±0.028	(8)	6.67 ±0.06	(8)	2.860 ±0.093	(8)
166.3	6.72 ±0.03	(8)	2.857 ±0.068	(8)	6.68 ±0.03	(8)	2.927 ±0.088	(8)
LEVEL "100" SOLUTION								
0.0	5.67 ±0.01	(3)	12.41 ±0.12	(3)	5.67 ±0.01	(3)	12.41 ±0.12	(3)
22.9	5.70 ±0.01	(8)	12.51 ±0.22	(8)	6.71 ±0.01	(8)	12.06 ±0.10	(8)
45.7	5.71 ±0.02	(8)	12.33 ±0.10	(7)	5.74 ±0.02	(8)	11.17 ±0.16	(8)
120.5	5.70 ±0.01	(5)	12.29 ±0.13	(5)	5.77 ±0.01	(8)	10.41 ±0.05	(6)
215.1	5.74 ±0.01	(5)	12.02 ±0.15	(4)	5.87 ±0.01	(7)	9.44 ±0.22	(4)

the course of the experiment in the refrigerated syringe samples and decreased almost 0.7 pH units in the samples stored at room temperature. In the same solution, DIC exhibited a slight overall decrease (0.03 mg/L) over the course of the experiment in the refrigerated samples, and increased by approximately 0.2 mg/L in the samples held at room temperature. The simultaneous decrease of pH and DIC in the refrigerated samples is not possible based on the known relationship between DIC and pH, and the observed change is a result of random experimental error.

For the Level "1" solution, pH measurements indicated no net change over the course of the experiment in the refrigerated samples and a maximum change of 0.1 unit from time = 0, which occurred at 91.4 hours. Samples held at room temperature showed a steady decrease in pH over time, with a net change of approximately 0.4 units between time = 0 and

161 hours. The DIC content of this solution changed very little in the refrigerated samples over the course of the experiment (approximately 0.05 mg/L net change). In the samples held at room temperature, the DIC content showed a net increase of approximately 0.15 mg/L.

Samples of the Level "10" solution that had been refrigerated exhibited a maximum change in pH of 0.04 units from initial measurements over the course of the experiment, and a net change of only 0.02 units. A similar pattern was observed in samples held at room temperature; a net decrease of 0.02 units was observed. The DIC content of refrigerated samples showed a net gain of 0.017 mg/L, while samples held at room temperature showed a net increase of 0.08 mg/L. The maximum difference from initial measurements was observed at 47.6 hours for both pH and DIC.

For the Level "100" solution, refrigerated samples exhibited a steady increase in pH over time, with a net change of 0.07 units, while samples held at room temperature exhibited a similar pattern of change, with a net change of 0.2 units. The DIC content of refrigerated samples showed a steady decrease over time, with a net change of approximately 0.4 mg/L for refrigerated samples and a net change of approximately 3 mg/L in samples held at room temperature.

For each solution, parameter, and temperature group, the mean values for each time period were averaged, and the variance was calculated. The same calculations were performed on the mean values for the QC check samples that had been analyzed along with the samples. For pH, the pH 4.00 QCCS was used initially. For DIC, the 2.00 mg/L C QCCS was used for all solutions except for the Level "100" solution; the 20.00 mg/L C QCCS was used for the Level "100" solution. A F-statistic was calculated from the ratio of the sample variance to the QCCS variance for each solution, parameter, and temperature group. The results of these tests are presented in Table A-4.

There was a significant effect ($p < 0.05$) of holding time on pH measurements for the Level "0" and Level "1" solutions that had been stored refrigerated. The other refrigerated solutions were not affected by holding time to a significant degree with respect to pH. The dissolved inorganic carbon content of all solutions that were stored refrigerated was not significantly effected by holding time.

The effects of holding time on pH and DIC were much more pronounced in samples that had been stored at room temperature. Only the Level "10" solution pH was not significantly affected by holding time. The DIC content of all but the most supersaturated solution (Level "100") was not affected by holding time in samples stored at room temperature. The stronger effects observed in the samples held at room temperature may have resulted from the laboratory having an ambient CO_2 level greater than 300 ppm.

The variance associated with measurements of the pH 4.00 QCCS was very small in all cases (0.0002). This solution has a much higher ionic strength than the synthetic sam-

ples analyzed in this experiment. The pH of this QCCS sample was also much lower than the circumneutral pH values observed in the synthetic samples. Solutions of lower pH generate a stronger potential for the meter to read, and the expected variation about this potential would be expected to be less than that expected from a potential generated on a circumneutral sample. The significant effects of holding time observed for the pH 4.00 QCCS may be a result of inherent properties of the instrumentation rather than a temporal change in the chemical concentration of the sample.

Table A-4. Summary of F-Tests Performed on Variances of Sample and QCCS Measurements for Solutions of Different Initial Dissolved Carbon Dioxide Concentrations (number of measurements is in parentheses.)

Solution	s ² (Samples)	s ² (QCCS)	F-Value
REFRIGERATED SAMPLES			
<u>pH Measurements</u>			
Level "0"	0.0027 (5)	0.0002 (5)	13.50*
Level "1"	0.0022 (5)	0.0002 (5)	11.00*
Level "10"	0.0004 (5)	0.0002 (5)	2.00 ^{ns}
Level "100"	0.0006 (5)	0.0002 (5)	3.00 ^{ns}
<u>DIC Measurements</u>			
Level "0"	0.0007 (5)	0.0028 (5)	0.25 ^{ns}
Level "1"	0.0007 (5)	0.0017 (5)	0.41 ^{ns}
Level "10"	0.0108 (5)	0.0064 (5)	1.69 ^{ns}
Level "100"	0.0337 (5)	0.0362 (5)	0.93 ^{ns}
ROOM TEMPERATURE SAMPLES			
<u>pH Measurements</u>			
Level "0"	0.0730 (5)	0.0002 (5)	365.0***
Level "1"	0.0343 (5)	0.0002 (5)	171.6***
Level "10"	0.0009 (5)	0.0002 (5)	4.5 ^{ns}
Level "100"	0.0057 (5)	0.0002 (5)	28.5**
<u>DIC Measurements</u>			
Level "0"	0.0095 (5)	0.0028 (5)	3.39 ^{ns}
Level "1"	0.0064 (5)	0.0017 (5)	3.76 ^{ns}
Level "10"	0.0079 (5)	0.0064 (5)	1.23 ^{ns}
Level "100"	1.4686 (5)	0.0362 (5)	40.57**

^{ns} not significant at $P = 0.05$.

* significant at $p < 0.05$.

** significant at $p < 0.01$.

*** significant at $p < 0.001$.

A pH 7.00 QCCS was also prepared each day. This solution was prepared almost identically to the synthetic samples, and thus it more closely mimics the chemical behavior of the samples, providing a more accurate representation of the expected analytical variance. The pH of this solution also more closely approximates the observed pH of the sample solutions. The pH 7.00 QCCS was analyzed only once on most days, and 18 total measurements were made over the course of these experiments. A variance based on these measurements was calculated and compared against the variances for pH measurements of samples. The results of these comparisons are presented in Table A-5. As expected, the QCCS had a larger variance than the pH 4.00 QCCS. In all cases, there was no significant effect of holding time on the pH of syringe samples that could be measured.

Table A-5. Comparisons of Variances for pH Measurements of Solutions Having Different Dissolved CO₂ Concentrations Versus a Low Ionic Strength pH 7.00 Quality Control Check Sample (number of measurements is in parentheses.)

Solution	s ² (Samples)	s ² (QCCS)	F-Value
REFRIGERATED SAMPLES			
Level "0"	0.0027 (5)	0.2627 (18)	0.010 ^{ns}
Level "1"	0.0022 (5)	0.2627 (18)	0.008 ^{ns}
Level "10"	0.0004 (5)	0.2627 (18)	0.002 ^{ns}
Level "100"	0.0006 (5)	0.2627 (18)	0.002 ^{ns}
ROOM TEMPERATURE SAMPLES			
Level "0"	0.0730 (5)	0.2627 (18)	0.278 ^{ns}
Level "1"	0.0343 (5)	0.2627 (18)	0.131 ^{ns}
Level "10"	0.0009 (5)	0.2627 (18)	0.003 ^{ns}
Level "100"	0.0057 (5)	0.2627 (18)	0.022 ^{ns}

^{ns} not significant at P = 0.05.

Most of the water samples collected during NSWS programs are supersaturated with dissolved CO₂ (3-20× atmospheric) (Linthurst et al., 1986). The results of this experiment indicate that samples collected in syringes can be held for up to 7 days with no measurable change in dissolved CO₂ concentration. It should be noted that the samples analyzed here were sterile, and natural water samples having biological activity associated with them may be much less stable at warmer temperatures. Experiment 4 evaluated the

possible effects of biological activity on sample stability.

Experiment 4

The results of measurements made at each time interval on natural water samples are summarized in Table A-6. The pH of refrigerated samples from both lakes showed a gradual decrease over the course of the experiment. Padden Lake exhibited a larger net decrease (0.17 pH units) than Bagley Lake (0.08 units). DIC values for refrigerated samples slowly increased throughout the experiment; Padden Lake exhibited a larger net change in DIC (approximately 0.3 mg/L vs. 0.05 mg/L for Bagley Lake).

The variance of sample measurements for each solution was compared to the variance of the pH 7.00 QCCS measurements or of the 2.00 mg/L C QCCS. Refrigerated samples from both lakes did not exhibit a significant effect of holding time for either pH or DIC. There was no significant effect of holding time on the pH of samples held at room temperature, but both lakes exhibited a significant change in DIC over time. The results of this experiment suggest that the use of pH measurement values instead of the hydrogen ion concentration values may be a less sensitive indicator of dissolved CO₂ concentrations than DIC.

Both of these lakes are similar in their chemical composition to target waters of NSWS programs. It appears that natural water samples can be stored for up to 7 days in sealed syringes without a significant change in dissolved CO₂ concentration if they are held in the dark at approximately 4 °C.

Conclusions

The results of these experiments indicate that water samples not necessarily in equilibrium with the atmosphere can be stored in sealed syringes for up to 7 days, if they are kept refrigerated, without a measurable effect on either DIC or pH.

The results of these experiments pertain only to pH and DIC, and no inference should be made regarding possible changes in other chemical parameters (e.g., aluminum) in water

Table A-6. Summary Statistics for Each Time Interval From Samples Collected From Padden and Bagley Lakes (values are presented as means \pm SD, with the number of measurements in parentheses.)

Time After Preparation (hours)	pH Measurements		DIC Measurements	
	Refrigerated	Room Temperature	Refrigerated	Room Temperature
PADDEN LAKE				
0.0	8.96 \pm 0.03 (12)	8.96 \pm 0.03 (12)	4.866 \pm 0.046 (12)	4.866 \pm 0.046 (12)
13.0	8.96 \pm 0.09 (4)	8.84 \pm 0.09 (4)	4.930 \pm 0.090 (4)	4.988 \pm 0.056 (4)
87.3	8.95 \pm 0.03 (4)	7.85 \pm 0.17 (4)	4.989 \pm 0.021 (4)	5.470 \pm 0.124 (4)
108.9	8.89 \pm 0.04 (6)	7.87 \pm 0.09 (5)	4.963 \pm 0.028 (6)	5.388 \pm 0.062 (6)
159.0	8.79 \pm 0.04 (6)	7.40 \pm 0.04 (6)	5.115 \pm 0.045 (5)	5.794 \pm 0.119 (6)
Mean:	8.91	8.18	4.973	5.301
Variance:	0.0054	0.4643	0.0085	0.1416
s ² (QCCS):	0.2627 (18)	0.2627 (18)	0.0018 (5)	0.0018 (5)
F-value:	0.021 ^{ns}	1.767 ^{ns}	4.722 ^{ns}	78.667 ^{***}
BAGLEY LAKE				
0.0	6.79 \pm 0.02 (12)	6.79 \pm 0.02 (12)	1.154 \pm 0.021 (12)	1.154 \pm 0.021 (12)
13.0	6.80 \pm 0.03 (4)	6.77 \pm 0.05 (4)	1.221 \pm 0.014 (4)	1.269 \pm 0.021 (4)
87.3	6.76 \pm 0.02 (4)	6.46 \pm 0.05 (4)	1.175 \pm 0.014 (4)	1.517 \pm 0.076 (4)
108.9	6.74 \pm 0.01 (5)	6.42 \pm 0.07 (6)	1.179 \pm 0.026 (6)	1.544 \pm 0.099 (6)
159.0	6.71 \pm 0.03 (6)	6.28 \pm 0.03 (6)	1.206 \pm 0.034 (6)	1.677 \pm 0.045 (6)
Mean:	6.76	6.54	1.187	1.432
Variance:	0.0014	0.0509	0.0007	0.0459
s ² (QCCS):	0.2627 (18)	0.2627 (18)	0.0020 (5)	0.0020 (5)
F-value:	0.005 ^{ns}	0.194 ^{ns}	0.350 ^{ns}	22.95 ^{***}

^{ns} not significant at P = 0.05.

^{***} significant at p < 0.001.

held in sealed syringes, as other chemical parameters may be sensitive to small changes in pH that were not measured in this study.

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Appendix B

Cubitainer Holding Time Study

by

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Introduction

The U.S. Environmental Protection Agency undertook a survey of approximately 3,000 lakes and 300 streams in the United States as part of the National Surface Water Survey (NSWS). A primary objective of the NSWS is to determine the degree to which surface waters in the United States are at risk as a result of acid deposition (Linthurst et al., 1986). A survey of this magnitude has many associated quality assurance and economic concerns. One concern is that the concentration of chemicals in samples may change from the time of collection to the time they are prepared for analysis (holding time).

In NSWS studies to date, samples were filtered and preserved at a field laboratory, which was centrally located in the region where samples are being collected, and then were transported by truck or air charter to an analytical laboratory for chemical analysis (Linthurst et al., 1986; Messer et al., 1986). Standard methods of filtration and preserva-

tion assured that minimal change occurred from the time samples were preserved to the time they were analyzed at the analytical laboratory. However, the degree to which holding time affects the chemistry of water samples is unknown.

The holding times of samples vary considerably depending on the distance from sampling site to the field laboratory, method of transportation, weather conditions, and terrain. During Phase I of the Western Lake Survey, conducted in the fall of 1985, for example, samples collected by ground crews sometimes required up to 2 days to be transported to a field laboratory, while samples collected by helicopter crews required only a few hours. If holding time affects the concentrations of chemical parameters in a sample, interpretation of data from samples with different holding times becomes difficult. If holding time has no effect on the concentration of parameters in a sample, less expensive methods of transporting samples can be used, and field laboratories would be unnecessary.

This study investigated changes in any of 25 chemical parameters in samples that were held 12, 24, 48, and 84 hours before preparation for analysis. The results may be useful in designing sampling strategies for future water quality surveys covering large or remote geographical areas, i.e., for surveys where the time between collection and preparation of samples is variable.

Materials and Methods

Collection and Chemical Analysis of Samples

Water samples were collected on June 24, 1985, from three lakes in New York, three streams in Pennsylvania, two streams in Maryland, and one stream each in South Carolina and Tennessee. Samples were collected over this wide area to determine if effects of holding time were due to phenomena of lakes and streams in certain geographical areas. The sampling locations are listed in Table B-1.

At each site, two 19-liter (5 U.S. gallons) Cubitainers were filled with water. The contents were then mixed by rocking the Cubitainers for five minutes. A Tygon tubing T-connector was attached to transfer water from both 19-liter Cubitainers simultaneously into eight 3.7-liter (1 U.S. gallon) Cubitainers. Each 3.7-liter Cubitainer was rinsed three times, was filled, and was sealed with no headspace. Holding times of 12, 24, 48, and 84 hours were randomly assigned to each Cubitainer. Each lake or stream, therefore,

had one pair of 3.7-liter Cubitainers for each holding time. Samples were shipped via charter aircraft to a field laboratory in Sylva, NC, and arrived within 12 hours of collection so that samples could be prepared and preserved at their assigned holding times. Preserved sample aliquots were shipped the following day to an analytical laboratory by overnight courier service. Samples were stored at approximately 4 °C during shipment. A detailed description of the chemical analyses and methodologies performed by the analytical laboratory can be found elsewhere (Hillman et al., 1986). All samples were analyzed within an acceptable time after filtration and preservation (Hillman et al., 1986; Drou   in preparation). The methods were the same as those used during Phase I of the Eastern Lake Survey (Linthurst et al., 1986), and during the pilot survey for the National Stream Survey (Messer et al., 1986).

Statistical Analysis

Standard single-factor repeated measures analyses of variance (RMANOVA; Winer, 1971) were performed for each parameter. Specifically, we tested the null hypothesis of equal mean concentrations of value of a particular parameter at 12, 24, 48, and 84 hours.

An assumption of the RMANOVA model is that the measurement error does not vary as a function of concentration. For Ca^{2+} , Mg^{2+} , total phosphorus, extractable aluminum, Na^+ , Cl^- conductance, an air-equilibrated dissolved inorganic carbon, and acid neutralizing capacity, log transformations were required

Table B-1. Locations of Lakes and Streams

Lake or Stream Name	County	State	Latitude	Longitude
Big Moose Lake	Herkimer	New York	43°49'45"N	74°51'00"W
Fly Pond	Herkimer	New York	43°44'52"N	74°54'05"W
West Lake	Herkimer	New York	43°45'20"N	74°55'15"W
Bear Creek	Lycoming	Pennsylvania	41°21'31"N	76°50'50"W
Cherry Run	Clinton	Pennsylvania	39°59'26"N	77°29'34"W
Lick Run	Clinton	Pennsylvania	41°19'02"N	77°30'52"W
Lyons Creek	Anne Arundel	Maryland	38°11'00"N	76°34'00"W
Morgan Creek	Kent	Maryland	39°15'20"N	76°02'30"W
Six Mile Creek	Pickens	South Carolina	34°46'54"N	82°50'57"W
Clear Creek	Anderson	Tennessee	36°10'00"N	84°00'00"W

to satisfy this assumption. Lyons Creek had extremely unusual data for total aluminum. The RMANOVA for total aluminum was performed both with and without data from this stream.

For each parameter, holding time is of practical significance when the precision among the holding times is less than the precision between standard samples with no holding time. Forty-one samples obtained from Big Moose Lake in New York in 1984 were used to estimate analytical precision and to evaluate laboratory bias and precision during Phase I of the Eastern Lake Survey (Best et al., in preparation). These "natural audit" samples were shown to be chemically stable during the Survey and therefore provided a useful estimate of the amount of variance which was due to the collection and analysis of samples. The relative standard deviation (standard deviation + mean) was used to estimate the precision of the Eastern Lake Survey natural audit data for each parameter (Permutt and Pollack, in preparation). For pH measurements, the absolute standard deviations were used. The relative and absolute standard deviation values were corrected for laboratory bias and trend (Permutt and Pollack, in preparation). The greater the value of the relative or standard deviation, the less is the precision and the greater is the variance in measuring a parameter.

The precision between two holding times can be estimated by the relative difference (difference + mean value) between two holding times. For pH measurements, precision between two holding times can be estimated by the absolute difference between the two holding times. If the relative (or absolute) difference between two holding times is less than the relative (or absolute) standard deviation of the natural audit samples, then the variance which is due to holding time is less than the variance which is due to the collection and analysis of samples. Therefore, statistically significant effects of holding time become questionable, or insignificant in the practical sense, when the relative (or absolute) differences between holding times are less than the relative (or absolute) standard deviation of the natural audit data.

When determining the practical significance of holding time, one should also con-

sider whether the effects are limited to a few lakes or streams or to the majority and whether the effect is the same for all lakes and streams sampled. Suppose that the concentration of a particular parameter increases at a certain holding time for some lakes and streams, while the concentration decreases or does not change at the same holding time for the remaining lakes and streams. In such a case, the effects of holding time may be due to site-specific phenomena. The practical significance of holding time for that parameter, regardless of the outcome of the RMANOVA, is questionable.

Results and Discussion

Plots of the data (Figure B-1) suggest that for all parameters, holding time did not have a strong effect over all lakes and streams. The results of the RMANOVA for each parameter (Table B-2) indicate that holding time had a statistically significant effect ($p < 0.05$) for 17 parameters. The results of groups of parameters are discussed in more detail below.

The Cations: Ca^{2+} , Mg^{2+} , K^+ , Mn , Fe , NH_4^+
(Figure B-1, Parts A-G)

Holding time had a statistically significant effect on the concentrations of Ca^{2+} , Fe (total ionic), Na^+ , and Mn (total ionic) ($p < 0.05$, Table B-2). No significant effect of holding time was observed for Mg^{2+} , K^+ , and NH_4^+ . The average concentration of Ca^{2+} and Fe increased up to 48 hours, then sharply decreased (Table B-2). However, this was primarily because of having data from only one stream for Ca^{2+} and from only three streams for Fe (Figure B-1, Parts A and F). Similarly, the mean decrease in the concentration of Mn between 12 and 48 hours is due primarily to data from three streams (Figure B-1, Part E).

Although statistical significance was observed, the practical significance of holding time on the concentrations of Ca^{2+} , Na^+ , Fe, and Mn is questionable. For Ca^{2+} and Na^+ , the relative difference in concentration between holding times was always less than the relative standard deviation of the ELS natural audit data (Table B-3). The average concentration of Ca^{2+} increased up to 48 hours, then sharply decreased (Table B-2). However, these

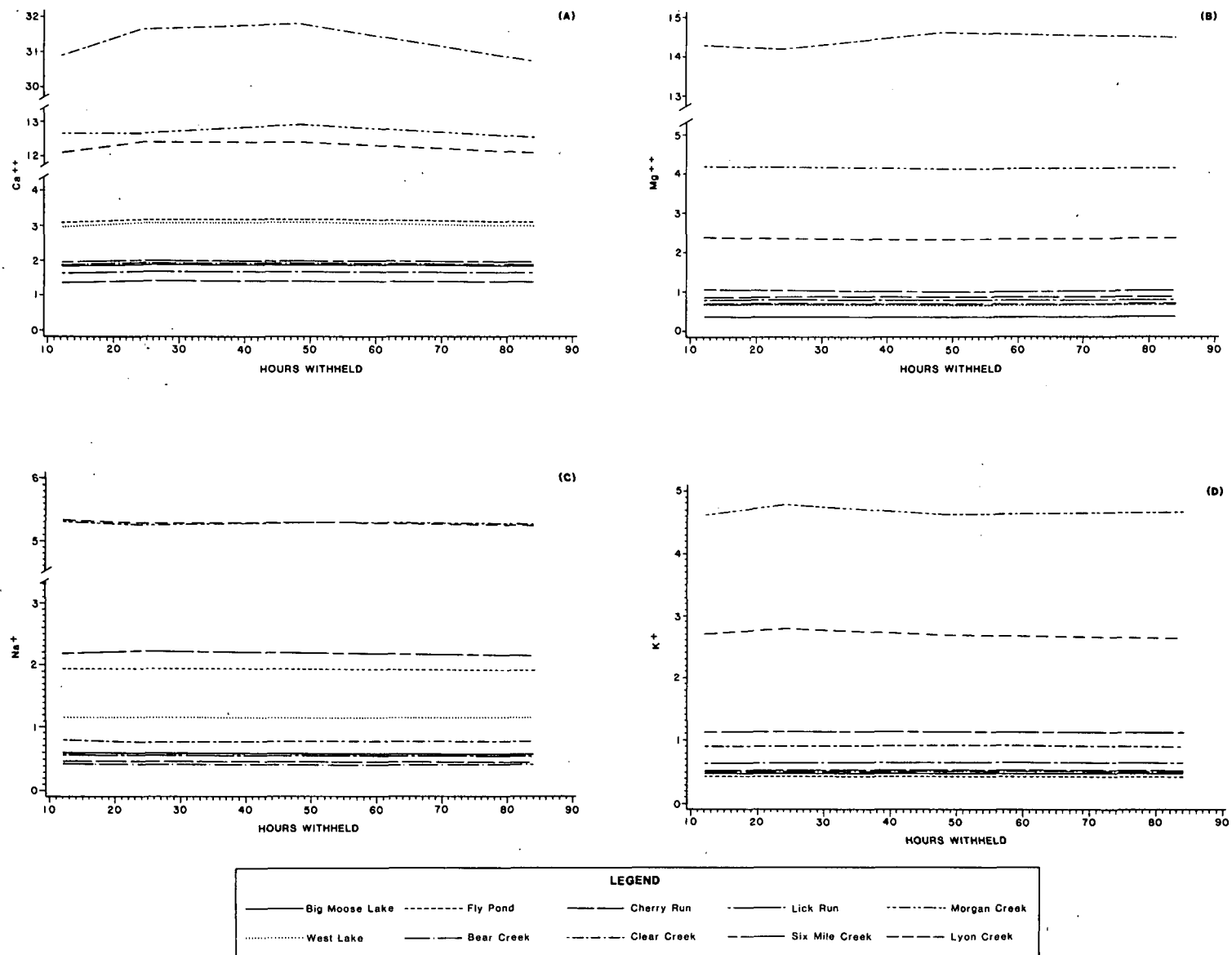


Figure B-1. Mean values for pairs of measurements at 4 holding times for 10 lakes and streams. (This figure is 7 pages total. Units are $\mu\text{eq/L}$ for acid-neutralizing capacity and base-neutralizing capacity; $\mu\text{S/cm}$ for conductance; pH units for pH_{ANC} , pH_{BNC} , and pH_{eq} ; and mg/L for the remaining parameters.)

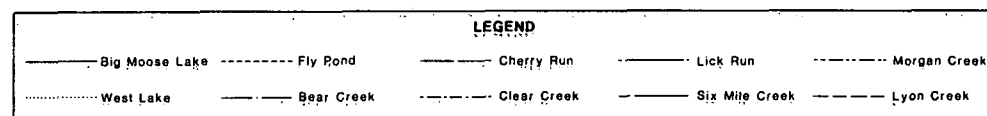
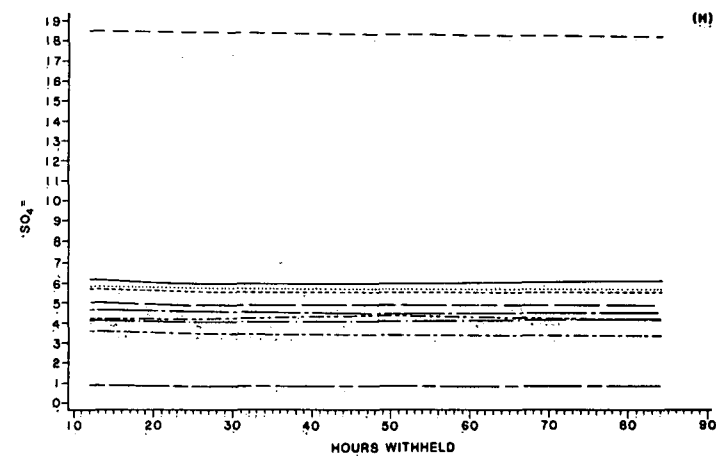
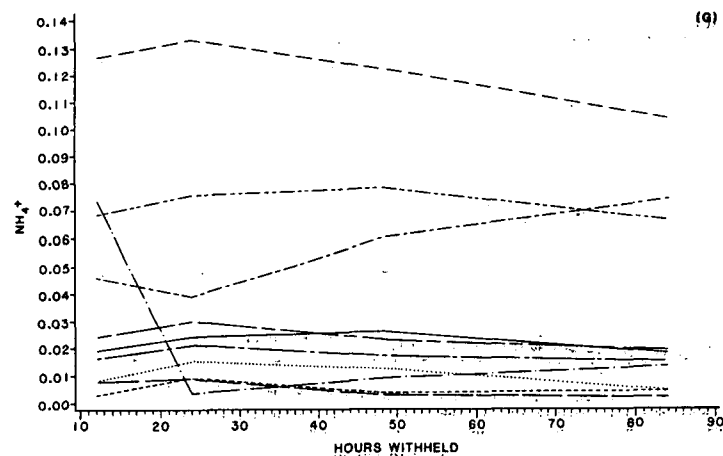
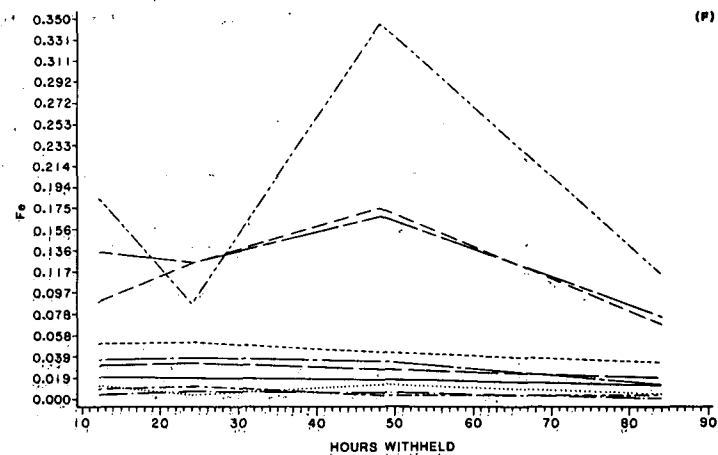
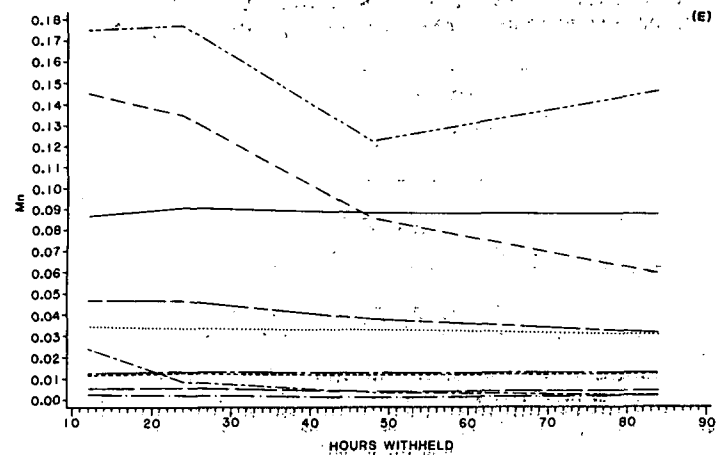


Figure B-1. Continued.

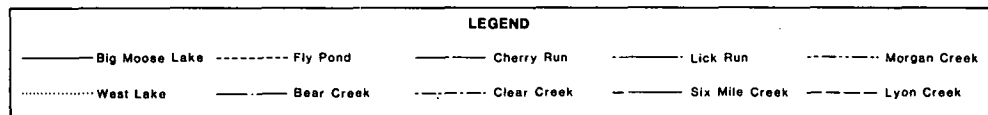
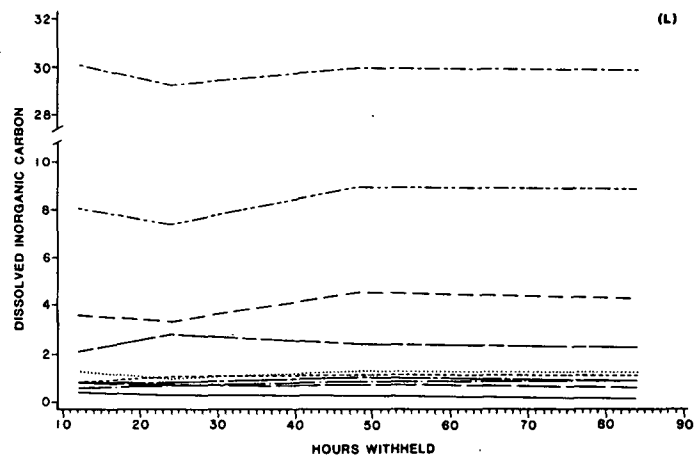
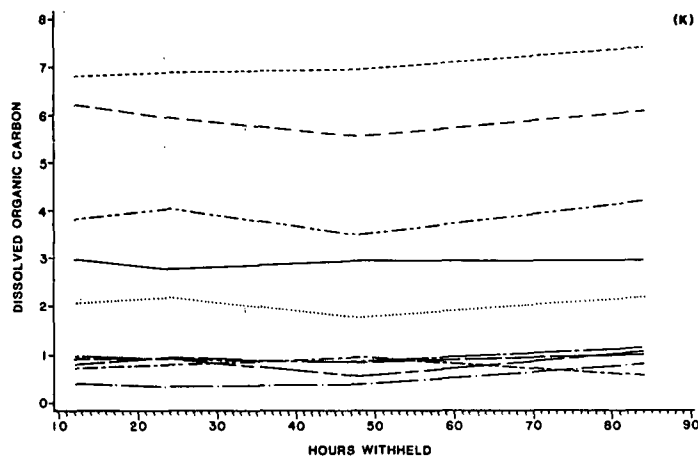
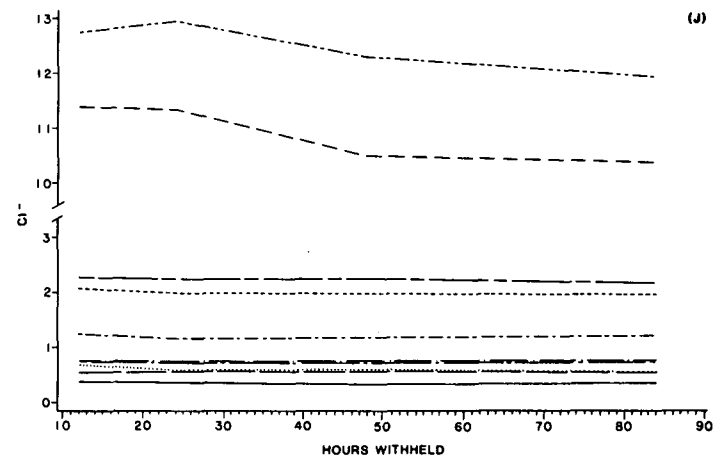
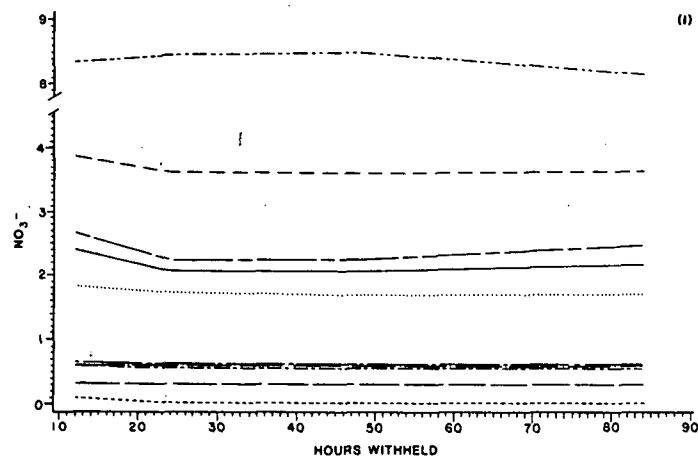


Figure B-1. Continued.

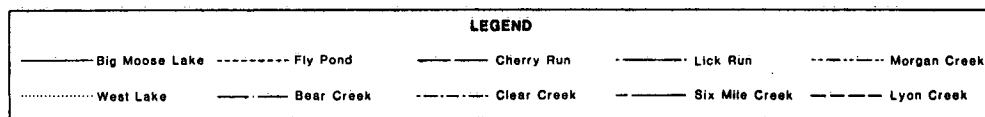
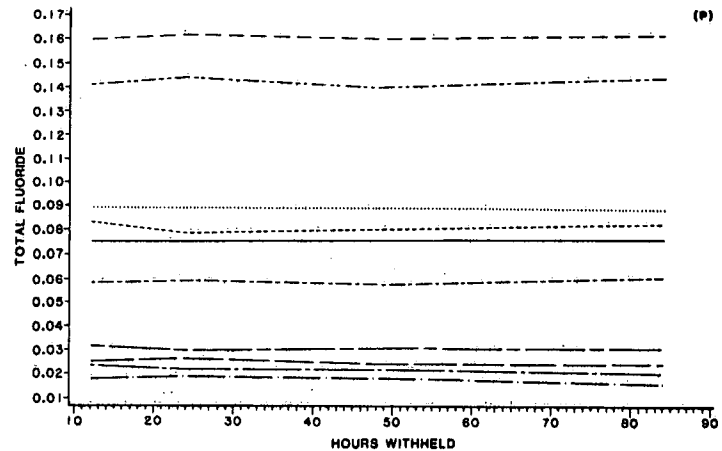
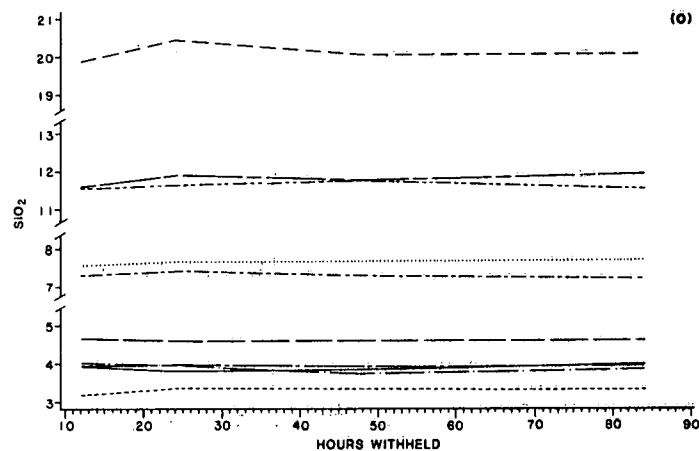
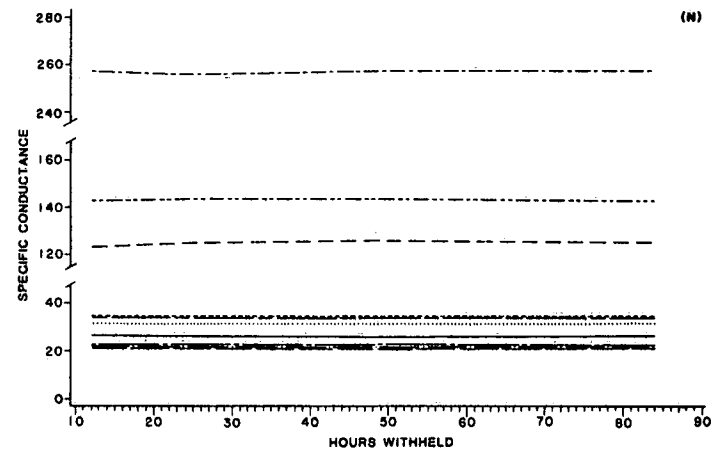
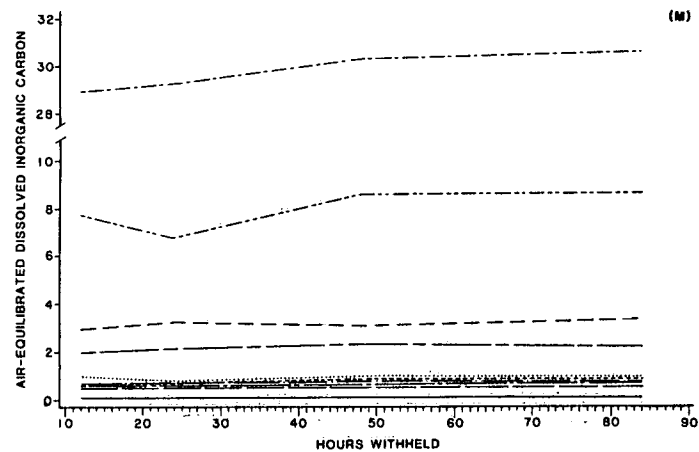


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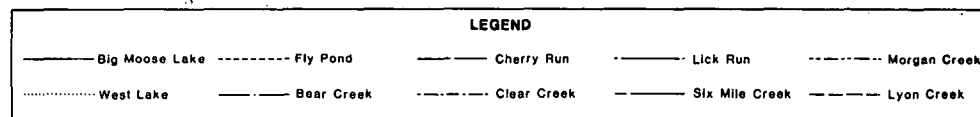
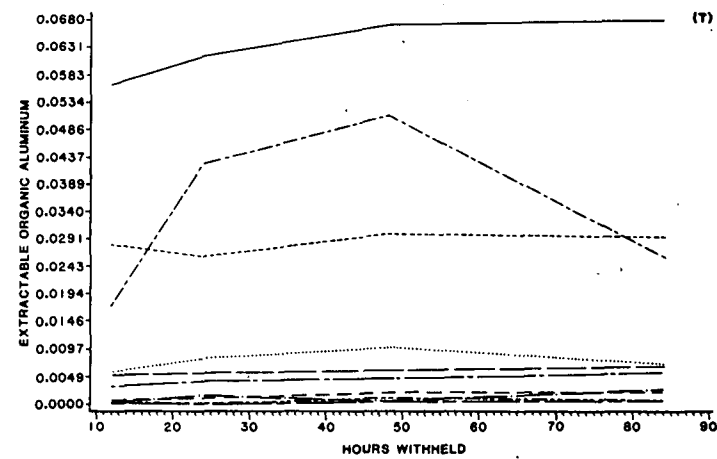
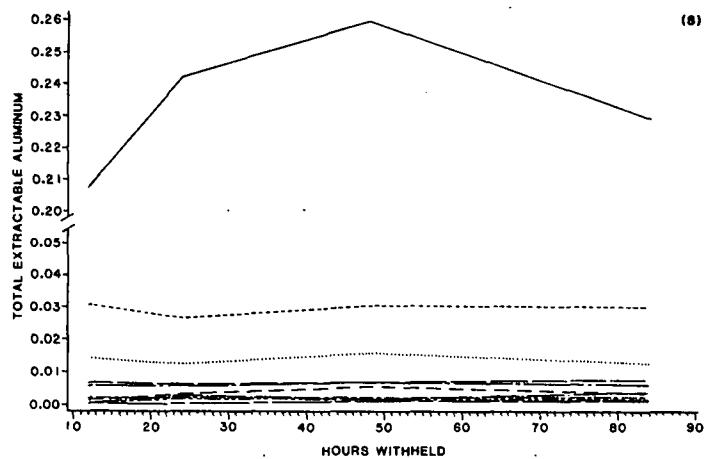
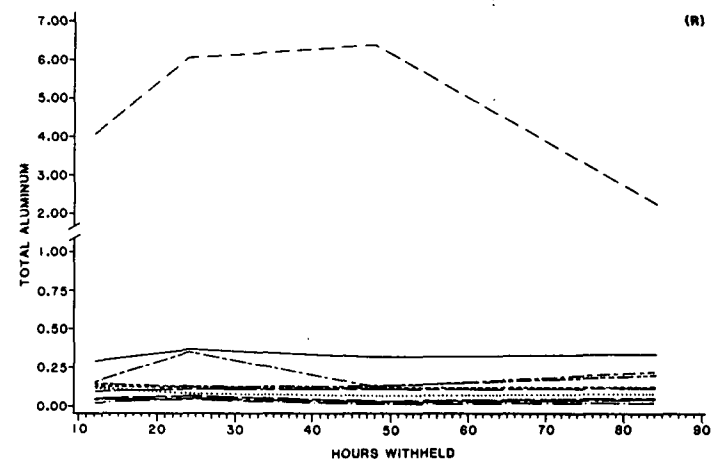
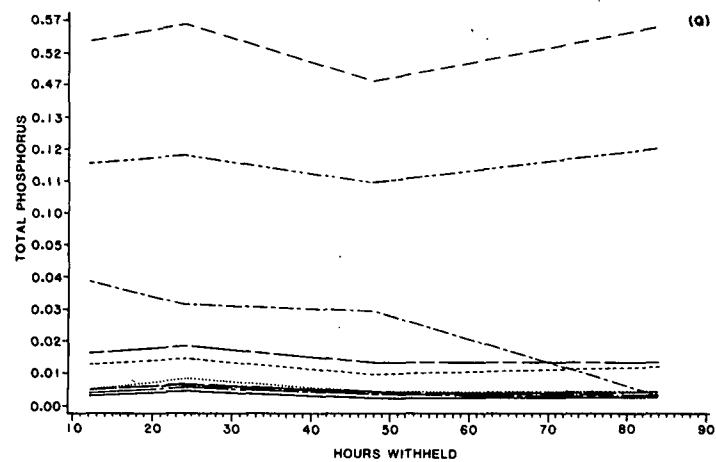


Figure B-1. Continued.

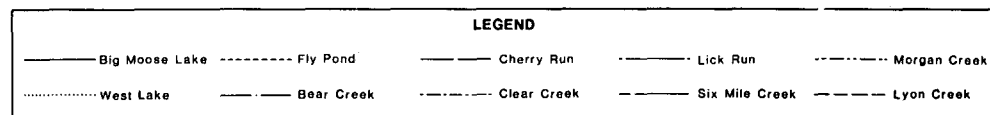
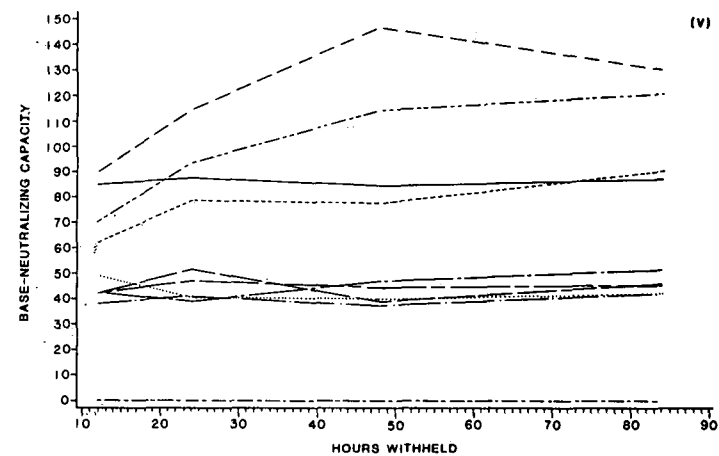
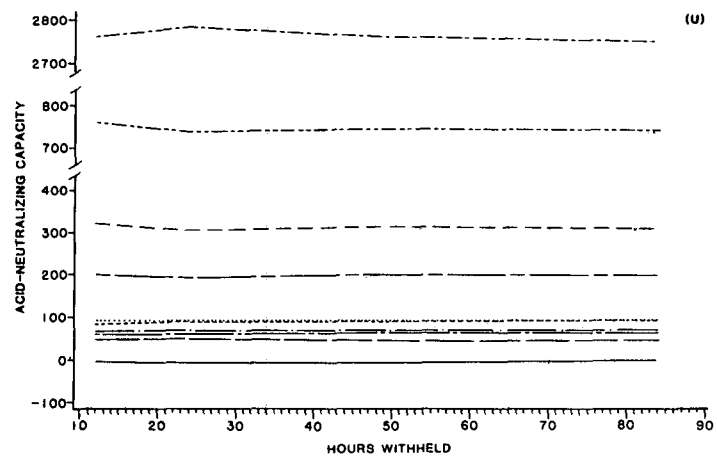


Figure B-1. Continued.

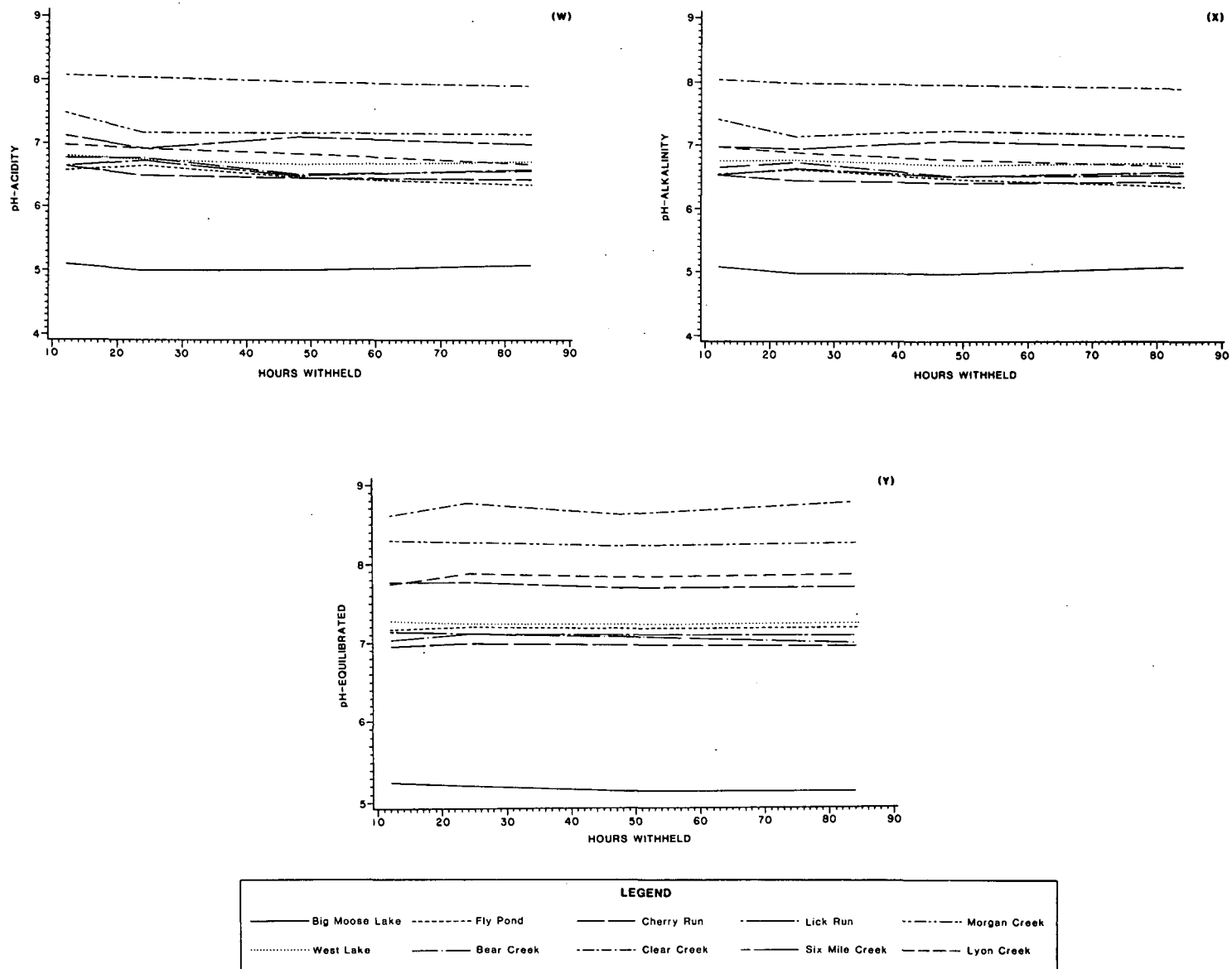


Figure B-1. Continued.

Table B-2. Treatment Means and Overall Standard Error (as determined by RMANOVA^a) of 25 Chemical Parameters at Four Holding Times for Three Lakes and Seven Streams. (Probabilities (p) < 0.05 for the repeated measured analysis of variance indicate a statistically significant effect of holding time).

Parameter; units	Holding Time (hours)				SE	p
	12	24	48	84		
Calcium; mg/L	7.012	7.185	7.230	7.019	0.035	<0.0001 ^a
Magnesium; mg/L	2.571	2.566	2.592	2.596	0.013	0.0042 ^a
Sodium; mg/L	1.874	1.868	1.864	1.840	0.004	<0.0001 ^a
Potassium; mg/L	1.238	1.274	1.254	1.243	0.009	0.0643
Manganese; mg/L	0.054	0.052	0.040	0.039	0.003	0.0096
Iron; mg/L	0.057	0.050	0.084	0.035	0.010	0.0420
Ammonium; mg/L	0.039	0.036	0.035	0.031	0.002	0.1871
Sulfate; mg/L	5.845	5.743	5.735	5.704	0.022	0.0002
Nitrate; mg/L	1.130	2.023	2.021	2.024	0.021	0.0092
Chloride; mg/L	3.276	3.269	3.134	3.071	0.050	0.0483 ^a
Dissolved organic carbon; mg/L	2.569	2.575	2.457	2.758	0.049	0.0002
Dissolved inorganic carbon; mg/L	4.842	4.734	5.137	5.017	0.094	0.0505
Dissolved inorganic carbon, air-equilibrated; mg/L	4.493	4.476	4.817	4.858	0.073	0.0005 ^a
Conductance; μ S/cm	71.42	71.48	71.80	71.61	0.125	0.0465 ^a
Silica; mg/L	7.754	7.876	7.798	7.814	0.032	0.7970
Fluoride; mg/L	0.070	0.071	0.070	0.071	0.000	0.3770
Phosphorus, total; mg/L	0.074	0.078	0.066	0.073	0.003	0.1370
Aluminum, total; mg/L	0.509	0.736	0.736	0.346	0.126	0.0875
Aluminum, total ^b ; mg/L	0.113	0.145	0.109	0.132	0.009	0.0592
Aluminum, extractable; mg/L	0.027	0.030	0.033	0.030	0.001	<0.0001 ^a
Aluminum, organic monomeric; mg/L	0.012	0.015	0.017	0.015	0.001	0.0342
Acid neutralizing capacity; μ eq/L	438.00	436.75	436.50	434.38	2.075	0.0456 ^a
Base neutralizing capacity; μ eq/L	52.103	59.303	63.053	65.653	2.518	0.0195
pH, initial BNC	6.816	6.738	6.663	6.644	0.023	<0.0001
pH, initial ANC	6.742	6.703	6.652	6.635	0.020	0.0015
pH, air-equilibrated	7.326	7.356	7.299	7.308	0.015	0.0514

^a RMANOVA performed by using log-transfer red values.

^b Data from Lyons Creek excluded.

changes were due primarily to data from Clear Creek. The remaining lakes and streams exhibited stable concentrations. For Ca^{2+} and Na^{+} , the mean change in concentration from 12 to 84 hours was 0.1 percent and 1.3 percent, respectively.

For Mn, the relative differences in concentration between samples held 24 and 48 hours and between 12 and 84 hours were 3 percent and 9 percent greater, respectively, than the relative standard deviation of natural audit samples (Table B-3). However, the relative difference in concentration between samples held 12 and 24 hours and between 48 and 84 hours was much less (19.2 percent and 20.5 percent) than the relative standard deviation of the natural audit data. Morgan Creek, Lyons Creek, and Six Mile Creek exhibited large decreases in concentration of Mn from 12 to 84 hours.

For the remaining lakes and streams, the concentration of Mn was stable from 12 to 84

hours. Similarly, Morgan Creek, Lyons Creek, and Six Mile Creek exhibited large fluctuations in the concentration of Fe from 12 to 84 hours. Relatively large increases in Fe were observed between 24 and 84 hours for these three streams, while large decreases were observed from 48 to 84 hours. The concentration of Fe increased from 12 to 24 hours for Lyons Creek, but decreased for Morgan Creek and Six Mile Creek. For the remaining lakes and streams, the concentration of Fe was stable from 12 to 84 hours. For Fe, the relative difference between 48 and 84 hours was 17.3 percent greater than the relative standard deviation of the ELS natural audit data. Between 12 and 24, 24 and 48, and 12 and 84 hours, the relative differences were less than the relative standard deviation of ELS natural audit data. The practical significance of the effects of holding time on Fe and Mn is questionable because of (1) the lack of an overall trend in Figure B-1, Parts E and F, (2) the effects of holding time being mixed and restricted to

Table B-3. Relative Difference (Difference Between Means of Holding Times in Question + Grand Mean of Holding Times in Question) Between the Means for Each Parameter for Holding Time Intervals of 12 to 24, 24 to 48, 48 to 84, and 12 to 84 hours.

Parameter	Holding Time Interval (hours)				RSD of Natural Audit Data ^a
	12-24	24-48	48-84	12-84	
Calcium (Ca ²⁺)	-0.022	-0.006	0.030	0.001	0.064
Magnesium (Mg ²⁺)	0.002	0.005	-0.001	0.001	0.019
Sodium (Na ⁺)	0.004	0.001	0.007	0.013	0.044
Potassium (K ⁺)	-0.029	0.016	0.009	0.004	0.044
Manganese (Mn)	0.038	0.261	0.025	0.322	0.230
Iron (Fe)	0.131	0.507	0.823	0.478	0.650
Ammonium (NH ₄ ⁺)	0.080	0.028	0.121	0.229	0.500
Sulfate (SO ₄ ²⁻)	0.017	0.001	0.005	0.024	0.072
Nitrate (NO ₃ ⁻)	0.052	0.001	-0.001	0.050	0.260
Chloride (Cl ⁻)	0.002	0.042	0.020	0.064	0.500
Dissolved organic carbon (DOC)	-0.002	0.075	-0.045	-0.073	0.088
Dissolved inorganic carbon (DIC)	0.023	-0.081	0.024	-0.036	0.150
DIC, air equilibrated (DIC _{eq})	0.004	-0.073	-0.008	-0.078	0.53
Conductance (COND)	-0.001	-0.004	0.003	-0.003	0.150
Silica (SiO ₂)	-0.016	0.010	-0.002	-0.008	0.074
Fluoride, total dissolved (F ⁻)	-0.014	0.014	-0.014	-0.014	0.039
Phosphorus, total (P)	-0.053	1.67	-0.098	0.014	1.28
Aluminum, total (Al)	-0.365	0.0	0.898	0.381	0.21
Aluminum, total ^b (Al)	-0.250	0.280	-0.190	-0.150	0.21
Aluminum, extractable (Al _{ext})	-0.105	-0.095	0.095	-0.105	0.320
Aluminum, organic monomeric (Al _{org}); µg/L	0.222	-0.125	0.125	0.222	
Acid neutralizing capacity (ANC); µg/L	0.003	0.001	0.005	0.008	2.49
Base neutralizing capacity (BNC); µg/L	0.129	-0.061	-0.041	0.225	0.34
pH, initial BNC (pH _{BNC}) ^c	0.078	0.075	0.019	0.172	0.03
pH, initial ANC (pH _{ANC}) ^c	0.039	0.051	0.017	0.107	0.03
pH, air equilibrated (pH _{eq}) ^c	0.030	-0.057	-0.009	-0.018	0.28

^a Absolute standard deviation was used for pH measurements for the natural audit samples.

^b Data from Lyons Creek removed.

^c Absolute difference.

three streams, and (3) the mixed results in precision in Table B-3.

The Anions: SO₄²⁻, NO₃⁻, and Cl⁻ (Figure B-1, Parts H-J)

Holding time had a statistically significant effect on SO₄²⁻, NO₃⁻, and Cl⁻ ($p < 0.05$, Table B-2). The mean concentration of all three variables decreased over time (Tables B-2 and B-3). However, the practical significance of these decreases is questionable. In all cases, the relative difference between holding times was less than the relative standard deviation of the ELS natural audit samples (Table B-3). Between 12 and 84 hours, the mean concentration of SO₄²⁻, NO₃⁻, and Cl⁻ decreased by 2.4 percent, 5 percent, and 6.4 percent respectively (Table B-3). Figure B-1, Parts H-J, suggests no strong trend for any of these parameters with respect to holding time.

Dissolved Inorganic and Organic Carbon (Figure B-1, Parts K - M)

Holding time had a statistically significant effect on the concentration of dissolved organic carbon (DOC) and air-equilibrated dissolved inorganic carbon (DIC_{eq}), but not on the concentration of dissolved inorganic carbon (DIC) (Table B-2). The practical significance of holding time, however, is questionable. For all of these parameters, the relative differences between holding times were always less than the relative standard deviations of ELS natural audit data (Table B-3). Figure B-1, Parts K and M, suggest no strong trend for these parameters with respect to holding time. Between 12 and 84 hours, the mean concentration of DOC increased by 11.5 percent while the mean concentration of DIC_{eq} increased by 7.8 percent (Table B-3). Only data from Fly Pond and Lick Run exhibited

steady increases in DOC from 12 to 84 hours. For DIC_{eq} , this increase was noticeable only in samples from Clear Creek and may have been due to the introduction of carbon dioxide into these samples.

Conductance (Figure B-1, Part N)

Holding time had a significant effect on this parameter (<0.05 , Table B-2). The practical significance of the effect of holding time, however, is questionable. The relative differences in mean concentration between holding times were always less than the relative standard deviations of ELS natural audit data (Table B-3). Conductance exhibited no definite trend over time and was stable for all streams (Figure B-1, Part N). Samples exhibited a mean increase of only $0.19 \mu\text{S/cm}$ (0.3 percent) from 12 to 84 hours (Table B-3).

SiO_2 , Total Fluoride and Total Phosphorus (Figure B-1, Parts O-Q)

Plots of mean concentrations over time for these three parameters (Figure B-1, Parts O-Q) reveal no trend. Holding time did not have a significant effect for these parameters ($p > 0.05$, Table B-2). The relative differences between holding times were always less than the relative standard deviations of the ELS natural audit data (Table B-3).

Aluminum Species (Figure B-1, Parts R-T)

Holding time had a statistically significant effect on the concentrations of total extractable aluminum (Al_{ext}) and organic monomeric aluminum (Al_{org}) (Table B-2). When the data for Lyons Creek were removed, holding time had a statistically significant effect ($p < 0.05$) on total aluminum (Al_{t}).

When the data for total aluminum from Lyons Creek were removed, the relative difference between 12 and 24 hours and between 24 and 48 hours exceeded the relative standard deviation of the natural audit data by 4 percent and 7 percent, respectively (Table B-3). The relative differences between 48 and 84 and between 12 and 84 hours were less than this relative standard deviation by 2 percent and 6 percent, respectively. Figure B-1, Part R, suggests stable concentrations for Al_{t} between 12 and 84 hours. The mean concentration exhibited both slight increases and decreases

(Table B-2), further suggestion that no overall trend is present. For these reasons, the practical significance of holding time on Al_{t} is questionable.

For Al_{ext} , the relative difference between holding times was always less than the relative standard deviation of the ELS natural audit data (Table B-3). Figure B-1, Part S, suggests no overall trend in the effect of holding time. Although large fluctuations in the concentration of Al_{ext} occurred for Big Moose Lake, the remaining sites exhibited stable concentrations between 12 and 84 hours. For these reasons, the practical significance of holding time for Al_{ext} is questionable.

Natural audit data were not available for Al_{org} , and this made an evaluation of the practical significance of holding time for this parameter more difficult. The mean concentrations of Al_{org} were quite low (Table B-2). The concentration of Al_{org} changed more for Clear Creek and Big Moose Lake than for any other lakes or streams during this experiment (Figure B-1). The concentration of Al_{org} for Clear Creek increased by 0.008 mg/L (22 percent) between 12 and 24 hours and by 0.009 mg/L (19 percent) between 24 and 48 hours. Between 48 and 84 hours, the concentration of Al_{org} in Clear Creek decreased by 0.025 mg/L (68 percent); this resulted in a net decrease of 0.008 mg/L (27 percent) between 12 and 84 hours. Samples from Big Moose Lake exhibited a gradual increase of 0.011 mg/L (17 percent) between 12 and 84 hours. For the remaining lakes and streams, the concentration of Al_{org} was stable between 12 and 84 hours. These results suggest that the practical significance of the effects of holding time on the concentration of Al_{org} is questionable.

Acid-Neutralizing Capacity (ANC) and Base-Neutralizing Capacity (BNC) (Figure B-1, Parts U-V)

Holding time had a statistically significant effect on BNC, but not on ANC (Table B-2). The practical significance of holding time on BNC, however, is questionable. The relative differences in BNC between holding times were always much less than the relative standard deviation of the natural audit data (Table B-3). The small mean increase in BNC, although not of practical significance, may have been due to an introduction of carbon

dioxide into some samples, particularly those from Morgan Creek and Lyons Creek (Figure B-1).

pH

(Figure B-1, Parts W-Y)

Holding time had a statistically significant effect on pH-alkalinity and pH-acidity, but not on pH-equilibrated (Table B-2). Between 12 and 84 hours, pH-alkalinity and pH-acidity decreased by an average of 0.107 and 0.152 pH units (2.3 percent and 1.6 percent), respectively. The introduction of carbon dioxide into some samples, particularly those from Morgan and Lyons Creeks, may have caused this decrease. The differences between holding times of 12 and 84 hours for pH-acidity and pH-alkalinity were greater than the absolute standard deviations for ELS natural audit data (Table B-3). Figure B-1, Part W and Part X, indicates steadily decreasing levels of pH-acidity and pH-alkalinity from 12 to 84 hours. The difference between holding times for pH-equilibrated was always less than the absolute standard deviation of the ELS natural audit data (Table B-3). Figure B-1, Part Y, indicates stable levels of pH-equilibrated from 12 to 84 hours.

The decrease in pH is expected because the audit sample has achieved equilibrium with atmospheric CO₂, while actual samples may be either undersaturated or oversaturated with respect to CO₂. The direction of the shift in pH will depend upon the proximity of the CO₂ concentration of the sample to the atmospheric CO₂ partial pressure at the location where the sample container is opened for analysis. Samples undersaturated with respect to the atmospheric partial pressure of CO₂ will decrease in pH because this gas diffuses into solution. Samples oversaturated will increase in pH because CO₂ degasses out of the sample. Thus the observed trend in pH is an overall response of samples to a decrease due to their CO₂ concentrations.

Cubitainers appear to be unsuitable for maintaining stability of pH (Schock and Schock, 1982). Burke and Hillman (Appendix A) observed stable pH readings for up to 7 days in samples held in sealed syringes and stored at 4 °C.

Conclusions

Although holding time had a statistically significant effect on 17 parameters, the practical significance in all cases is questionable. When statistically significant effects of holding times were observed for a parameter, at least one of the following was true: (1) the relative difference between holding times was less than the relative standard deviation of the natural audit data, or (2) graphically, effects of holding time appear to be restricted to a minority of the lakes and streams sampled and are site-specific phenomena. A major uncertainty in this study is the effect of holding samples up to 12 hours after collection. In surveys covering large geographical areas, it may be logistically impossible to filter and preserve many samples less than 12 hours after collection. If samples can be transported to an analytical laboratory, filtered and preserved within 84 hours after collection, the economic cost of a survey can be decreased by eliminating field laboratories, by collecting both samples with ground crews instead of with helicopter crews or by shipping samples by standard air instead of overnight courier.

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