&EPA

Eastern Lake Survey - Phase II National Stream Survey - Phase I

Processing Laboratory Operations Report

Aquatic Effects Research Program

SUBREGIONS OF THE NATIONAL STREAM SURVEY - PHASE I

Northern
Appalachians (2Cn)

Valley and Ridge (2Bn)

Poconos/Catskills (1D)

Southern Blue Ridge (2As)
(Pilot Study)

Ozarks/Ouachitas (2D)

Mid-Atlantic
Coastal Plain (3B)

Piedmont
(3A)

Florida (3C)

Southern Appalachians (2X)

EPA 600/4-88/025

Eastern Lake Survey-Phase II
National Stream Survey-Phase I

Processing Laboratory Operations Report

A Contribution to the
National Acid Precipitation Assessment Program

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

Environmental Monitoring Systems Laboratory - Las Vegas, NV 89114
Environmental Research Laboratory - Corvallis, OR 97333

Notice

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This document is one volume of sets which fully describe the Eastern Lake Survey-Phase II and the National Stream Survey. The complete set for each project includes the major data report, quality assurance plan, quality assurance report, analytical methods manual, field operations report, and laboratory operations report. The National Stream Survey set also includes the pilot survey final report.

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Abstract

The National Surface Water Survey was designed to characterize surface water chemistry in regions of the United States believed to be potentially sensitive to acidic deposition. The National Stream Survey was a synoptic survey designed to quantify the chemistry of streams in areas of the United States known to contain low alkalinity waters. Phase II of the Eastern Lake Survey was designed to address temporal variability of chemical and biological characteristics of a subset of Phase I lakes. This document describes the centralized processing laboratory operations associated with the 1986 surveys.

The processing laboratory was located in Las Vegas, Nevada. Personnel at the laboratory processed water samples received from the field and shipped prepared aliquots to contracted analytical laboratories for subsequent analyses. Dissolved inorganic carbon, pH, total monomeric aluminum, organically bound monomeric aluminum, true color, turbidity, and conductivity were measured at the processing laboratory. A total of 3,377 lake, stream, and snowpack samples were processed and analyzed during the 1986 studies.

The centralized laboratory operation was successful. Samples were prepared for shipment to the analytical laboratories within the specified holding time in all cases. No personnel safety incidents occurred during the study. Recommendations regarding laboratory operations are included in this report to assist in the preparation of similar projects.

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Abbreviations and Symbols

Abbreviations

ACS	-- American Chemical Society
ASTM	-- American Society of Testing and Materials
BTU	-- British thermal unit
CEC	-- cation-exchange column
CPR	-- cardiopulmonary resuscitation
DIC	-- dissolved inorganic carbon
ELS	-- Eastern Lake Survey
ELS-I	-- Eastern Lake Survey-Phase I
ELS-II	-- Eastern Lake Survey-Phase II
EMSL-LV	-- Environmental Monitoring Systems Laboratory-Las Vegas
EPA	-- Environmental Protection Agency
FIA	-- flow injection analysis (or analyzer)
FN	-- natural field audit
HOx	-- 8-hydroxyquinoline/sodium acetate reagent
ID	-- identification
Lockheed-EMSCO	-- Lockheed Engineering and Management Services Company, Inc.
MIBK	-- methyl isobutyl ketone
NBS	-- National Bureau of Standards
NLS	-- National Lake Survey
NSS	-- National Stream Survey
NSS-I	-- National Stream Survey-Phase I
NSWS	-- National Surface Water Survey
NTU	-- nephelometric turbidity units
PC units	-- platinum-cobalt units
PCV	-- pyrocatechol violet
QA	-- quality assurance
QC	-- quality control
QCCS	-- quality control check sample (or sample)
RD Pair	-- routine and duplicate sample pair
%RSD	-- percent relative standard deviation
RO	-- reverse osmosis
SVS-P	-- Spring Variability Study-Pilot
TD	-- trailer duplicate sample
WLS	-- Western Lake Survey

Symbols

AC	-- alternating current
amp	-- ampere
°C	-- degrees centigrade
g	-- gram
L	-- liter
m	-- meter
M	-- molar
MΩ·cm	-- megaohm centimeter, resistivity unit
mg	-- milligram, 10^{-3} g
mL	-- milliliter, 10^{-3} L
mm	-- millimeter, 10^{-3} m
n	-- number of observations
N	-- normal
ppm	-- parts per million
psi	-- pounds per square inch
r^2	-- coefficient of correlation
rpm	-- revolutions per minute
V	-- volts
w/v	-- weight to volume
$\overline{X}$	-- mean
μg	-- microgram, 10^{-6} g
μL	-- microliter, 10^{-6} L
μm	-- micron, 10^{-6} m
μS/cm	-- microsiemen per centimeter, conductivity unit
%	-- percentage
>	-- greater than
<	-- less than
|x|	-- absolute value of x
Δx	-- change in x

Section 1

Introduction

The National Surface Water Survey (NSWS) was conducted under the direction of the U.S. Environmental Protection Agency (EPA). The NSWS, as part of the National Acid Precipitation Assessment Program's Aquatic Effects Research Program, was designed to characterize surface water chemistry in regions of the United States believed to be potentially sensitive to acidic deposition. The NSWS was composed of the National Lake Survey (NLS) and the National Stream Survey (NSS). The NLS consisted of the Eastern Lake Survey (ELS) and the Western Lake Survey (WLS).

Phase I projects of the NSWS were synoptic surveys designed to quantify the chemistry of lakes and streams in areas of the United States known to contain low alkalinity waters. Phase II projects were designed to determine temporal variability of chemical characteristics of a subset of Phase I lakes and streams. Pilot studies were conducted prior to Phase I projects in order to test equipment, logistics, and protocols.

The EPA's Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV), has been charged with the responsibility for conducting NSWS field and processing laboratory operations. Laboratory, field sampling, managerial, and quality assurance (QA) personnel were provided by Lockheed Engineering and Management Services Company, Inc. (Lockheed-EMSCO).

This report discusses the Las Vegas processing laboratory operations for the six surveys conducted in 1986 (Table 1). The Spring Variability Pilot Study (SVS-P) and the Snowpack Study were done in conjunction with ELS-Phase II (ELS-II). The objective of SVS-P was to obtain data describing the spacial and temporal variability of lake chemistry during snowmelt. The Snowpack Study was conducted in order to determine the relationship between snowpack conditions and the extent and severity of episodic lake acidification.

Table 1. Outline of National Surface Water Surveys for 1986

Survey	Laboratory processing dates (1986)	Field operations report reference
Spring Variability Pilot Study	FEB 21-APR 3	
Snowpack Study	MAR 20-22; MAY 1-23	
National Stream Survey-Phase I	MAR 18-MAY 16	Hagley et al., in preparation
Eastern Lake Survey-Phase II:		Merritt and Sheppe, in preparation
Spring	MAR 25-MAY 4	
Summer	JUL 24-AUG 12	
Fall	OCT 9-NOV 15	

The main function of the processing laboratory was to prepare and preserve water samples received from the field and to ship the prepared aliquots to a contracted analytical laboratory for subsequent analyses. Dissolved inorganic carbon (DIC), pH, aluminum (total monomeric and organically bound monomeric), true color, turbidity, and conductivity were measured at the processing laboratory in Las Vegas, Nevada. The analytical methods used by the processing and contracted analytical laboratories are presented in Hillman et al. (1986) and Kerfoot et al. (in preparation). Changes in or modifications to these methods

are discussed in this report. A list of instrumentation, equipment, and supplies used for these procedures is provided in Appendix A. QA plans for ELS-II (Engels et al., in preparation) and NSS-I (Drousé et al., 1986) were prepared. Quality control (QC) procedures were incorporated into all laboratory analyses.

Section 2

Processing Laboratory Preparation

Organization

Laboratory Trailer Description

Six laboratory trailers were constructed for Phase I of NLS. A field laboratory was stationed at each field site in order to process samples as soon as possible following collection. The field laboratory operations are described in Morris et al. (1986). A trailer floor plan is presented in Appendix B, Figure B-1. The trailers were constructed according to the following specifications:

- Prototype trailer
  - tow-behind design
  - length 24 feet, width 8 feet, height 12.5 feet

- Additional five trailers
  - gooseneck design with fifthwheel hitch
  - length 31 feet, width 8 feet, height 12.7 feet

- Work space and storage capacity of each trailer
  - length 24 feet, width 7.5 feet, height 7.5 feet
  - storage capacity 480 cubic feet (compartment storage)
  - counter space 18 linear feet

- Trailer requirements
  - 110 V and 220 V AC, single-phase 80-amp electrical power
  - minimum water pressure of 50 psi
  - access to sewer drain or leach field

- Trailer equipment
  - laminar flow hood containing high efficiency purification apparatus

filters (0.3-μm pore size) capable of delivering Class 100 air
  - Millipore Milli-RO reverse osmosis purification system, 95-L reservoir, Millipore Milli-Q system capable of delivering American Society for Testing and Materials (ASTM) Type I deionized water (ASTM, 1984)
  - two freezers, refrigerator/freezer
  - two heating/air-conditioning units (5,000-BTU heating capacity and 13,200-BTU cooling capacity)

- Trailer safety features
  - eye-wash station
  - first aid kit
  - two fire extinguishers
  - storage cabinet for flammable solvents
  - vented cabinet for concentrated acids
  - safety shower

Centralization of Laboratory Operations

The results of two experiments (Burke and Hillman, 1987, and M. A. Stapanian, personal communication) indicated that the maximum sample holding time before aliquot preparation could be extended from 12 hours to 24 hours. This permitted centralization of processing laboratory facilities at a warehouse in Las Vegas. Samples were shipped from the field overnight by a commercial courier service and processed within 24 hours of collection.

Several factors influenced the decision to centrally locate the laboratory trailers. The six available trailers were inadequate to accommodate all field sites necessary for concurrent stream and lake studies. In particular, the NSS-I sampling schedule would have neces-

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sitated frequent trailer relocation efforts, each move requiring two days of field time. Housing the trailers in a single location provided an organized area for sample receipt and supply shipment, and the protected location provided a cleaner work environment than when the trailers were stationed in the field, unsheltered from weather conditions. Chemicals were stored in fireproof cabinets in the warehouse. A floorplan of the warehouse is shown in Appendix B, Figure B-2. The purchase of a flow injection analyzer (FIA) for monomeric aluminum determination for each trailer was not possible because of the expense of the instrument. One FIA was purchased for the single location and was sufficient to analyze all samples.

For the centralized laboratory operation, each trailer was dedicated to one or two procedures. For example, all extractable aluminum aliquots were prepared in one trailer for all surveys (Section 4, Extractable Aluminum). This process required the use of methyl isobutyl ketone (MIBK), a hazardous liquid. MIBK was confined to a specially vented trailer, minimizing the potential exposure to personnel and localizing the storage of hazardous waste.

Laboratory Personnel

When the trailers were located in the field, each laboratory was staffed by five persons: a field laboratory coordinator, a supervisor, and three analysts. For the centralized laboratory operations, the staff consisted of a laboratory coordinator, one or two supervisors, and from 6 to 18 analysts. Two supervisors were required for the spring surveys, one for the ELS-II summer seasonal study, and the coordinator and supervisor positions were combined for the ELS-II fall seasonal study. A list of personnel who worked in the processing laboratory during 1986 is presented in Appendix C, Table C-1. The laboratory coordinator was responsible for the overall operations at the processing laboratory, including the daily organization of samples, the shipment of samples to the analytical laboratories, and the completion of all data forms (Appendix D). The laboratory supervisor was responsible for the daily operations at the processing laboratory. The supervisor ensured that samples were handled in accordance with approved methodologies and QA guidelines. Other supervisory responsibilities included

laboratory safety, troubleshooting instrument malfunctions, and reviewing the analytical results. Analysts prepared aliquots for subsequent analytical laboratory analysis and performed DIC, pH, FIA-aluminum, true color, conductivity, and turbidity analyses (Section 4). Depending on the number of samples received, a number of analysts were assigned to each procedure.

Training and Safety

Twenty-two individuals were trained at the processing laboratory during five training sessions conducted in the spring of 1986. Shorter training sessions were conducted at the start of summer and fall operations because all analysts were trained during previous NSWS studies. Prior to 1986 laboratory operations, a draft methods manual was prepared. Analysts were expected to be familiar with all procedures outlined in this document.

Methods

The supervisors and analysts with previous NSWS experience conducted the training programs. Training objectives are summarized in Table 2. Laboratory procedures were taught in modular form to small groups over a three-day period. Instructors described and demonstrated each method. The analysts achieved competency during supervised practice sessions. New analysts, hired after the start of processing, were assigned to positions which were understaffed. They received on-the-job training which consisted of a day observing the analysts during sample processing, followed by a question and answer session. For summer and fall training sessions, analysts reviewed laboratory procedures and tested the analytical instruments under the direction of the laboratory supervisor.

Laboratory safety instruction included the location and use of safety equipment and fire exits, hazardous material handling and disposal, and emergency procedures.

At the end of each training session, all analysts completed a written examination covering laboratory and safety procedures. Analysts assigned to process extractable aluminum aliquots (Section 4) prepared a practice extraction to test their accuracy

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(percent recovery of a known aluminum standard). Before each processing period, the supervisors conducted a practice run simulating an operational day.

Health and safety requirements scheduled for completion during training included: medical surveillance examinations, certification in cardiopulmonary resuscitation (CPR) and first aid, and respirator and safety glasses fittings.

Discussion and Recommendations

The success of the modular training program was based on two items. First, instruction was given to small groups or individuals followed by closely supervised practice time. Second, experienced analysts assisted the supervisor with instructing new analysts. This practice reinforced skills in previously trained analysts and distributed the teaching load.

The modular approach is most effective within a designated training period before samples arrive. In the spring, training time was organized around the new laboratory set-up and sample processing. The supervisors trained new personnel as the schedule permitted. First aid, CPR classes, and medical surveillance examinations were not completed until later dates. For summer and fall operations, all training objectives were completed before samples arrived.

Efficiency of future training programs could be improved in two ways. First, certification in first aid and CPR as a prerequisite for employment would save both time and money. Second, a slide or video presentation detailing processing, analytical, and safety procedures should be prepared and shown in order to familiarize new analysts with methods and equipment and to serve as a review for experienced personnel.

Communications

All information transferred between the laboratory and the field sites was routed through a communications center in Las Vegas. This central communications center played an integral role in the success of the concurrent surveys.

The responsibilities of the communications center included the following:

- Informing the laboratory coordinator of the projected sample load and of any field sampling difficulties affecting the laboratory.

- Tracking sample shipments from a field site to the processing laboratory.

- Resolving sample identification problems and data discrepancies.

- Tracking sample shipments from the processing laboratory to the analytical laboratories and notifying the latter of any sample processing problems.

- Relaying field supply requests to the laboratory coordinator and warehouse manager and tracking the shipment of requested materials.

- Recording daily field, processing laboratory, and shipping activities in a logbook.

Section 3

Quality Assurance

Rigorous QA measures were followed to maintain consistency in laboratory procedures. Details of the QA plan are presented in Drousé et al. (1986) and Engels et al. (in preparation).

Sample Batches

A sample batch consisted of all samples processed on a given day for each survey.

Sample Types

Four types of water samples (routine, duplicate, blank, and audit samples) were processed and analyzed. Collection procedures are presented in Merritt and Sheppe (in preparation) and Hagley et al. (in preparation). A *routine* sample consisted of a 4-L container (Cubitainer), a bulk sample for aliquot preparation, and four 60-mL syringes, one each for DIC, FIA-aluminum, pH, and preparation of the extractable aluminum aliquot (Section 4). A *duplicate* sample, a second sample collected immediately following the collection of the routine sample, included a Cubitainer and four syringes and was treated in the same manner as a routine sample. One routine-duplicate pair (RD pair) was included with each batch of samples. A *blank* sample included a Cubitainer and two syringes (FIA-aluminum and extractable aluminum). Two types of blank samples, field and laboratory blank samples, were processed and analyzed. Field blank samples consisted of deionized water sent from the laboratory to the field, run through the sampling equipment, and returned to the laboratory for processing. Laboratory blank samples were deionized water samples prepared at the laboratory and incorporated into a sample batch for processing. An *audit* sample is a solution with a known chemical composition used to monitor the performance of the processing and analytical laboratories. Two categories of audit samples were used: field and laboratory audit samples. Field audit samples were received in 2-L bottles and were prepared and analyzed at the processing laboratory in the same manner as a routine sample. These samples were ordered in advance and were stored at the processing laboratory at 4 °C. A field audit sample represented a sample known to be an audit by the processing laboratory staff but having a composition unknown to the analysts. When received at the analytical laboratory, the field audit was of unknown sample type and composition (a double blind test). A laboratory audit sample was received from an assigned audit laboratory as a complete set of aliquots. The laboratory audit sample was prepared by the audit laboratory staff following the same protocols used in the processing laboratory (Table 9). Arriving the day they were required, the laboratory audit samples were relabeled at the processing laboratory and were incorporated into a sample batch by the laboratory coordinator. The laboratory audit sample was a double blind sample to analysts at the analytical laboratory. A description of the audit sample types was originally presented in Morris et al. (1986). There were natural (well-characterized, filtered, lake water) and synthetic sample types of both field and laboratory audit samples. Radian Corporation (Austin, Texas) prepared field and laboratory audit samples for all surveys. In addition, EMSL-LV prepared synthetic laboratory audit samples used during the ELS-II fall seasonal study. Synthetic rainwater samples prepared by the National Bureau of Standards (NBS) (Gaithersburg, Maryland) were also used as laboratory audit samples during the ELS-II fall seasonal study. Sample codes for all sample types are shown in Appendix D, Table D-1.

Data Requirements

Quality control check samples (QCCS) were prepared daily for all methods (except true color) to monitor the reliability of the results. The type of QCCS used for each method is presented in Table 3. A QCCS was analyzed after a specified number of samples were measured; and control limits were determined for each QCCS. Control charts for selected QC solutions are presented in Section 5 of this report.

Agreement between routine and duplicate field samples for processing laboratory parameters was determined daily. If the precision requirements were not met, the pair was reanalyzed at the processing laboratory. As a check on processing laboratory instrument precision, a sample was selected randomly each day by the laboratory coordinator as the trailer duplicate (TD) and was analyzed in replicate. The RD pair and TD agreement precision requirements are listed in Table 3.

For pH, the processing laboratory result was required to agree with the field result within 0.50 pH units for each lake sample, and within 0.30 pH units for each stream sample. If the results did not meet these criteria, the sample was reanalyzed at the processing laboratory. Field versus laboratory pH results for NSS-I are discussed in Section 4.

For the FIA-aluminum procedure (Section 4), the instrument detection limit was determined to be 7.0 μg/L Al. The detection limit was calculated as three times the standard deviation of repetitive, nonconsecutive measurements of a low aluminum standard (Kerfoot et al., in preparation). The detection limit QCCS, a sample containing aluminum at a concentration nearly three times the detection limit (20 μg/L Al), was analyzed once per batch. A non-acidified deionized water blank was analyzed once at the beginning and once at the end of the daily analysis. When the 75 μg/L Al QCCS was analyzed with the cation-exchange column (CEC) engaged,

Table 3. Quality Assurance Outline for Processing Laboratory Analyses

Parameter	Quality control check sample	Maximum quality control check sample interval spring	summer/fall	Quality control check sample limit	Routine-duplicate pair and trailer duplicate precision requirement
pH	1 x 10⁻⁴ N H₂SO₄	5	10	4.00 ± 0.10 pH units	0.10 pH units
Flow injection analysis- monomeric aluminum determination	75 μg/L Al	10	10	75.0 ± 7.5 μg/L Al 75.0 ± 15.0 μg/L Al (spring-channel 2)	10% 20%
Conductivity	1 x 10⁻⁴ N KCl 5 x 10⁻⁴ N KCl 1 x 10⁻³ N KCl	10 10 10	NA NA NA	14.7 ± 1.5 μS/cm 73.9 ± 7.4 μS/cm 147.0 ± 14.7 μS/cm	10% 10% 10%
Dissolved inorganic carbon	2 mg/L C	8	10	2.000 ± 0.200 mg/L C	10%
Turbidity	5 nephelometric turbidity units (NTU)	8	10	5.0 ± 0.5 NTU	10%
Color	None	NA	NA	NA	5 platinum- cobalt units

the channel 2 (organically bound monomeric aluminum) result was required to be within 20% of the blank value or the sample was reanalyzed after identification of the cause for the high result.

Analysis of a calibration blank (deionized water) was required for the conductivity and DIC procedures (Section 4). For the DIC method, the daily calibration blank result was required to be less than 0.100 mg/L C. Each week 20 consecutive blank samples were analyzed for DIC. The detection limit, which was calculated as three times the standard deviation of the blank sample results, was required to be less than 0.100 mg/L C. For conductivity measurements, the daily calibration blank result was required to be less than 0.9 μS/cm.

Section 4

Daily Laboratory Procedures

Analysts organized supplies and equipment, prepared reagents and standards, and calibrated instruments before samples arrived from the field sites. The laboratory coordinator organized samples (by survey) into sample batches, then distributed samples to the analysts. After processing was complete, analysts prepared samples for shipment to the analytical laboratories. Samples were analyzed at the contracted analytical laboratories within 48 hours to 28 days of collection based on the holding times specified in Hillman et al. (1986). The laboratory coordinator reviewed the analytical results, completed the data forms, and forwarded the forms to QA personnel. Laboratory personnel cleaned the facility and prepared for the next day's operations. The flow of samples, from collection through processing, is illustrated in Figure 1.

Sample Organization

Methods

Samples were packed with frozen chemical refrigerant packs in shipping containers (coolers). They were shipped by an overnight courier or by a commercial airline to the processing laboratory. Samples arrived at the laboratory by 9:30 a.m. the day following collection. When commercial airlines were used, laboratory personnel claimed the shipment at the airport. Due to cost and inconvenience, commercial airlines were used only when the overnight courier was not in operation (Sunday) or when the overnight courier pick-up deadline was missed in the field (less than five times).

Each shipping cooler contained from one to three Cubitainers, the associated syringes, frozen chemical refrigerant packs, and field data forms. The syringes, sorted by site identification number, were secured in plastic containers. To organize the samples, the laboratory coordinator (1) collected field data forms, (2) measured each cooler temperature to the nearest 0.1 °C with an NBS-traceable thermometer by placing the thermometer between the Cubitainers, (3) recorded site ID number, sample type information (Section 3) and sample temperature on sample log-in sheet, (4) matched each Cubitainer with the associated syringes by the site ID number and sample type, (5) randomly assigned a sample ID number to the sample and recorded batch and sample ID numbers on each container and on the sample log-in sheet, (6) incorporated scheduled audit samples into batches, and (7) distributed samples to analysts. The supervisors and analysts prepared to process samples during batch organization (Morris et al., 1986; Hillman et al., 1986).

The coordinator reviewed the field data forms and transcribed the sample ID and temperature information from the sample log-in sheet to the field data forms. A copy of the sample log-in sheet was distributed to QA personnel. The field data forms for ELS-II and NSS-I are presented in Merritt and Sheppe (in preparation) and Hagley et al. (in preparation), respectively. Three copies of the four-part field form were sent to the processing laboratory for each sampled site. The white original and yellow copy were sent to QA personnel and the pink copy was retained at the processing laboratory. A summary sheet, which was distributed to each trailer, included the field pH results, identification of the TD, RD pair, and blank samples (Section 3), and any special remarks concerning the sample (i.e., low sample volume, broken syringe tip, no analysis required, etc.). A copy of the summary sheet was forwarded to QA personnel. After sample

Quality Assurance Samples

ROUTINE SAMPLES	FIELD BLANK	FIELD DUPLICATE
4 Syringes (60 mL)	2 Syringes	4 Syringes
1 Cubitainer (4 L)	1 Cubitainer	1 Cubitainer

AUDIT SAMPLES	
FIELD	LABORATORY
1 Container (2 L)	7 Preserved Aliquots

Shipped to Processing Laboratory at 4 °C via Overnight Courier

PROCESSING LABORATORY *(Next Day)*

Samples Organized into Batch

Sample Processing Information Recorded on Field Data Forms

SYRINGES — — CUBITAINER

FIA - Aluminum

Dissolved Inorganic Carbon

pH

True Color

Turbidity

Conductivity

Data Transcribed to Data Form

Aluminum Extraction Performed and Aliquot Prepared

Shipping Form Prepared

ALIQUOT PREPARATION
1. Filtration
2. Preservation
3. Storage at 4 °C

Seven Aliquots Packed for Shipment and Sent to Analytical Laboratories via Overnight Courier

QUALITY ASSURANCE — — *(Next Day)*

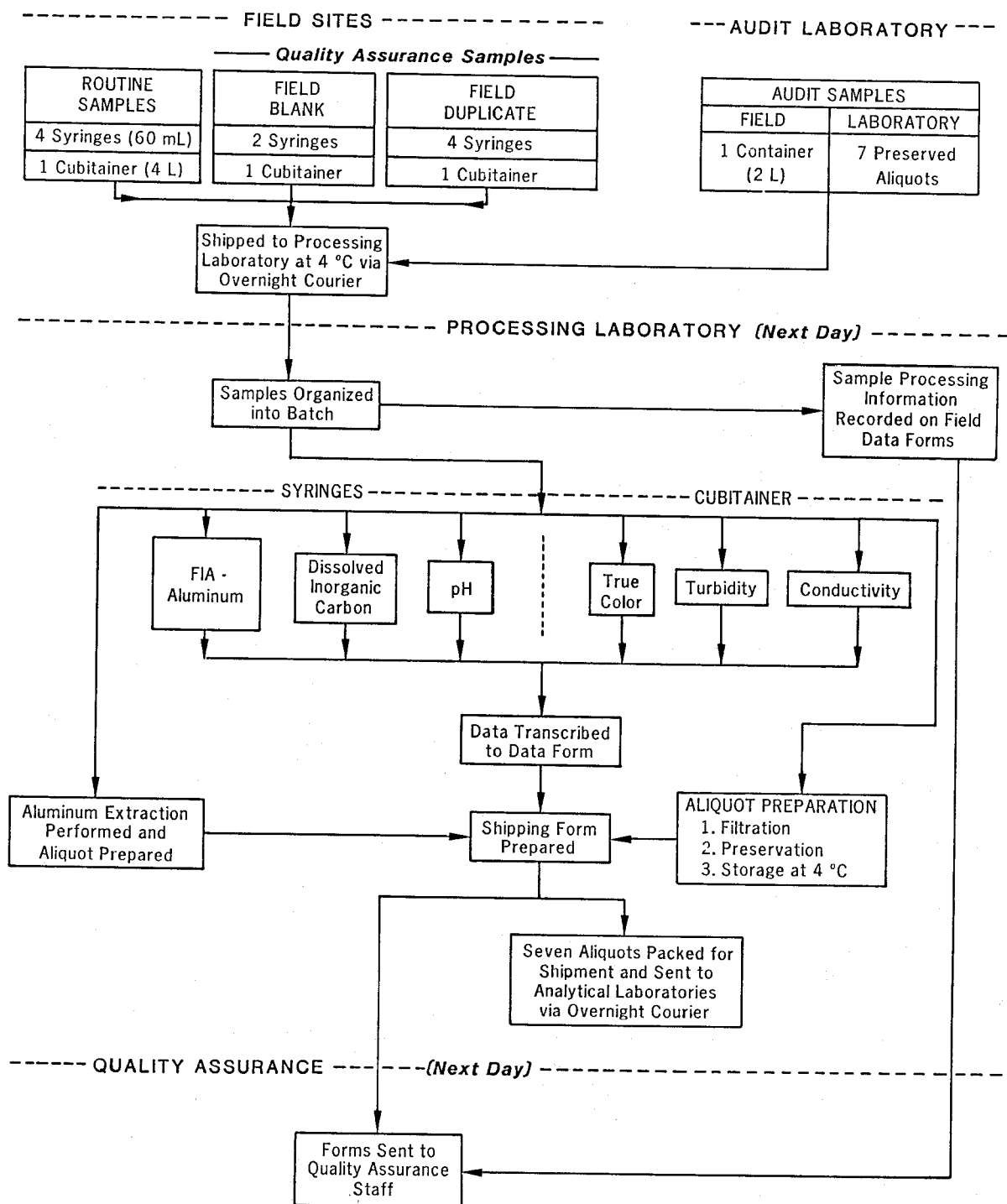Forms Sent to Quality Assurance Staff

Figure 1. Flow of samples and data from the field through the processing laboratory.

processing was completed, the coordinator completed the three-page laboratory batch/QC data form (Appendix D, Figure D-1). The white original and pink copy of this form were sent to QA personnel and the yellow copy remained at the processing laboratory. A four-part shipping/receiving form (Appendix D, Figure D-2) was completed by the coordinator and the copies were distributed as follows: white original to QA personnel; yellow copy to the sample management office (Alexandria, Virginia); pink and gold copies to the analytical laboratory.

During the ELS-II summer seasonal study, field samplers collected a number of special project samples, including preserved hypolimnetic, triplicate, chlorophyll, and zooplankton samples. The responsibilities of processing laboratory personnel regarding these samples are presented in Table 4. Analysis of preserved hypolimnetic samples provided data to study the potential loss of dissolved iron and manganese from hypolimnetic water samples due to exposure to oxy-

gen during normal routine sample collection. Triplicate samples were collected for an inter-laboratory bias experiment. Each day, processing laboratory personnel prepared two batches of aliquots from the triplicate Cubitainer: the routine batch and the bias experiment batch. Each batch (routine and bias) was sent to a separate analytical laboratory. Processing of the triplicate samples is discussed later in this section (Aliquot Preparation). Batch/QC data form sample codes for the ELS-II summer seasonal study are shown in Appendix D, Table D-2.

Discussion

The organization of samples into batches during the spring required a great deal of time due to the large number of samples received. When more than 30 samples arrived on a given day, two people organized the sample batches. All sample information was verified by checking sampling schedules and field data forms. The communications center resolved any sample identification discrepancies.

Table 4. Eastern Lake Survey-Phase II Summer Seasonal Study

	Special Project Responsibilities	
Sample	Description	Procedure
Preseved Hypolimnetic	250-mL aliquot; preserved with 0.2 mL HNO$_3$ (concentrated)	1. Assign batch, sample ID numbers 2. Incorporate audit samples (Appendix D, Table D-2) into batch 3. Check pH of all samples 4. Record information in logbook 5. Prepare 15-mL split and blank sample 6. Ship samples to Environmental Monitoring Systems Laboratory, Las Vegas, Nevada
Triplicate	4-L Cubitainer	1. Assign two batch and sample ID numbers to each Triplicate Cubitainer 2. Prepare two batches of aliquots 3. Incorporate audit (Appendix D, Table D-2) and blank samples into each batch 4. Ship each set to assigned analytical laboratory daily
Chlorophyll	10-mL vial containing filter (0.8 μm pore size, polycarbonate)	1. Assign a batch and a sample ID number to each vial 2. Incorporate audit samples into batch. Natural audit samples from Lake Mead, Nevada; standards prepared by Environmental Monitoring Systems Laboratory, Cincinnati, Ohio) 3. Store at -20 °C 4. Record information in logbook 5. Ship samples to Fresh Water Institute of Winnipeg, Manitoba, Canada weekly
Zooplankton	250-mL glass jar; preserved with formalin (4%)	1. Record information in logbook 2. Ship samples to Academy of Natural Sciences, Philadelphia, Pennsylvania at end of survey

pH (Closed System)

Introduction

Samples were collected in syringes to minimize the variation in pH as a result of CO_2 gas transfer between the sample and the atmosphere (Burke and Hillman, 1987). The pH was measured in an 8-mL sealed chamber (Hillman et al., 1986) using an Orion model 611 pH/millivolt meter and an Orion Ross model 8104 combination electrode.

Methods

The pH procedure is documented in Hillman et al. (1986) and is illustrated in Figure 2. Samples were equilibrated to room temperature. A 1×10^{-4} N H_2SO_4 solution was used as a QCCS. QC requirements are pre-sented in Section 3. The pH meter was standardized using NBS-traceable pH buffer solutions (certified pH 4.00 ± 0.01 and pH 7.00 ± 0.01 at 25 °C). Specific modifications of the pH method incorporated to increase measurement efficiency included the following:

* A protocol was developed for the use of two pH meters for one batch when the batch size was greater than 20 samples. A dilute pH 7 buffer solution was prepared by placing 5.000 ± 0.001 g of concentrated NBS-traceable pH 7 buffer in 1 L of deionized water. The dilute buffer, which has an empirically derived value of 7.31 ± 0.07 pH units (mean ± two standard deviations, n = 49), was used as an intermeter comparability check solution. Table 5 summarizes the steps and indicates the time of initiation.
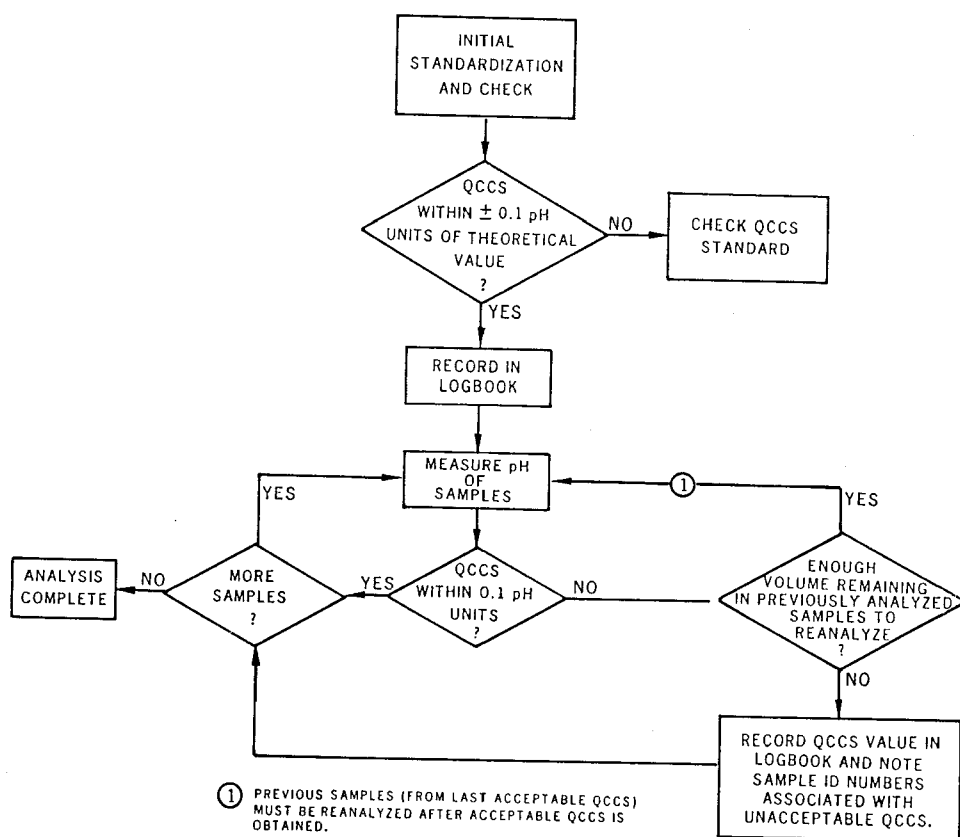

Figure 2. Flowchart for pH determination.

Table 5. Protocol for Simultaneous Use of Two pH Meters

Procedure	Spring	Summer	Fall
1. Designate primary and secondary pH meter	x	x	x
2. Analyze first half of batch on primary meter and second half on secondary meter	x	x	x
3. Analyze the routine-duplicate pair on the same meter	x	x	x
4. Analyze a trailer duplicate on both meters		x	x
5. Use a natural audit sample as a comparability check of each batch on both meters	x	x	
6. Use a dilute pH 7 buffer solution as comparability check with each pH 4 QCCS on both meters		x	x
7. If check sample values do not agree within 0.05 pH units and recalibration does not succeed, analyze all samples on primary meter		x	x

- The maximum QCCS interval was increased from one analysis every five samples during the spring surveys to one analysis every ten samples during the summer and fall seasonal surveys.

- A stable pH reading was redefined to be a pH value that does not vary more than 0.02 pH units in one direction during a one-minute interval for the summer and fall surveys. A two-minute interval was used for the spring surveys.

- Performance of the pH meter two-point temperature calibration was changed from daily intervals during the spring surveys to weekly intervals during the summer and fall surveys.

Results

Samples used as intermeter comparability checks and their associated ranges and between meter ΔpH values are listed in Table 6. Natural field (FN) audit samples are described in Section 3. The FN audit sample pH difference ($|\Delta$pH$|$) was greater than the dilute pH 7 buffer results for a given analysis day. The frequency of unacceptable QC checks between meters (%$|\Delta$pH$|$ > 0.05 pH units) was also greater for the FN audit samples than for the dilute pH 7 buffer samples (0-33% vs. 0%).

Figure 3 is a plot of the difference between NSS-I field and processing laboratory pH values. QA protocol required that these measurements agree within 0.3 pH units (NSS-I only). If they did not, the sample was required to be reanalyzed at the processing laboratory.

QCCS results are presented in Section 5 (Figure 8, and Tables 13 and 14). FN audit sample results are presented in Figure 15 and in Table 15.

Discussion

The time required for a sample to reach a stable pH value varied from seven minutes to two hours, although most samples reached a stable pH in approximately 20 minutes. During the spring surveys, as many as 90 samples were received daily, requiring the use of two pH meters per batch. Analysts used four meters and measured two batches simultaneously to decrease the total analysis time. Batch sizes justified the use of two pH meters during the summer seasonal study also.

The use of two pH meters per batch required the development of a protocol to address the question of comparability of the results between meters. To verify intermeter comparability, a QCCS which closely approximated the chemistry of NSWS samples was desired. The FN audit samples listed in Table 6

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Table 6. Comparison of Intermeter Check Samples for Spring and Summer 1986

| Sample Type	Date Used 1986	Observed Range by pH electrode		$|\Delta pH|$ by day	% $|\Delta pH|$ > 0.05 pH units
		I	A		
Spring					
FN-8	MAR 20-MAR 26	5.08-5.20	5.05-5.24	0.00-0.04	0%
FN-7	MAR 27-APR 2 APR 15-APR 19	6.90-6.96	6.84-6.99	0.00-0.10	7%
FN-6	APR 1-APR 16	6.62-7.01	6.61-7.03	0.00-0.24	30%
Summer					
FN-7	JUL 24-JUL 26	6.61-6.85	6.59-6.83	0.00-0.19	33%
FN-8	JUL 28-JUL 29	5.00-5.20	5.05-5.18	0.02-0.05	20%
20:1 pH 7 buffer	JUL 26-JUL 29	7.28-7.29	7.28-7.29	0.00	0%
200:1 pH 7 buffer	JUL 30-AUG 8	7.26-7.38	7.24-7.37	0.00-0.05	0%

BATCH NUMBER ⟶
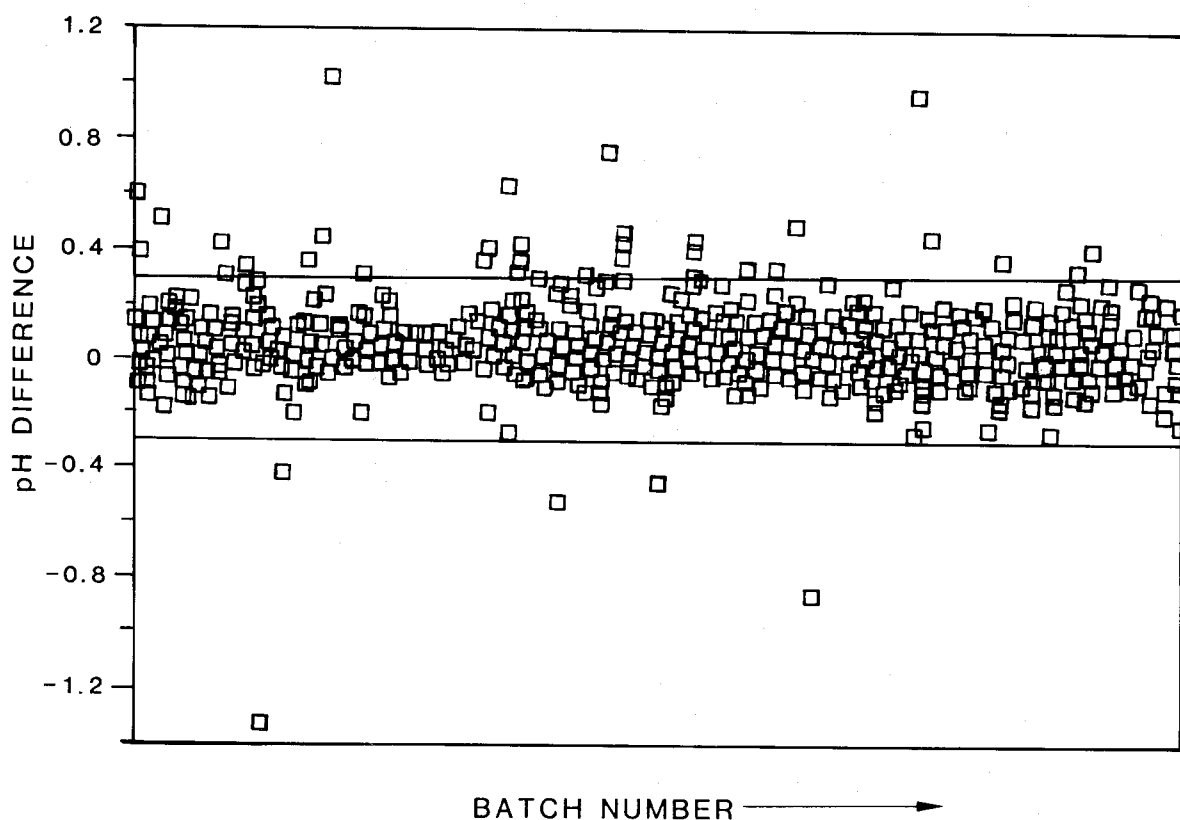
Figure 3. The pH difference between NSS-I field values and processing laboratory values.

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served as the intermeter comparability check during the spring surveys and initially during the summer seasonal survey. These audit samples proved unsatisfactory for several reasons. First, agreement within 0.05 pH units between meters was difficult to obtain due to unexplained within audit sample variability (Table 6). For example, in the summer survey the FN sample collected from Seventh Lake (FN-7) failed to meet criteria (%|ΔpH| > 0.05 pH units) 33% of the time. Failure to meet the agreement criteria required recalibration of meters and reanalysis of the previous samples from the last acceptable intermeter comparability check. Second, the time required for the FN samples to reach equilibrium averaged approximately 30 minutes. When routine field samples were slow to stabilize, these comparability audit samples added considerable analysis time. Third, the additional audit samples were a cost factor.

During summer processing, a new intermeter check sample, a dilute pH 7 buffer solution, was introduced. Initially a 20:1 dilution of the NBS-traceable pH 7 calibration buffer solution was used, yielding acceptable results. A 200:1 dilution was chosen later because its ionic strength was closer to that of the pH 4 QCCS and FN audit samples. The 200:1 dilution gave comparable readings on two pH meters (0% failure to meet 0.05 pH unit agreement criteria, Table 6). A mean value of 7.31 ± 0.07 for this comparability check sample was determined empirically based on statistical analysis of the summer survey data.

The precision of the 1×10^{-4} N H_2SO_4 QCCS measurements during the spring surveys is presented in Section 5, Figure 8 and Tables 13 and 14. The maximum interval among QCCS measurements was increased from one measurement every five samples to one measurement every ten samples before summer processing, based on consistent QCCS results obtained in all previous surveys. The deviation of the mean pH value (4.06 ± 0.05) from the theoretical value (pH 4.00 ± 0.1) was probably due to a larger error in the liquid junction potential of the electrode than previous theories would predict (Metcalf, 1987). For future surveys, we recommended that the value of the QCCS be corrected from 4.00 ± 0.1 to 4.06 ± 0.05 pH units. This change more accurately reflects the apparent pH of the standard using the system described. Statistical tests have

demonstrated the good precision of the Orion Ross combination electrode (Metcalf, 1987).

A Hydrolab Surveyor II was used in the field to measure the *in situ* pH during ELS-II (Merritt and Sheppe, in preparation). Orion Ross combination electrodes (model 8104) and Beckman pHI-21 portable pH meters were used for NSS-I field pH measurements (Hagley et al., in preparation). The acceptance criteria between field and laboratory pH measurements were 0.50 pH units for ELS-II samples and 0.30 pH units for NSS-I samples. Field pH results from each survey were compared with the laboratory results immediately following analysis at the processing laboratory. If agreement criteria were not met, the sample was reanalyzed at the laboratory to verify the pH value obtained at the laboratory. Comparison of the field and laboratory results served as a check on the function of the laboratory instrumentation and as an indicator of field instrument operation. As demonstrated in Figure 3, field versus laboratory pH agreement is excellent and confirms two items. First, the pH of samples in sealed syringes was stable for at least 24 hours following field collection. Second, the precision of the measurements was high (r^2 = 0.988) despite the fact that pH meters made by different manufacturers were used for field and laboratory pH measurements.

Flow Injection Analysis Monomeric Aluminum Determination

Introduction

The FIA-aluminum procedure is a computer-controlled colorimetric method used to accurately and quickly measure the concentrations of various dissolved monomeric aluminum fractions. The system is an automated continuous flow system in which two sample streams are measured concurrently. One stream (channel 1) is analyzed directly for total monomeric aluminum which includes inorganic monomeric and organically bound monomeric species. The second stream (channel 2) is passed through a CEC containing Amberlite 120 resin which removes the inorganic monomeric aluminum fraction (Driscoll, 1984) measuring only the organically bound monomeric

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species. This method permits the indirect determination of the inorganic monomeric aluminum fraction which has been related to high fish mortality (Baker and Schofield, 1982). Although extractable aluminum and total aluminum in an unfiltered sample also were measured by the analytical laboratories using graphite furnace atomic absorption spectroscopy, the FIA-aluminum method provided specific information about inorganic monomeric aluminum, the species believed to be toxic to fish.

Methods

Samples were collected in the field in sealed syringes and stored at 4 °C until analysis. A sample was loaded from the syringe through a syringe filter (acid-washed, 0.45-μm pore size) into the two FIA sample loops (10-μL). The sample first filled the channel 1 sample loop, then passed through the CEC to fill the channel 2 sample loop. The two discrete sample volumes were delivered to the reaction manifold by separate carrier streams of deionized water. A peristaltic pump was used to deliver reagents that mixed with the separate sample streams. A masking reagent was added in order to eliminate iron interference. Pyrocatechol violet (PCV), which forms a colored complex with aluminum, was added to the streams, then a buffer solution was added to adjust the reaction pH to 6.1 to maximize color development. The sample streams passed through separate colorimeter flowcells which measured the absorbance of the PCV-Al^{3+} complex at 580 nm. The measured absorbances were proportional to the concentration of total monomeric aluminum and organically bound monomeric aluminum present in the sample. The absorbance peak areas were converted to readings in μg/L Al using a computer program. The FIA-aluminum method is presented in Kerfoot et al. (in preparation). The colorimeter, reaction manifold, and software package were developed by LaChat/Quick Chem.

A synopsis of the FIA-aluminum method is presented in Table 7. This working method is documented in Henshaw et al. (in preparation). A 75-μg/L aluminum standard was prepared from a certified 1000-mg/L aluminum standard and used as a QCCS. A calibration curve was calculated each day using 0, 25, 100, 200, and 350-μg/L Al standards that were prepared from a separate certified 1000-mg/L

Al standard. A 20-μg/L Al detection limit standard and a reagent blank sample (deionized water) were analyzed each day. QC requirements are presented in Section 3.

Table 7. Flow Injection Analysis-Aluminum Procedure

A. Precalibration

1. Prepare reagents, standards, and quality control solutions.
2. Warm up system components; begin pumping reagents until baseline is stable.
3. Initiate background computer program and chart recorder.
4. Input sample information to computer.
5. Adjust "ZERO" to 100 and "GAIN" to 4.00 for each channel.

B. Calibration

1. Place sample inlet into first of the five standards (acidified blank, 25, 100, 200, 350-μg/L Al standards). Analyze each standard two times.
2. Turn switch to "CAL" position.
3. Start program.
4. Place sample inlet into second standard after two injection cycles.
5. Calibration data is printed after the fifth standard.
6. Obtain raw calibration data.

C. Samples

1. Analyze 75-μg/L Al quality control check sample (with and without the cation-exchange column), high calibration standards, 600-μg/L Al quality control check sample, 20-μg/L Al detection limit sample, and deionized water blank.
2. Place syringe pump in line and set pump on "7 mL/min".
3. Place syringe with filter on syringe pump.
4. Turn switch to "SAMPLE" position.
5. Initiate sample analysis.
6. Analyze 75-μg/L Al quality control check sample every 10 samples, once with cationexchange column and once without cationexchange column.
7. At completion of sample analysis, analyze 75-μg/L Al quality control check standard, detection limit standard, and blank.

D. System Shut-down

1. Stop background program.
2. Obtain raw sample data.
3. Run deionized water and cleaning solution through reagent lines.
4. Turn off system components.

Results

For the fall seasonal study, control limits were determined for a natural audit sample

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(Big Moose Lake, Adirondack Mountains, New York State) based on 14 calibrations by a single operator. This sample was analyzed daily to monitor the status of the CEC. The statistical analysis is presented in Table 8, and is based on 14 instrument calibrations. QCCS control charts for the FIA-aluminum method are presented in Section 5, Figures 9 and 10. QCCS statistical results are presented in Table 13. Natural field audit sample results are presented in Figure 17 and Table 15.

Table 8. Natural Field Audit Sample Results for Flow Injection Analysis-Aluminum

	Total Al Channel 1 (μg/L Al)	Organic Al Channel 2 (μg/L Al)
n	36	36
X̄	147.7	44.5
Two Standard Deviations	12.58	10.74
Range	135.1-160.3	33.8-55.2

Discussion and Recommendations

Numerous problems delayed the development of a workable FIA-aluminum method before spring sample processing began. The instrument was not received until mid-January. Further development of the method available was required. Previous applications of the method included an acidified carrier stream and sample acidification. For NSWS samples, it was decided to use a deionized water carrier and not to acidify the samples in order to minimize changes in pH and, hence, in aluminum speciation.

The main instrumental problem involved the CEC. During the spring surveys, the sample flow for channel 2 (organically bound monomeric aluminum) was as follows: the sample stream first filled the channel 2 sample loop, passed through the CEC, then entered the reaction manifold. It was necessary to manually remove the CEC from the sample line for the analysis of standards and QC solutions, then replace the CEC for sample analysis. This removal and replacement of the CEC was time-consuming and often resulted in the introduction of air into the sample analysis line. Due to these problems with the CEC, the

QCCS limit was extended to 75.0 ± 15.0 μg/L Al for channel 2 during the spring surveys. The channel 1 QCCS limit remained at 75.0 ± 7.5 μg/L Al.

The major sample-related problem was the high aluminum concentrations measured in NSS-I samples. This led to the development of a high-range analysis procedure. High calibration standards (500, 750, and 1000 μg/L Al) were analyzed each day following the 0-350 μg/L Al calibration. A 600-μg/L Al standard was analyzed as the high-range QCCS. If a sample aluminum concentration was between 350 and 600 μg/L Al the 600-μg/L Al QCCS was subsequently analyzed. If the high QCCS was within 10% of its theoretical concentration, the sample result was accepted. If the sample aluminum concentration was between 600 and 1000 μg/L Al or the high QCCS criteria were not met, a high calibration curve was determined manually from a linear regression of peak area versus concentration of the high calibration standards (350, 500, 750, and 1000 μg/L Al). An expanded calibration was performed for samples with aluminum concentrations exceeding 1 mg/L Al using standard concentrations of 1.000, 2.000, and 3.500 mg/L Al and a QCCS of 2.500 mg/L Al (±10% limit). The gain settings were changed to 1.00. Any sample aluminum concentration exceeding 3.500 mg/L Al was diluted with deionized water which was adjusted to the sample pH by titration with 0.001 N H_2SO_4 (Ultrex) until the absorbance was on scale at a gain setting of 1.00 (Kerfoot et al., in preparation).

As a result of the instrument and sample-related problems, the spring FIA-aluminum procedure required excessive processing time and produced a backlog of 395 samples. The backlogged samples were analyzed as time permitted during the spring surveys with the assistance of methods development personnel. The data were qualified (flagged) because the samples were not analyzed within the specified sample holding time of 24 hours. The effects of holding time on aluminum speciation have not been determined conclusively.

The methods development group corrected the FIA problems prior to the summer seasonal survey. During the spring surveys, routine FIA calibration was done with aluminum standards ranging from 0-150 μg/L Al.

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Experimentation with the calibration showed that it was linear to 1000 μg/L Al and that the best precision and sensitivity could be achieved by performing a calibration using standards from 0-350 μg/L Al. By installing a switch and placing the CEC *before* the channel 2 sample loop, the operator could control the activation of the CEC easily. This reduced both the possibility of air introduction and the total analysis time considerably. Reagent concentrations and flow rates were varied in order to optimize the method. A pH meter and strip chart recorder were added to monitor the system. Additional QC data requirements were introduced. Method revision details are described in Kerfoot et al. (in preparation).

During the summer seasonal survey, the FIA-aluminum analysis proceeded with minimal difficulty. Highly turbid samples could not pass through the syringe filter without introducing air into the sample injection line. Once these samples were identified, they were centrifuged (for 90 seconds at setting of 40 equal to 1500 rpm) and analyzed successfully. For three days during the summer survey, channel 2 did not function properly as evidenced by the low values obtained for a natural audit sample known to contain a measurable concentration of organically bound monomeric aluminum. This resulted in the modification of the protocol to include the routine analysis of this natural audit sample collected from Big Moose Lake in New York State (FN-8 for the summer survey and FN-10 for fall activities). The calculated ranges for this internal QCCS (Table 8) were not implemented as strict limits, but were used as a guideline to monitor the status of both channels of the FIA.

For each QCCS interval, the 75-μg/L Al QCCS was analyzed one time without the CEC and one time with the CEC. The control charts presented in Section 5, Figures 9 and 10 demonstrate the comparability between channel 1 and channel 2. Without the CEC engaged, only total monomeric aluminum is measured.

The successful development of a viable method for monomeric aluminum determination and a final data requirement plan (Section 3) continued throughout the sample processing period. Many protocol revisions were necessary after completion of the spring surveys.

The continued development of the FIA-aluminum method during sample processing produced a reliable FIA method for ELS-II summer and fall seasonal studies.

Conductivity

Introduction

Conductivity, defined as the ability of an aqueous solution to carry an electric current, can be roughly linearly correlated with the ionic strength of a solution when the conductivity of the sample is less than 100 μS/cm (25 °C). Processing laboratory conductivity measurements were made only on NSS-I samples, using a YSI Scientific model 32 conductivity meter and a YSI model 3417 conductivity cell with a theoretical cell constant of 1.00 cm^{-1}.

Methods

The method adopted for conductivity measurement was a modification of the procedure described in Hillman et al. (1986). Samples were poured from the Cubitainer into two 50-mL centrifuge tubes (a rinse solution and a measurement solution) and equilibrated to room temperature. Three QC solutions were used for conductivity measurements: a 1 x 1^{-4} N, 5 x 10^{-4} N, and 1 x 10^{-3} N KCl solutions measuring 14.7, 73.9, and 147.0 μS/cm, respectively (theoretical values at 25 °C). The stock solution was a 1 N KCl solution prepared from reagent grade KCl dried for 2 hours at 105 °C. A 147.0 μS/cm KCl standard (prepared from a second 1 N KCl stock solution) was used as a calibration standard. The conductivity of a deionized blank sample was measured each day. QC requirements are presented in Section 3. Deviations were detected in the output from the conductivity meter temperature compensation circuitry. The automatic temperature probe was not used. Measured conductivities of the QC standards and deionized blank sample were corrected to 25 °C using a temperature correction factor table and a pocket calculator. Figure 4 is a flowchart for the conductivity procedure.

Results

QCCS control charts are presented in Section 5, Figures 11, 12, and 13. The QCCS

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ELECTRONICS
CHECK
WITH RESISTORS

VALUES
WITHIN 1% OF
THEORETICAL
VALUES
? — NO

YES

CALIBRATION
PROCEDURE
TO CHECK
PROBE CELL
CONSTANT

CONSULT CONDUCTIVITY
METER OR CONDUCTIVITY
PROBE OPERATIONS MANUAL
AND NOTIFY SUPERVISOR

ACCEPTABLE
VALUES
FOR $147\mu Scm^{-1}$ CALIBRATION
STANDARD
AND
BLANK
? — NO

YES

QCCS
WITHIN
10% ? — NO

REMAKE AND
REMEASURE
SOLUTIONS

ACCEPTABLE
RANGE
?

NO

YES

YES

MORE
SAMPLES
?

MEASURE
SAMPLES AND
RECORD IN LOGBOOK

①

NO

FINAL CELL
CONSTANT CHECK

ANALYSIS
COMPLETE

① PREVIOUS SAMPLES (FROM LAST ACCEPTABLE QCCS)
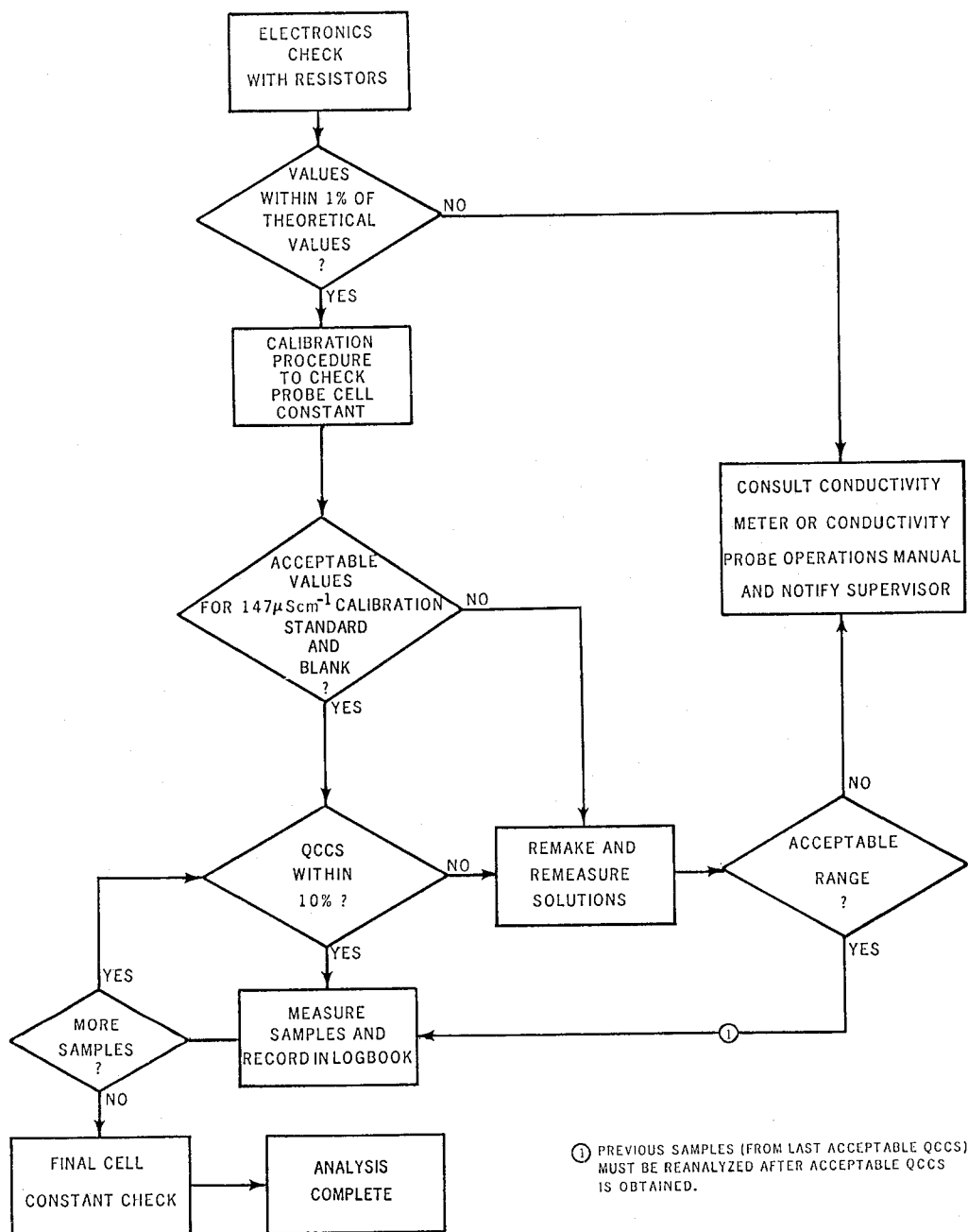MUST BE REANALYZED AFTER ACCEPTABLE QCCS
IS OBTAINED.

Figure 4. Flowchart for conductivity method.

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statistical results are presented in Table 13. FN audit sample results are presented in Figure 18 and Table 15.

Discussion and Recommendations

During the spring surveys, analysts were trained as time permitted. This resulted in some analysis inconsistencies. As analysts became familiar with the revised method and the instrument, these problems were resolved.

The conductivity cell used early in the spring was determined to be faulty when the blank sample and cell constant (K_c) values were reviewed. A replacement YSI conductivity cell was substituted after Batch ID 2129 (Figure 18).

Several modifications in the available procedure (Hillman et al., 1986) were necessary for the successful measurement of conductivity. First, it was necessary to correct the measured conductivity values to 25 °C using a table of temperature correction factors. These computations were necessary to evaluate the accuracy of the QCCS and to monitor the cell constant during analysis. In the future, it would be more efficient to equilibrate all samples and standards to 25 °C in a water bath. Second, the deionized water used to prepare the calibration standard and QCCS contributed to the overall conductivity and had to be considered in calculating the actual K_c and QCCS values. The following equations were used:

$$K_c = \frac{K_t}{(K_m \times T) - (B_m \times T)} \quad (1)$$

$$S_c = (S_m \times K_c \times T) - (B_m \times T) \quad (2)$$

where

B_m = measured value of blank (deionized water)

K_c = temperature-corrected cell constant

K_m = measured value of calibration standard

K_t = theoretical value of calibration standard at 25 °C

S_c = temperature and blank corrected specific conductance of QCCS

S_m = measured value of QCCS

T = temperature correction factor

Dissolved Inorganic Carbon

Introduction

The DIC concentration of water samples was measured for all surveys. DIC measurements, in combination with pH measurements, provide an indication of the relative buffering capacity of aquatic systems. Samples were collected in syringes to prevent CO_2 exchange between the sample and the atmosphere (Burke and Hillman, 1987). A Dohrmann/Xertex (DC-80) carbon analyzer was used for the infrared spectrophotometric measurement of DIC.

Methods

Sample syringes were stored at 4 °C until DIC analysis. The DIC method is detailed in Hillman et al. (1986). Samples were filtered using disposable 0.45-μm pore size syringe filters. A 2-mg/L C DIC standard was used as a QCCS and a 10-mg/L C standard (prepared from a separate stock solution) was used for the calibration procedure. The stock solutions were 1000-mg/L C solutions prepared from reagent grade Na_2CO_3 dried at 110 °C for 2 hours. A deionized water blank was analyzed each day. QC requirements are presented in Section 3. Increasing the maximum QCCS interval from one analysis every eight samples to one analysis every ten samples before summer processing was the only procedural change. A DIC method flowchart is illustrated in Figure 5.

Results

A control chart for the 2-mg/L C QCCS is presented in Section 5, Figure 14. The QCCS statistical results are presented in Table 13. FN audit sample results for DIC analysis are presented in Table 15 and Figure 16.

Discussion and Recommendations

A batch of 20 samples required three hours to analyze. With two to four batches arriving each day during the spring surveys, two carbon analyzers were run simultaneously. Several batches were cross-checked using both carbon analyzers, and the values were found to be within 10% of each other. Each
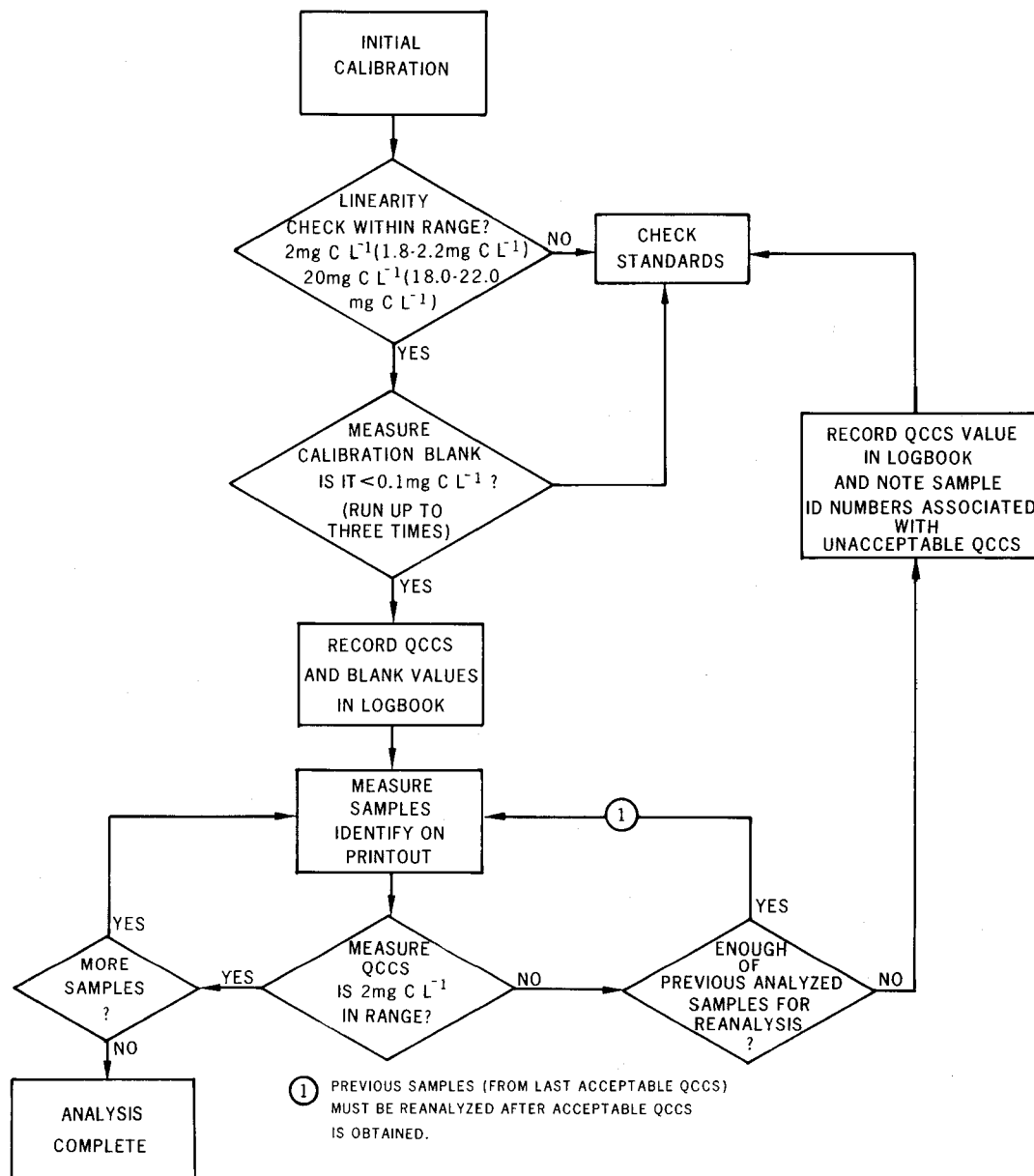
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Figure 5. Flowchart for dissolved inorganic carbon analysis.

batch was analyzed using only one carbon analyzer to minimize within batch variability (i.e., a batch was never split and analyzed using two instruments.)

Due to the long storage time before the beginning of the laboratory operations in 1986, several instruments had to be returned to the manufacturer for servicing. Problems discovered by the manufacturer included unoiled air pumps, soiled permeation driers, and plugged flow restrictors. Weekly and monthly maintenance procedures were established (Table 11). A complete check-out of each instrument should be performed before laboratory operations begin, and a detailed maintenance record should be kept.

When the trailers were located in the field, inside and outside gas regulators were used to control carrier gas flow to the carbon analyzers. It was convenient for analysts to control the gas flow from within the trailer in the field, but the extra fittings increased the possibility of gas fluctuations. When gas leaks were discovered, recalibration and reanalysis of samples was necessary. The inside N_2 regulators were removed when laboratory operations were consolidated eliminating the extra gas fittings.

During the spring surveys an area-wide power failure interrupted the analysis of samples. Samples were processed the following day and the data were qualified (flagged). Reserve power units were installed in the processing laboratory as a precaution against loss of instrument memory and calibration in the event of future power failures. The reserve power units could maintain a minimal power supply for one to three hours.

The decision to increase the maximum QCCS analysis interval after spring processing was based on the accuracy and precision of the 2-mg/L C QCCS (Figure 14) and results from all previous surveys.

Aliquot Preparation

Introduction

A set of seven aliquots was prepared from each Cubitainer. The samples were required to be processed within 24 hours from the time of collection. The parameter to be measured at the analytical laboratory (Table 9) dictated how samples were prepared and preserved at the processing laboratory.

Methods

A set of aliquots was prepared from each Cubitainer bulk sample (Hillman et al., 1986). The preparation techniques, order of priority, and chemical parameters measured at the analytical laboratory for each aliquot are presented in Table 9. Analytical methods used by the contracted analytical laboratories and sample holding times are presented in Hillman et al. (1986).

For ELS-II seasonal studies, an additional split sample was prepared for trace metal analysis by graphite furnace atomic absorption spectrophotometry at Indiana University (Bloomington, Indiana) under the direction of Dr. J. White. The preparation of this split is outlined in Table 9.

In preparation for shipment, each aliquot was sealed with electrical tape and individually placed in a plastic bag tied with a twist-tie. All aliquots for each sample (except the extractable aluminum aliquot) were placed in a one-gallon Ziploc bag. Samples were shipped in coolers with frozen chemical refrigerant packs. Extractable aluminum aliquots were shipped in a separate shipping cooler with frozen chemical refrigerant packs. Details regarding the shipment of extractable aluminum aliquots are discussed in the Extractable Aluminum discussion of this section. The sample shipping form (Appendix D, Figure D-2) was completed and distributed as described in the Sample Organization discussion of this section.

The summer seasonal survey included special projects particular to temperate lake stratification conditions. The sample organization and analyses of preserved hypolimnetic, chlorophyll, and zooplankton samples are discussed in the Sample Organization discussion of this section and Table 4. Two additional split samples were prepared at the processing laboratory during ELS-II, the summer seasonal study: a total nitrogen and phosphorus sample and a triplicate sample.

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Table 9. Aliquot Preparation

Aliquot	Processing	Container volume	Preservation acid	Chemical parameters measured	Priority order
1	Acid, filtered	250 mL	HNO_3	Metals (Ca, Fe, K, Mg, Mn, Na)	4
2	Acid, filtered	15 mL	None	Extractable Al	3
3	No acid, filtered	250 mL	None, no headspace	Cl^-, F^-, NO_3^-, SO_4^{2-}, SiO_2	2
4	Acid, filtered	125 mL	H_2SO_4	Dissolved organic carbon, NH_4^+	6
5	Unfiltered	500 mL	None, no headspace	Acid/base neutralizing capacity, conductivity, dissolved inorganic carbon, pH	1
6 ELS-II, SVS-P	Unfiltered	125 mL	H_2SO_4	Total P	7
6 NSS-I	Acid, filtered	125 mL	H_2SO_4	Total dissolved P	7
7	Unfiltered	125 mL	HNO_3	Total Al	5
Split, ELS-II	Acid, filtered	15 mL	HNO_3	Trace metals (Cd, Cu, Ni, Pb, Mn)	8

1. Total nitrogen and phosphorus split

Description: Unfiltered, 125-mL, H_2SO_4 preserved, stored in specially prepared HCl-washed containers; shipped to EMSL-LV the following day. The samples were analyzed using a colorimetric FIA method.

2. Triplicate sample for interlaboratory bias experiment

Description: One set of aliquots (1 and 3-7, listed in Table 9) shipped daily with the routine batch; one set of half-sized aliquots (1 and 3-7) shipped daily with the bias batch to a separate analytical laboratory.

Aliquot labels used for the 1986 surveys are represented in Appendix D, Figures D-3 and D-4.

Results

The batch series, total number of batches, analytical laboratories used, and sample types processed are listed in Table 10. A total of 3,377 samples were processed.

Discussion and Recommendations

During the spring surveys, as many as seven analysts were assigned to filtration; a team of two analysts assumed all preservation responsibilities. In subsequent surveys, the batch sizes dictated that one to three analysts were needed to filter samples. One additional analyst was assigned to preserve the aliquots. Each analyst assigned to filtration could process a maximum of 15 samples per day.

Stream samples usually filtered slowly. The use of two-stage filtration units might speed up future large-scale operations. These units, which employ a coarse filter in addition to the fine filter that was used, would eliminate excessive filtration times.

During the spring surveys, three blank samples were contaminated with nitric acid. This was attributed to contamination between acid-washed and non-acid-washed filtration units. A plastic barrier was constructed and used to separate acid and non-acid filtration units in subsequent surveys.

Table 10. Processing Summary

	Spring Variability Pilot Study	National Stream Survey Phase-I	Eastern Lake Survey-PhaseII-Seasonal Studies				
			Snowpack Study	Spring	Summer	Bias Experiment-Summer	Fall
Batch series	3000	2100	4000	3500	3600	3650	3700
Number of batches	17	68	20	29	17	17	26
Analytical Laboratories[a]	PBS & J, Versar	NY State, Global	EMSI	PBS & J, Versar	PBS & J	Versar, PBS & J	Versar
Routine	128	1,395	277	146	295	26	239
Duplicate	18	65	51	29	31	-	26
Audit	27	134	20	43	44	20	93
Blank	30	68	86	29	25	2	30
Total	203	1,662	434	247	395	48	388

[a]PBS & J = Post, Buckley, Schuh, and Jermigan, Inc (Orlando, Florida)
Versar (Alexandria, Virginia)
NY State = New York State Department of Health (Albany, New York)
Global = Global Geochemistry Corporation (Canoga Park, California)
EMSI = Environmental Monitoring Services, Inc. (Thousand Oaks, California)

For the first part of the spring surveys, the aliquots were not always refrigerated for one hour prior to the taping of the lids, which was the procedure for the earlier surveys. This was due to the high number of samples encountered and the overnight courier deadline of 3:30 p.m. each day. The analytical laboratories reported that a few of the aliquot bottles had leaked during shipment. To alleviate this problem, the aliquots were stored at 4 °C for at least one hour before the lids were taped, minimizing the expansion and contraction of the bottle seal.

Due to the uncertainty of the weather conditions in the field, weekend sample processing was frequently necessary. Because the overnight courier did not operate at full capacity on Sunday, samples processed on Saturdays were held by the courier for Monday delivery to the analytical laboratory. Samples processed on Sunday were shipped on Monday.

Extractable Aluminum

Introduction

An extractable aluminum procedure using MIBK was used to determine aluminum concentrations in natural waters (Barnes, 1975). Sample aliquots were filtered, mixed with an 8-hydroxyquinoline/sodium acetate reagent (HOx), and buffered with ammonium acetate to a pH of 8.3. At this pH, dissolved aluminum species complexed with the HOx in solution. These complexes were extracted from the mixture by adding MIBK. The complex was transferred to the organic layer by agitation, then was removed by pipet. The prepared aliquots were shipped daily to the analytical laboratories for analysis by graphite furnace atomic absorption spectroscopy.

Methods

Extractable aluminum samples were collected in syringes by the field crews. The syringes were held at 4 °C until preparation. The method for extractable aluminum using MIBK is presented in Figure 6. The prepara-
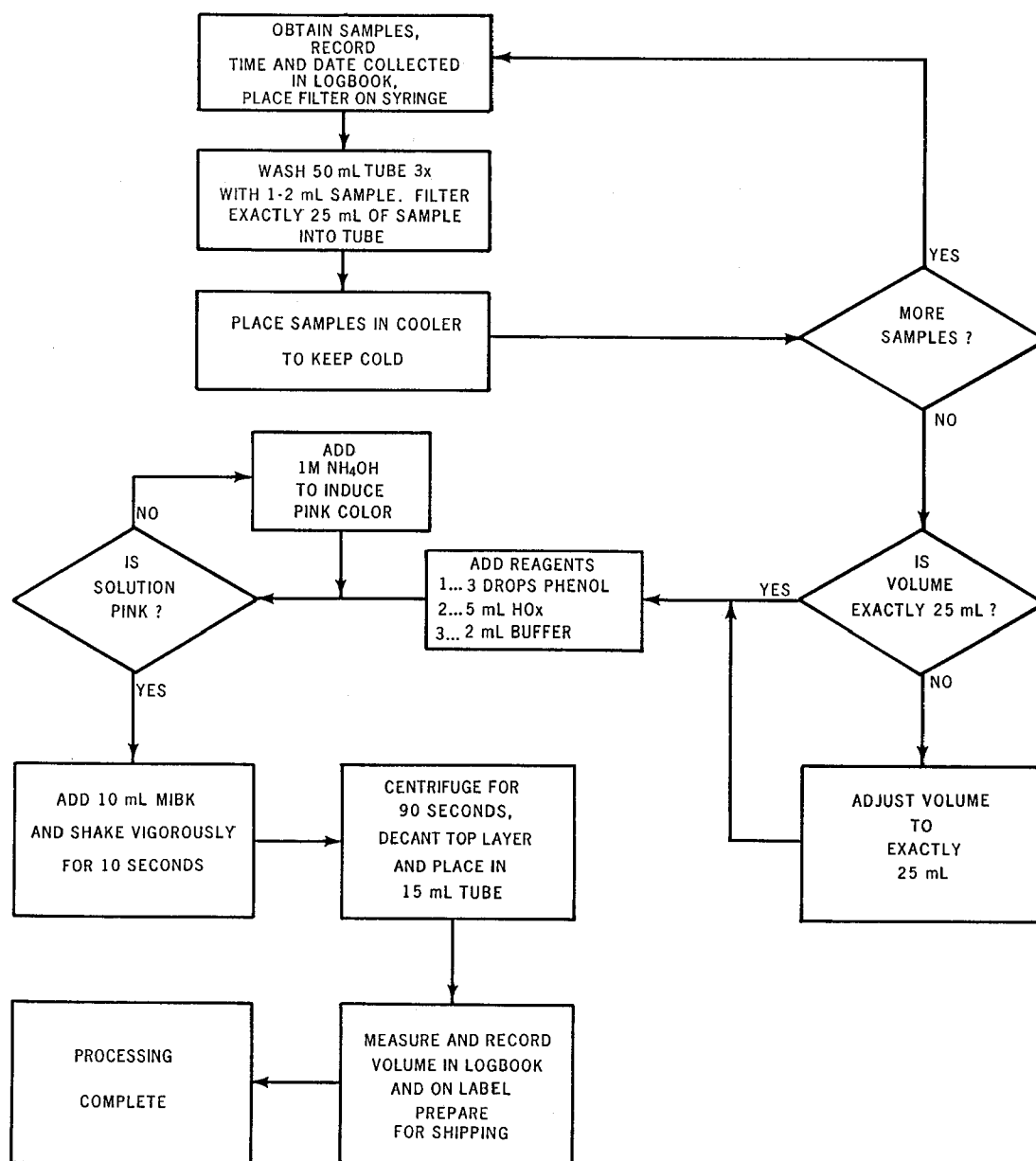
Figure 6. Aluminum extraction method flowchart.

tion techniques and the priority of this aliquot are presented in Table 9 (Aliquot 2). A calibrated photoionization detector was used to monitor organic vapor (MIBK) levels in the trailer. Personnel who performed extractable aluminum analyses were required to wear respirators. Method changes for the 1986 surveys are described below:

- Samples were filtered from the syringe into 50-mL centrifuge tubes using acid-washed syringe filters instead of obtaining a portion of filtered samples from aliquot 1.

- Glacial acetic acid was used in place of hydrochloric acid for the buffer preparation.

- Analysts wore two pairs of gloves when handling MIBK as an added safety precaution.

- The extractable aluminum aliquots were shipped to the analytical laboratory separately.

Discussion and Recommendations

Glacial acetic acid was substituted for hydrochloric acid in the buffer solution because chlorine and ammonia contamination was detected by the analytical laboratories in the blank samples. This was attributed to the fuming characteristics of the buffer solution during preparation using hydrochloric acid.

To guard against leakage during sample shipment to the analytical laboratory, the 15-mL centrifuge tubes were taped lengthwise with electrical tape. Special Styrofoam carriers were fashioned to hold tubes upright during shipment. These aliquots were packaged in a separate cooler.

Analysts' technique was a major source of variability in the recovery of extractable aluminum. The performance of each analyst was tested prior to the survey and the percent recovery of spiked samples was reviewed. When possible, one or two operators were assigned to prepare this aliquot throughout a survey.

Preparation (including acid-washing) of 20 syringe filters required one analyst approximately one hour. For previous surveys, a filtered portion of sample was obtained during the preparation of Aliquot 2 (Table 9) in order to prepare the extractable aluminum aliquot. This eliminates the need for filter preparation and the additional filtration from the syringe. Since the extractable aluminum aliquot would be prepared from the Cubitainer bulk sample, one less syringe per sample would be collected in the field.

Though the extractable aluminum procedure proved a reliable method for measurement of aluminum concentrations when prepared by a single analyst, the FIA-aluminum method provides more specific information concerning particular aluminum species. Because a reliable FIA-aluminum method has been developed, we recommended that the extractable aluminum method be eliminated. Sole use of the FIA method provides specific aluminum species data, reduces contract laboratory costs, and substantially reduces the volume and handling of hazardous waste in the laboratory.

Color and Turbidity

Introduction

Color in natural waters has been closely correlated to the amount of dissolved organic carbon. Dissolved organic compounds may act as chelators for metals such as aluminum. True color was measured using a Hach CO-1 color determination kit, in which a color disc was rotated over the blank until the color matched the sample color. The results were expressed as American Public Health Administration platinum-cobalt (PC) units.

Turbidity, a measure of suspended organic and inorganic material in the water column, affects light transmission. The nephelometer projects an optical beam through the unfiltered sample contained in a special optical cuvette. Particulate matter in the sample scatters the light which is then measured with a photodetector. The digital readout, in nephelometric turbidity units (NTU), is a measure of the concentration of the particles in the solution.

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Methods

Methods for true color and turbidity are documented in Hillman et al. (1986). The applicable range of the Hach color determination kit is 0-500 PC units. A number of NSS-I samples had color values exceeding 500 PC units and required the development of a high-range color procedure. The analyst decanted the sample and the deionized water blank to the 5-mL mark on the color tube and added 5 mL of deionized water to the sample tube. The sample and the deionized water were mixed thoroughly, and the volume was reduced to 5 mL using a disposable pipet. The color value was read using the procedure for samples with color values between 100 and 500 PC units. The value was multiplied by ten and recorded with a comment on how the final color value was determined.

Figure 7 illustrates the turbidity method. A 5 NTU standard was used as a QCCS; a 10 NTU standard was used as a calibration standard. The linearity of the nephelometer was checked using 2, 5, and 20 NTU standards. The maximum QCCS interval was increased from one analysis every eight samples (spring) to one analysis every ten samples (summer and fall).

A matrix-corrected dilution equation for high turbidity (>200 NTU) samples was modified from Hillman et al. (1986). Analysts poured 25-30 mL of filtered sample into a cuvette and measured turbidity. Unfiltered sample (5 mL) was added to a 50-mL centrifuge tube with 45 mL of filtered sample and mixed thoroughly. Analysts poured 25-30 mL of the diluted sample into a cuvette and the turbidity was measured using the standard
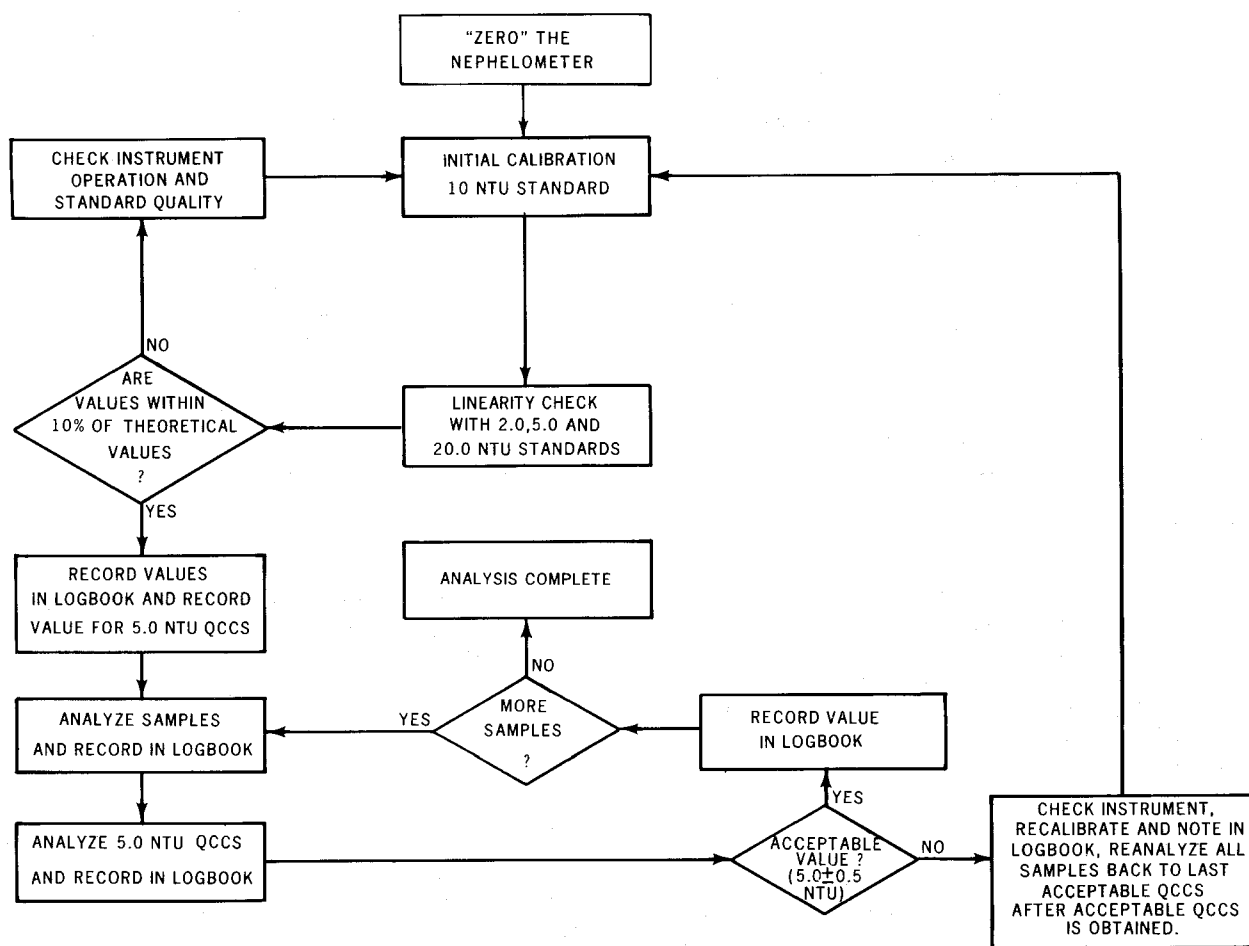
Figure 7. Flowchart for turbidity method.

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protocol. The final turbidity was calculated using the following equation:

$$\text{Actual turbidity} = 10 \left[\cfrac{\text{Turbidity of diluted sample}}{10} \right] - 9 \left[\cfrac{\text{Turbidity of filtered sample}}{10} \right]$$

High-range samples were reanalyzed at the end of the batch with the appropriate QCCS measured before and after the high-range samples. Samples with turbidity values ranging from 20-50 NTU required the use of a 20-NTU QCCS; sample values ranging from 51-175 NTU required the use of a 50-NTU QCCS; values ranging from 176-199 NTU required the use of a 175-NTU QCCS.

Discussion and Recommendations

High-range methodology for both the color and turbidity procedures was developed.

The decision to increase the maximum QCCS interval for turbidity before the summer survey was based on the high precision of the 5-NTU QCCS during previous surveys. A further extension of the maximum QCCS interval to include an initial check, a mid-batch check, and a final check independent of batch size is recommended based on previous results.

Equipment Maintenance

The laboratory staff performed regular maintenance on all instruments and the water systems one day per week.

Methods

Appendix A provides a list of instruments, equipment, and supplies used by the processing laboratory. A list of weekly maintenance is presented in Table 11. All maintenance procedures were recorded in logbooks. Records for all refrigerators, freezers, and water systems were kept in daily logs.

A reverse osmosis (RO) system provided Type I reagent grade water (ASTM, 1984) in each trailer. Due to the poor quality of the Las Vegas feedwater, these systems required frequent upkeep. Cartridge replacement and system maintenance were done as directed by the water system instruction manuals. A Milli-RO water purification system which included the RO membrane was employed. A polishing system (Milli-Q) was used to produce the high quality water required for processing. A complete water system was composed of both a Milli-RO and a Milli-Q unit.

Table 11. Equipment Maintenance

General Weekly Maintenance--
- Check balance, pipet, and Repipet calibrations.
- Check inventory and restock trailers.
- Change water in eyewash stations.
- Check all emergency showers and fire extinguishers.
- Replace prefilters of the water systems.

Method Weekly·Maintenance--
- Turbidity - Repour all standards.
- Filtration - Soak filtration units.
- pH - Drain and refill electrodes.

- DIC - Change all pump tubing.
  - Refill tin scrubbers and reaction vessels.
  - Prepare reagents and stock solutions.
  - Check scrubber line cartridges.
  - Perform detection limit check.

- Extractable aluminum - Check organic vapor meter calibration.
  - Prepare reagents as needed.
  - Check calibration of Repipets.

- FIA-aluminum - Replace pump and Teflon tubing.
  - Clean flow cells and rotary valves.
  - Prepare reagents as needed.
  - Download data files.[a]
  - Perform detection limit check.[a]

[a] These items should be incorporated in the future but were not done during these surveys.

Results

Analysis of the incoming feedwater supply to the warehouse showed that the conductivity was 1,072 μS/cm and the hardness (as $CaCO_3$) was 336 mg/L.

Discussion and Recommendations

We recommend that a day be set aside each week for scheduled maintenance only. Changes in the sampling itinerary due to poor weather conditions did not always permit a scheduled maintenance day. Performing maintenance while samples are being processed should be avoided.

Type I reagent water has a resistivity value 16.67 MΩ·cm (0.06 μS/cm) (ASTM, 1984). Large sample loads during the spring surveys created a high demand on the water systems. Individual cartridges had to be replaced frequently. A system could process approximately 300 gallons of water with a resistivity value of 18 MΩ·cm before losing its purification ability (approximately every two to three weeks with daily use). During the reduced demand of the summer survey, frequent (and expensive) cartridge replacement was still necessary to maintain operations because the one-year life expectancy of the RO membranes was near expiration. An unsuccessful attempt was made to preserve the old RO membranes at the completion of the ELS-II summer seasonal study. New RO membranes were installed in each system prior to the beginning of fall sampling. The systems performed successfully with minimal attention throughout the fall seasonal study.

The instruction manual for the RO membranes specified that the maximum conductivity of the feedwater should be no greater than 833 μS/cm. The Las Vegas feedwater conductivity value was measured at 1,072 μS/cm. This feedwater supply analysis shows that the Milli-Q ion-exchange cartridges were working under great stress to produce acceptable water. Instead of replacing all of the cartridges associated with both systems, only the Milli-RO prefilter and precarbon cartridges and the Milli-Q ion-exchange cartridges were replaced to obtain Type I water. This was a successful, cost-saving measure that resulted in minimal system "down time." It would be most efficient to rent or purchase some type of pretreatment system for either the incoming water line feeding the warehouse or for each trailer individually. Suggestions confirmed by the manufacturer included the use of a water softener or a large ion-exchange unit on the feedwater supply. Demand on the water systems, age of the RO membranes, and the composition of the incoming water affected the maintenance of the water systems.

Field Support

Introduction

Field support for NSWS sampling teams was centralized by combining the laboratory and warehouse operations. Field standards for conductivity and pH were prepared and shipped from the laboratory; field supplies were shipped simultaneously from the warehouse.

Methods

Standards and equipment were shipped according to a prearranged schedule. The communications center coordinated all shipping requests. Table 12 provides a list of all items shipped by the processing laboratory.

Table 12. Field Supplies

1 x 10^{-4}, 5 x 10^{-4}, 1 x 10^{-3} N KCl standards
1 x 10^{-4} N H$_2$SO$_4$ QCCS, pH 4, pH 7 NBS buffer solutions
3 M KCl
Deionized water
Frozen chemical refrigerant packs
Syringe containers
pH electrodes
Syringe valves
Shipping containers (coolers)

Conductivity and pH standards were prepared in 20-L carboy containers, then transferred to 4-L Cubitainers for shipping. Standards were packed in frozen chemical refrigerant packs and shipped in hard plastic coolers. Standards and deionized water were prepared as needed for the spring surveys. All summer and fall seasonal study standards were prepared before the survey began.

Laboratory personnel also prepared the following items for the summer survey:

- HCl-leached, 125-mL bottles for total nitrogen and phosphorus samples
- Deionized, water-leached, 2-L bottles for chlorophyll samples
- Deionized water-rinsed filters and 250-mL bottles spiked with HNO$_3$ for preserved hypolimnetic samples
- Buffered formalin solution for zooplankton samples
- Chlorophyll audit samples prepared from Lake Mead (Nevada)
- Field audits for preserved hypolimnetic and total nitrogen and phosphorus samples

Discussion and Recommendations

During the start-up phase of the spring surveys, the large demand for field supplies created a backlog of supply orders at the laboratory. Development of a weekly shipping schedule and additions to the laboratory staff alleviated the problem. Laboratory personnel assigned to supply the field teams operated on a second shift (1300-2100 hours) to more efficiently utilize laboratory space and available water systems. For the summer and fall operations, field standards were prepared before sample processing began and were refrigerated until needed.

Laboratory freezer space was limited. Commercial freezer space was rented during the spring surveys to freeze the large number of cold packs necessary for shipping standards and samples.

Snowpack

Introduction

The snowpack survey was designed and conducted by Dr. D. DeWalle of Pennsylvania State University in conjunction with ELS-II. The objectives of the survey were to determine the relationship between snowpack conditions and the extent and severity of episodic lake acidification and to examine snowpack spacial and temporal variation. Nine watersheds were sampled one time each to study snowpack spacial variability. Temporal variability sampling was conducted on two watersheds for a six-week period. The processing laboratory staff measured pH and DIC and prepared aliquots for shipment to an analytical laboratory.

Methods

Snowpack sample processing differed from lake and stream sample processing in the following ways:

(1) Samples were equilibrated to room temperature.

(2) pH aliquots were poured from melt buckets into 50-mL centrifuge tubes and measured in an open system (i.e., no pH sample chamber).

(3) DIC sample syringes were drawn from the melt buckets.

(4) Cubitainers were filled with the remaining volume from the melt buckets. Analysts prepared aliquots 1, 3, and 5 as half-sized aliquots and aliquot 4. See Table 9 for aliquot descriptions.

(5) Two 50-mL trace metal split samples were prepared, preserved with HNO_3, and sent to Dr. DeWalle (Pennsylvania State University) for analysis.

Results

A tabulation of snowpack samples processed is presented in Table 10.

Discussion and Recommendations

Snowpack samples were scheduled to be processed before NSS-I samples arrived. Delays in the start-up of the processing laboratory resulted in a backlog of samples at Pennsylvania State University. Three batches were processed in March. QA personnel noted that the samples had not been organized properly (by sampling date) into batches before shipment and required that all samples be shipped to Las Vegas, stored in commercial freezer space, and properly organized into batches. Further processing was postponed until May. Once the frozen samples arrived at the processing laboratory, they were melted, processed, and shipped within one day and analyzed by the contracted analytical laboratory within the required holding time. The effect of storage on the frozen samples was not assessed.

Trial samples were shipped to Las Vegas to test snowpack protocols. The plastic bags containing the samples leaked during the melting procedure leaving inadequate sample volume for processing and analysis. The decision was made to ship samples to the laboratory in plastic bags, then transfer the samples to plastic buckets for melting.

Samples were processed in the following priority order when sample volumes were low: (1) pH, (2) DIC, (3) aliquots, and (4) splits.

For a batch of 20 samples, two hours were needed to wash 20 melting buckets; two hours were needed to transfer the samples from the plastic bags to the buckets; and 16-20 hours were required to melt the samples for processing the following day. Sample organization and aliquot preparation required an additional two hours. Processing time was minimal (two to three hours). The pH of the snowpack samples stabilized quickly (within five minutes) and samples filtered rapidly.

Snowpack sample processing was delayed until the samples were sorted properly and the NSS-I sample load stabilized. Once these problems were resolved, the flow of snowpack samples through the processing laboratory proceeded without incident.

Section 5

Results

Quality Control Check Sample Results

Analysis of the pH QCCS is presented in this section along with control charts for FIA-aluminum, conductivity, and DIC QCCS results. Table 13 summarizes the QCCS results. The verified results will be available in future QA reports.

pH

Figure 8 is a frequency distribution demonstrating the accuracy and precision of the 1×10^{-4} N H_2SO_4 QCCS based on 485 samples analyzed during the spring surveys of 1986. The mean pH value was 4.06, which was within QCCS limits of 3.90 to 4.10 pH units. The precision as two standard deviations was ± 0.05 pH units. The statistical comparability of electrodes used for these

measurements is given in Table 14 (Metcalf, 1987). A similar mean of 4.05 ± 0.04 (mean ± two standard deviations) was obtained for the ELS-II fall seasonal data (n = 52).

FIA-Aluminum

Figures 9 and 10 are control charts for the 75-μg/L Al QCCS for FIA-aluminum analysis. Figure 9 depicts channel 1 results and Figure 10 depicts channel 2 results. The CEC is not engaged so channel 1 and channel 2 both measure total monomeric aluminum. The control lines are drawn at values representing ±10% and ±20% of the mean. The statistical results are summarized in Table 13.

Conductivity

Control charts for the conductivity QCCS are presented in Figures 11 through 13. Three

Table 13. Quality Control Check Sample Results

Parameter	Survey	Quality control check sample	$\bar{X}$	Two standard deviations	n
pH (pH units)	Spring	1×10^{-4}N H_2SO_4	4.06	0.05	485
Flow injection analysis-aluminum channel 1 (μg/L Al)	Eastern Lake Survey-Phase II (summer)	75μg/L Al	74.5	6.16	34
Flow injection analysis-aluminum channel 2 (μg/L Al)	Eastern Lake Survey-Phase II (summer)	75μg/L Al	73.6	8.26	34
Conductivity (μS/cm)	National Stream Survey-Phase I	1×10^{-4}N KCl 5×10^{-4}N KCl 1×10^{-3}N KCl	15.5 74.2 146.3	1.58 3.92 6.58	78 78 78
Dissolved inorganic carbon (mg/L C)	Spring Variability Pilot Study	2 mg/L C	2.115	0.142	34

NOTE: These results have been calculated from the raw data which were input directly from the processing laboratory Batch/QC data forms (Appendix D, Figure D-1).
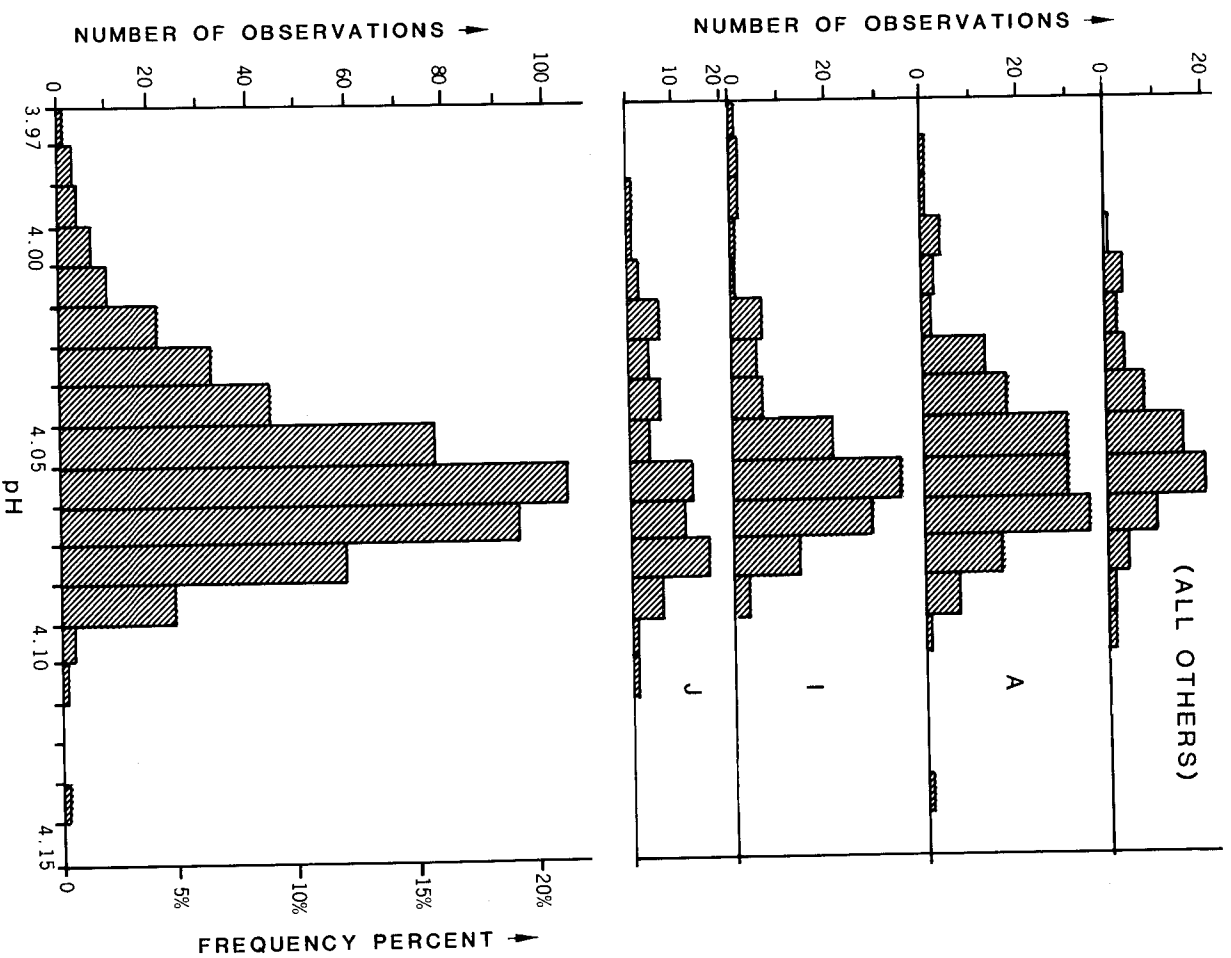
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Figure 8. Frequency distributions of the pH quality control check sample results.

Upper: Histogram of the 485 pH measurements grouped by electrodes A, I, J, and the six remaining electrodes (all others).

Lower: Histogram of 485 measurements of 1×10^{-4} N H_2SO_4 standard using nine different Ross pH combination electrodes (Metcalf, 1987).

Table 14. Descriptive Statistics of pH Quality Control Check Sample Frequency Distributions Grouped by Electrode (Metcalf, 1987)

Statistical variables	All electrodes	Electrode A	Electrode I	Electrode J	Remaining electrodes
n	485	171	141	92	81
$\bar{X}$	4.056	4.056	4.056	4.059	4.053
Standard Deviation	0.023	0.022	0.022	0.026	0.020
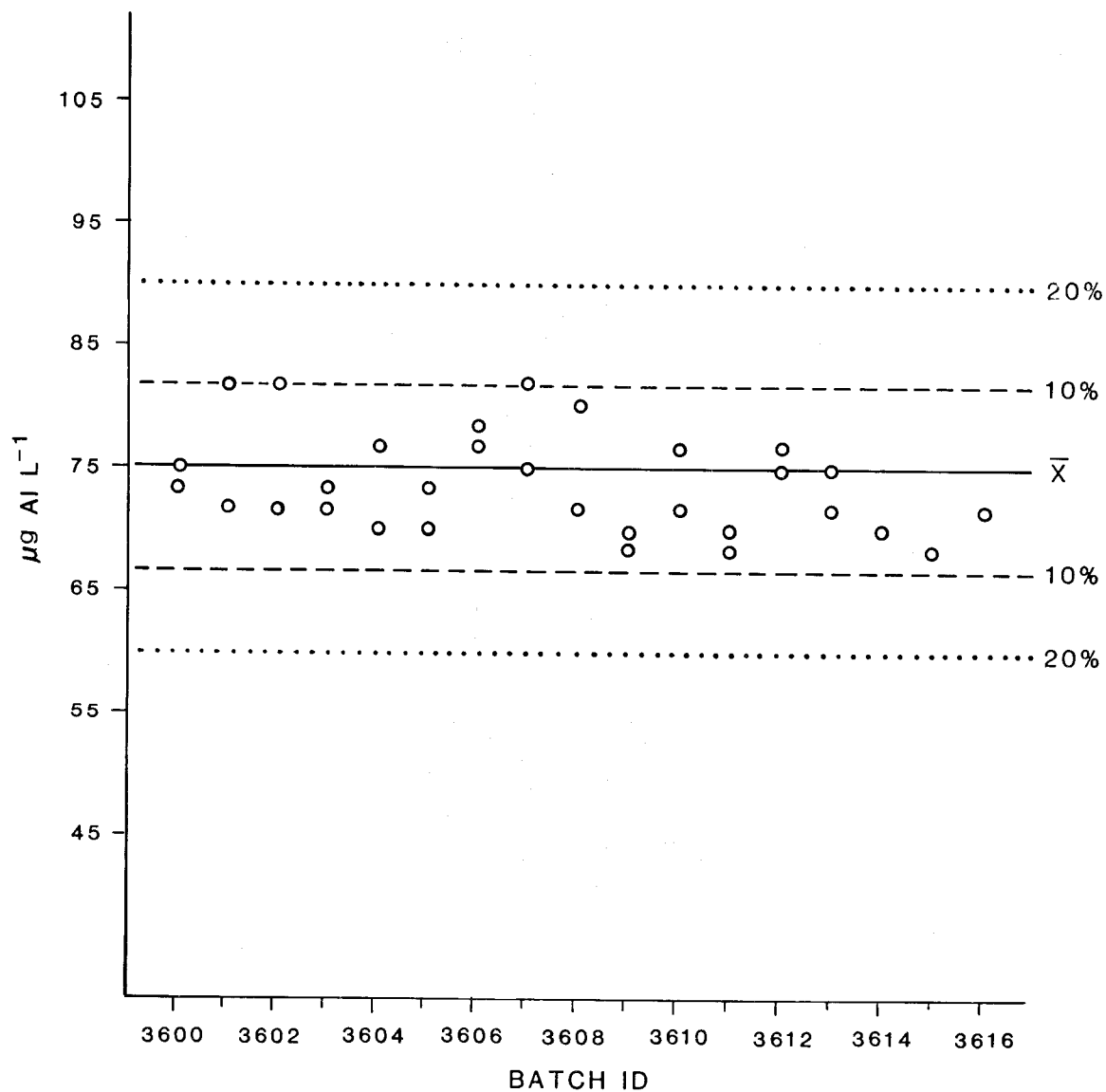
Figure 9. Control chart for flow injection analysis-aluminum quality control check sample (channel 1). 75-μg/L Al quality control check sample values versus Batch ID for the Eastern Lake Survey-Phase II (summer). Percent difference (%) from the mean ($\bar{X}$).
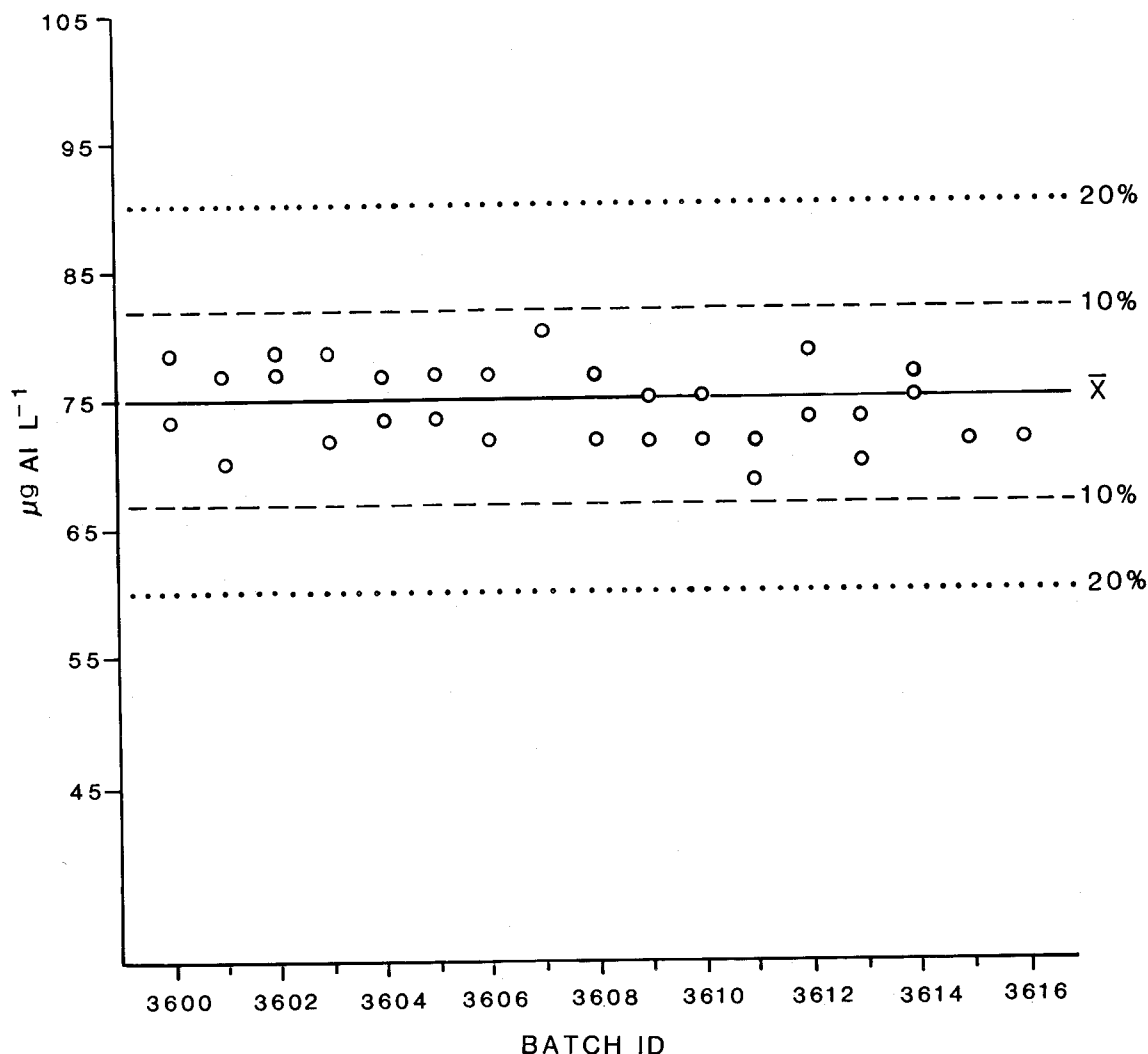
34

Figure 10. Control chart for flow injection analysis-aluminum quality control check sample (channel 2). 75-µg/L Al quality control check sample values versus Batch ID for the Eastern Lake Survey-Phase II (summer). Percent difference (%) from the mean ($\overline{X}$).

standards were used as QC solutions: 1 x 10^{-4}, 5 x 10^{-4}, and 1 x 10^{-3} N KCl solutions. The control lines are drawn at values representing ±5%, ±10%, and ±20% of the mean for the low conductivity standard and ±5% and ±10% of the mean for the medium and high conductivity standards. The statistical results are presented in Table 13.

DIC

Figure 14 is a control chart for the 2-mg/L C DIC QCCS with control lines drawn at values representing ±10% and ±20% of the mean. The statistical results are presented in Table 13.
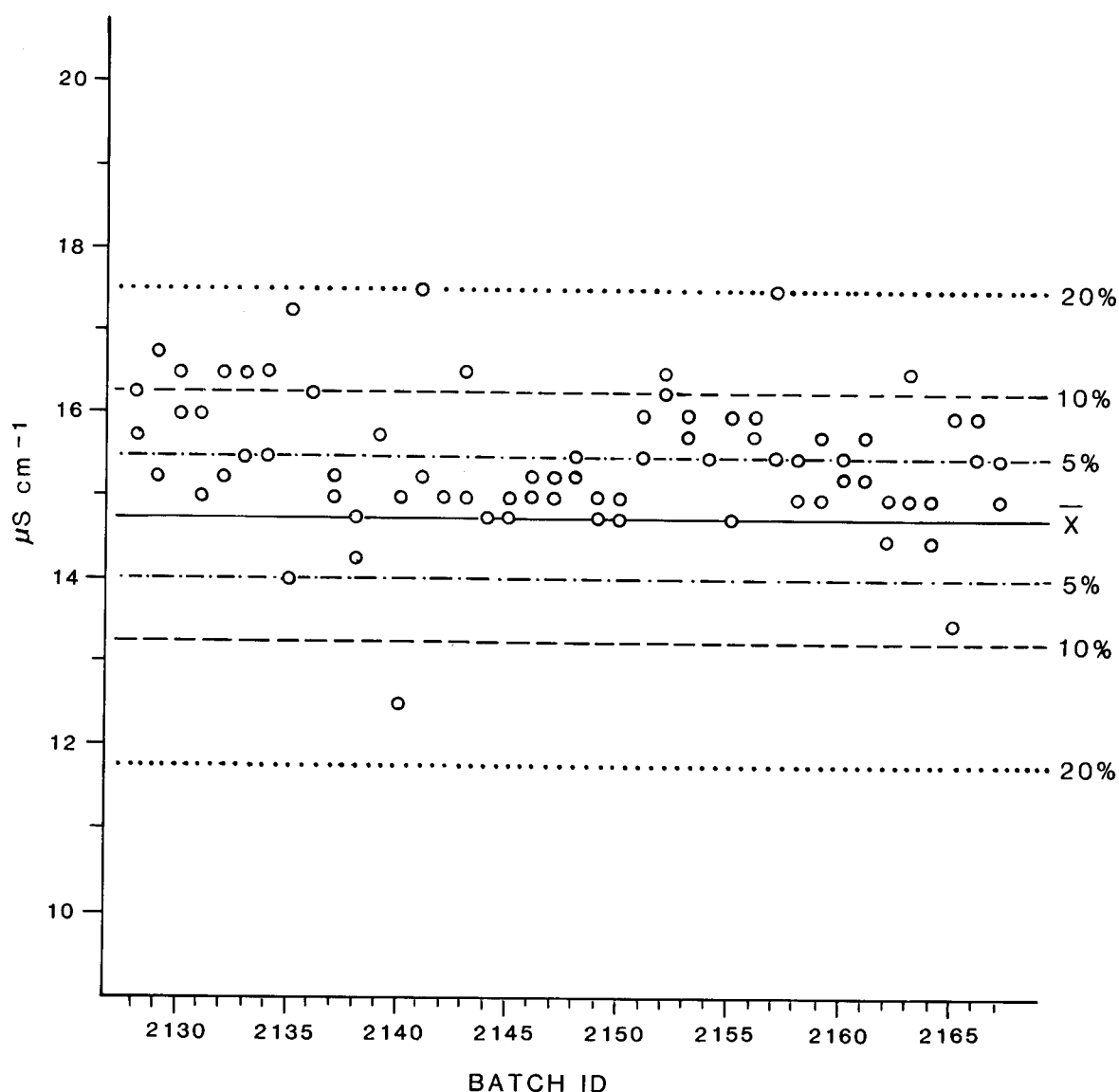
Figure 11. Control chart for 14.7-μS/cm conductivity control check sample (channel 2). Low quality control check sample values versus Batch ID for the National Stream Survey-Phase I. (Values corrected to 25 °C). Percent difference (%) from the mean ($\overline{X}$).

Natural Field Audit Sample Results

Several FN audit sample types were measured at the processing laboratory. These samples were collected, filtered, homogenized, and split into aliquots by Radian Corporation (Austin, Texas). FN-6, FN-7, and FN-8 audit samples were collected from Bagley Lake (Cascade Mountains, Washington), Seventh Lake (Adirondack Mountains, New York), and Big Moose Lake (Adirondack Mountains, New York). Sample codes are presented in Appendix D, Table D-1.
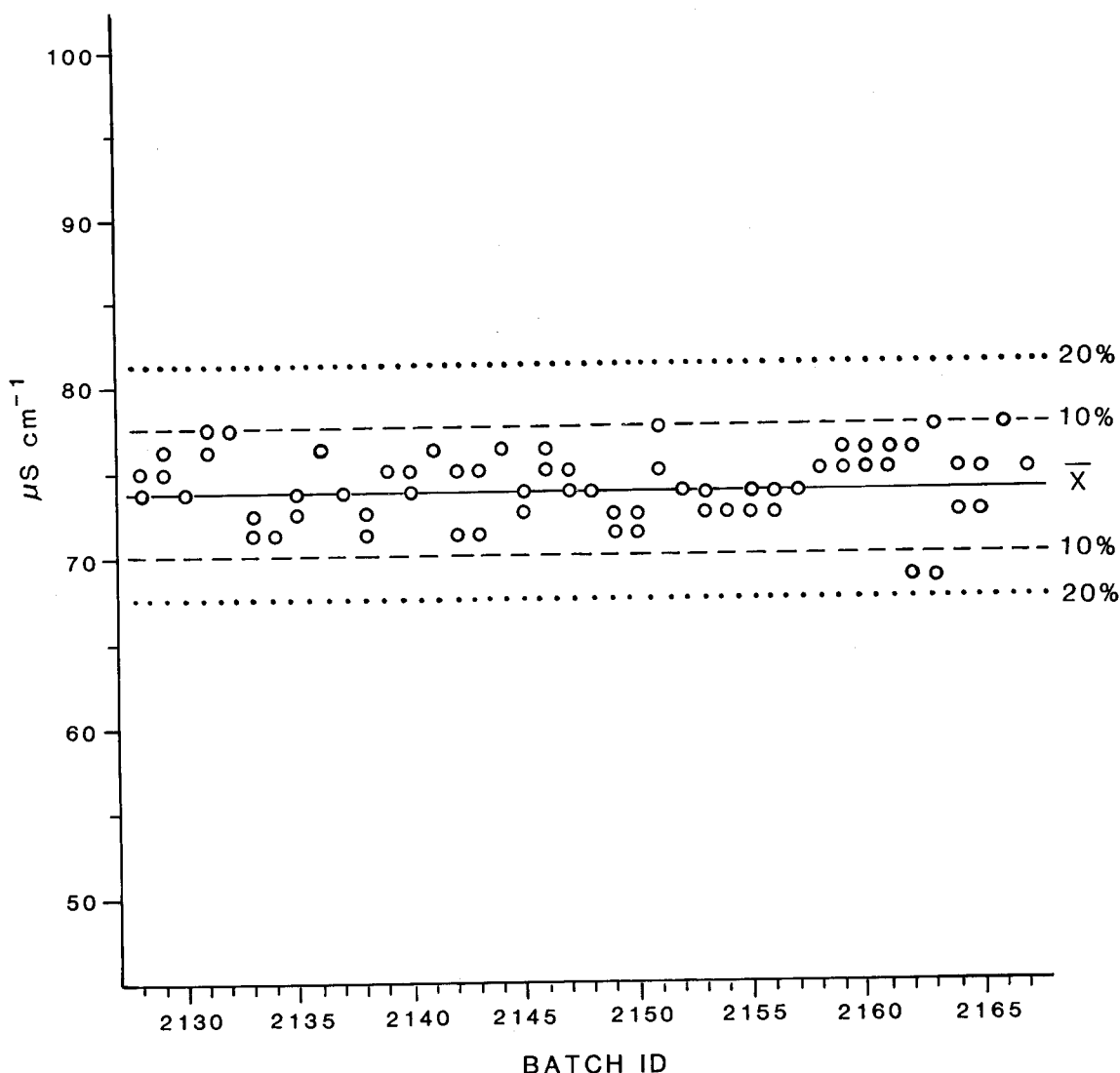
Figure 12. Control chart for 73.9-μS/cm conductivity control check sample. Medium quality control check sample values versus Batch ID for the National Stream Survey-Phase I. (Values corrected to 25 °C). Percent difference (%) from the mean (X̄).

Figures 15 and 16 are plots of the FN-7 and FN-8 audit sample results for pH and DIC for all surveys except the Snowpack Study (FN-7 was not used for NSS-I). FIA-aluminum audit sample results (FN-7 and FN-8) for ELS-II (fall) are presented in Figure 17. Table 15 includes summary statistics for the FN-7 and FN-8 samples analyzed for pH, FIA-aluminum, and DIC.

A distribution of results for the FN-6 audit sample is shown in Figure 18. There were 23 observations and the mean ± two standard deviations value was 15.7 ± 5.16 μS/cm. The faulty conductivity cell (discussed in Section 4) was replaced with a functioning cell before Batch 2130 was analyzed.
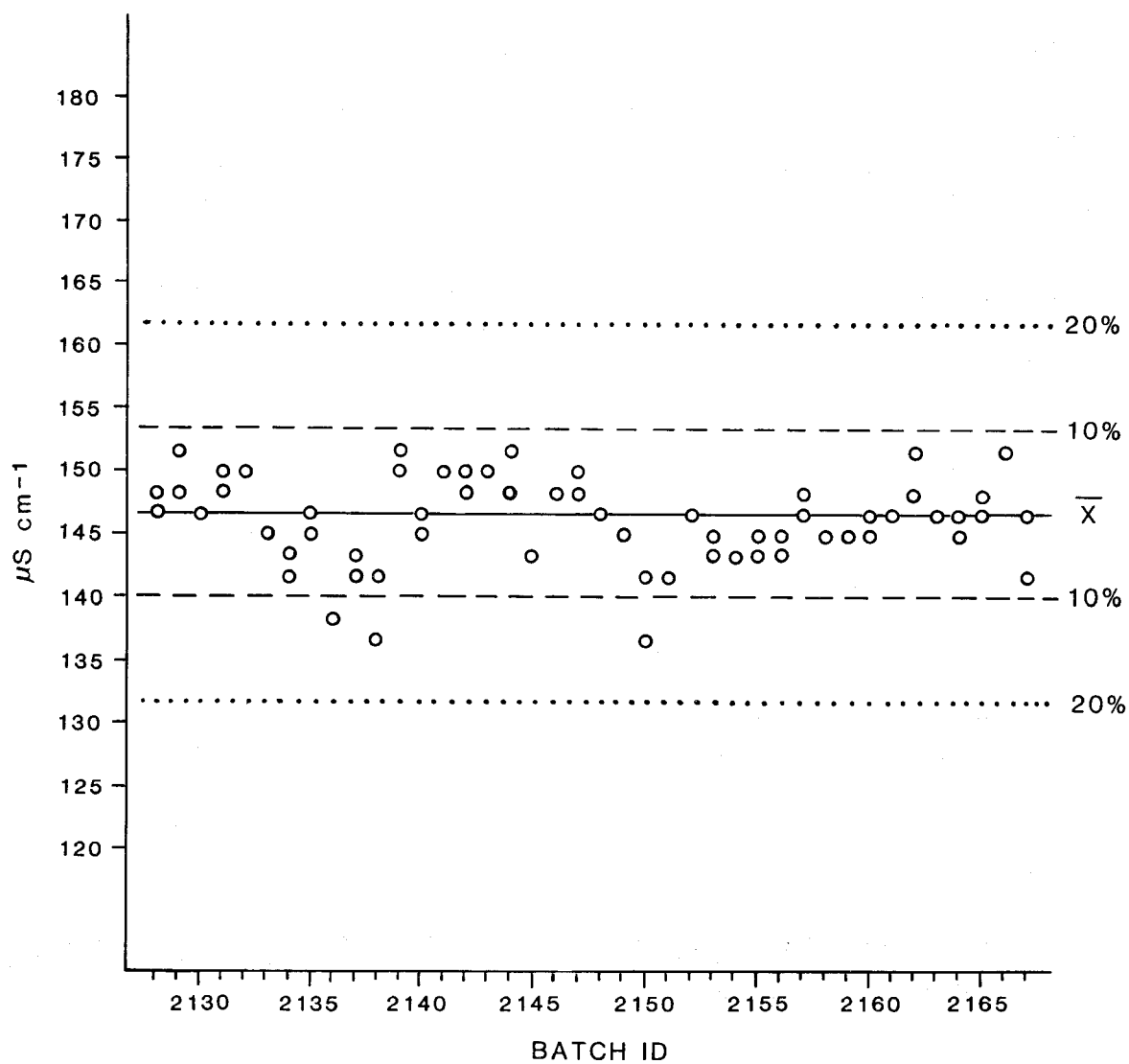
Figure 13. Control chart for 147.0-μS/cm conductivity control check sample. High quality control check sample values versus Batch ID for the National Stream Survey-Phase I. (Values corrected to 25 °C). Percent difference (%) from the mean (X̄).
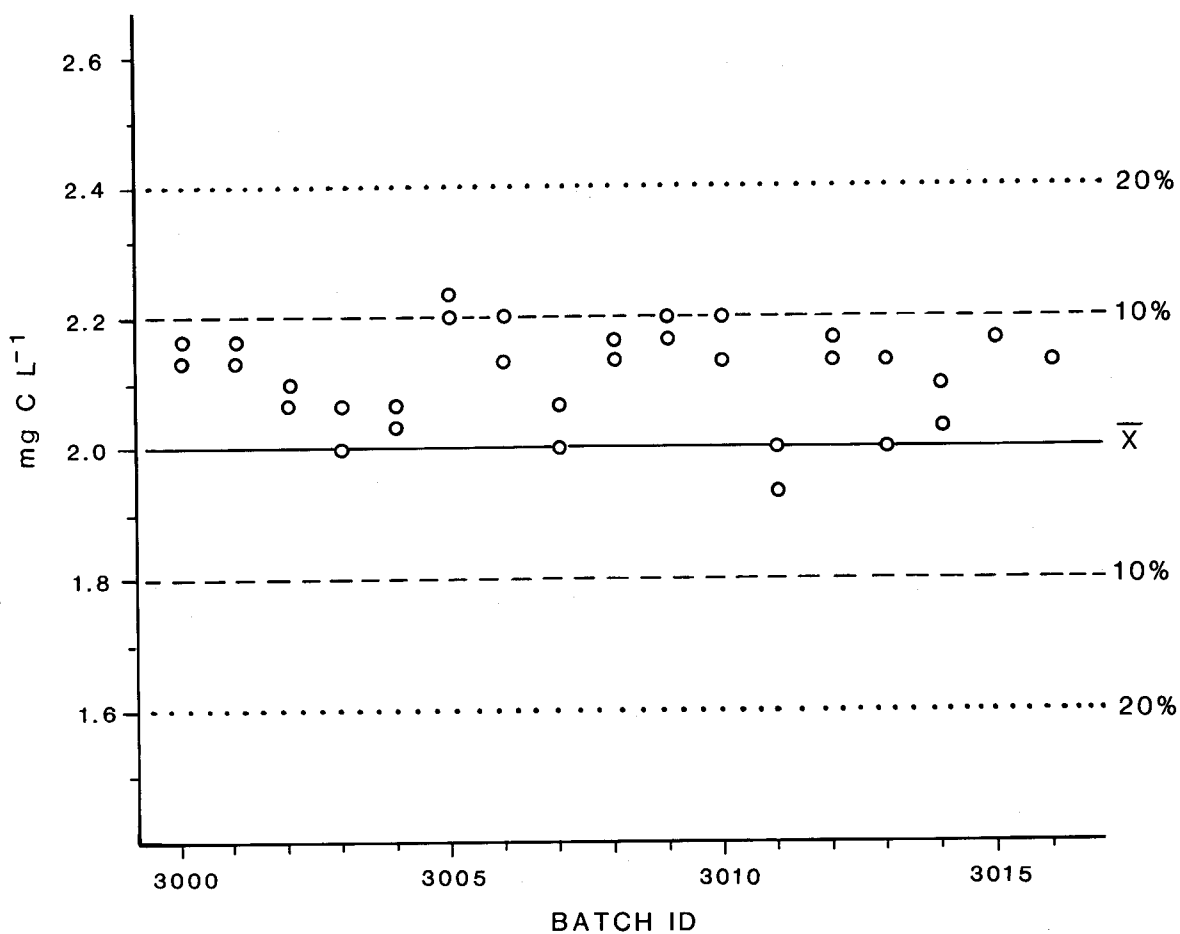
Figure 14. Control chart for dissolved Inorganic carbon quality control check sample. 2-mg/L C quality control check sample values versus Batch ID for the Spring Variability Pilot Study. Percent difference (%) from the mean ($\overline{X}$).
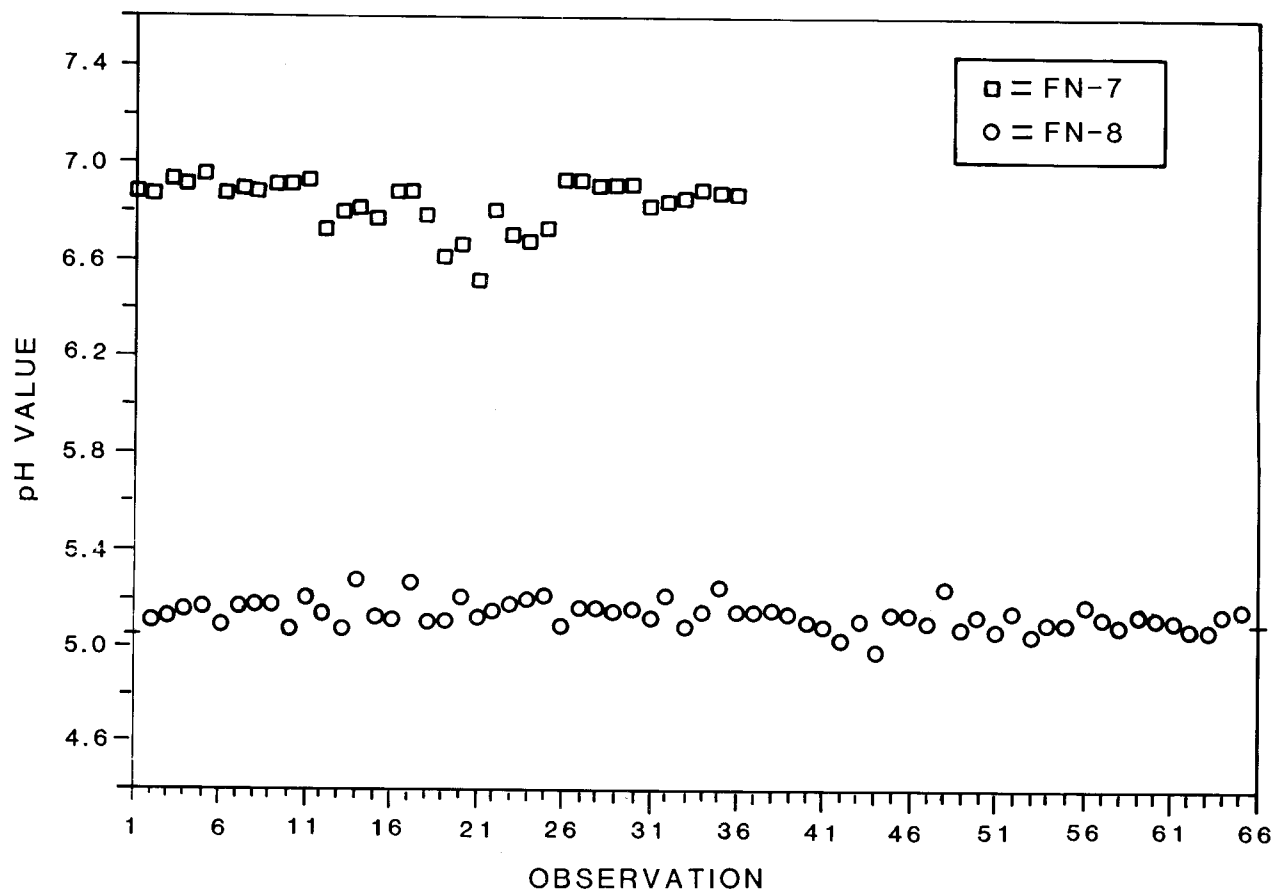
Figure 15. pH natural field audit sample results versus observation. FN-7 and FN-8 results for three 1986 spring surveys.
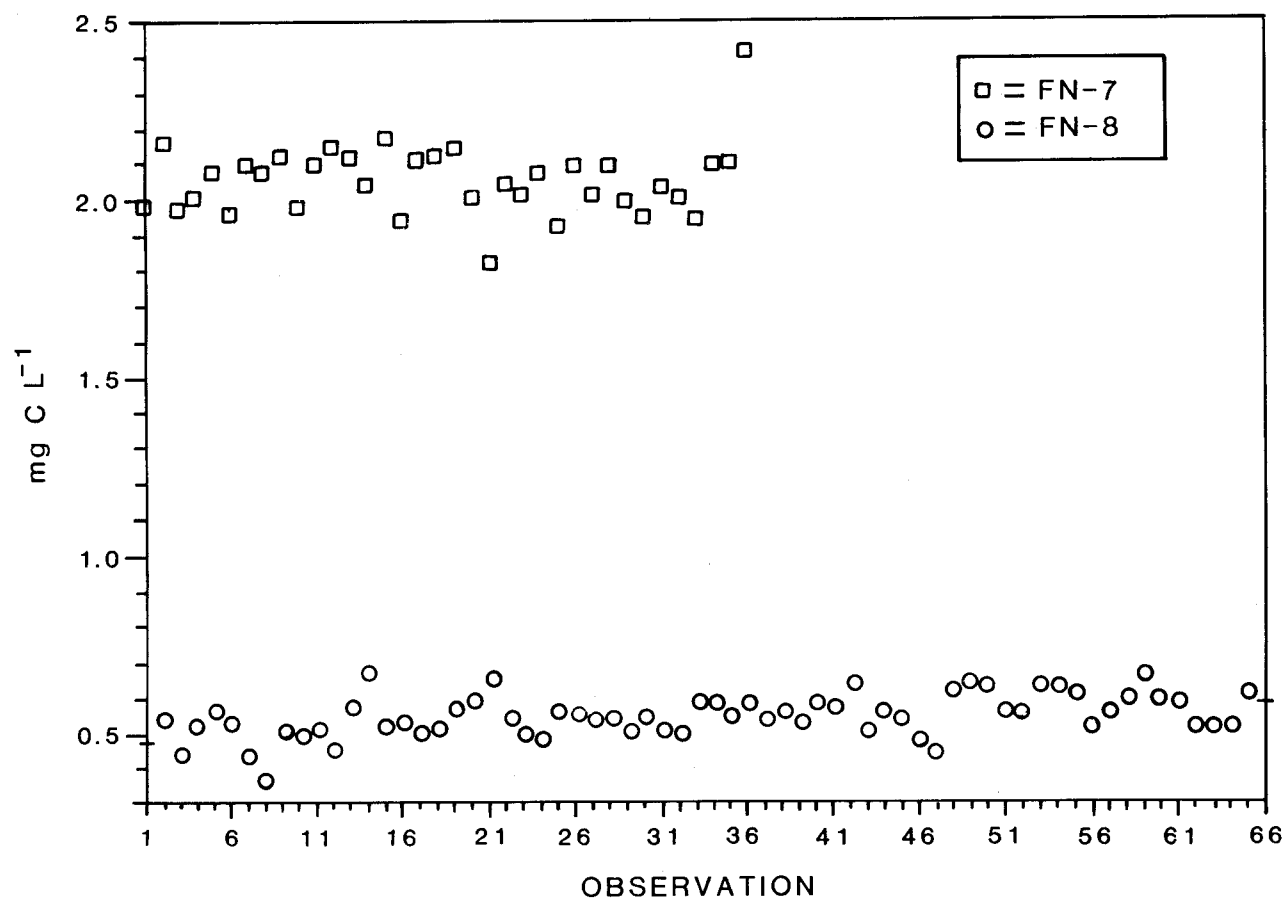
40

Figure 16. Dissolved inorganic carbon natural field audit sample results versus observation. FN-7 and FN-8 results for three 1986 spring surveys.
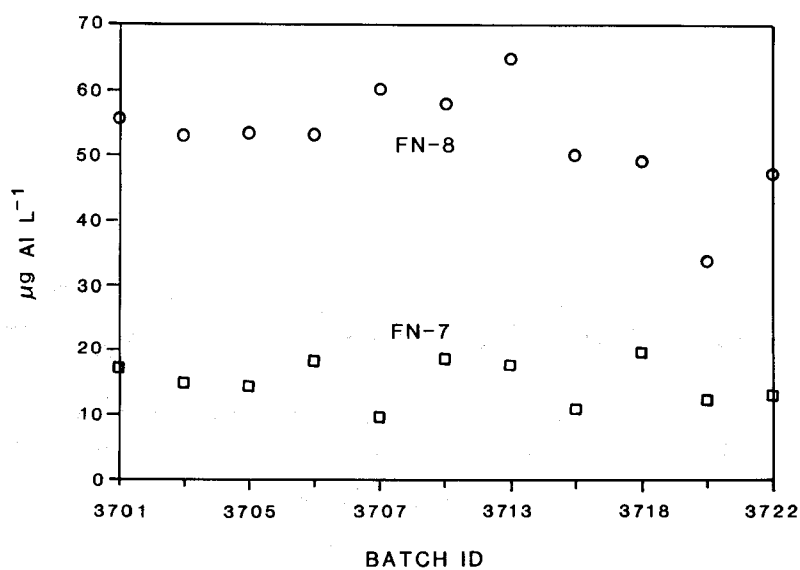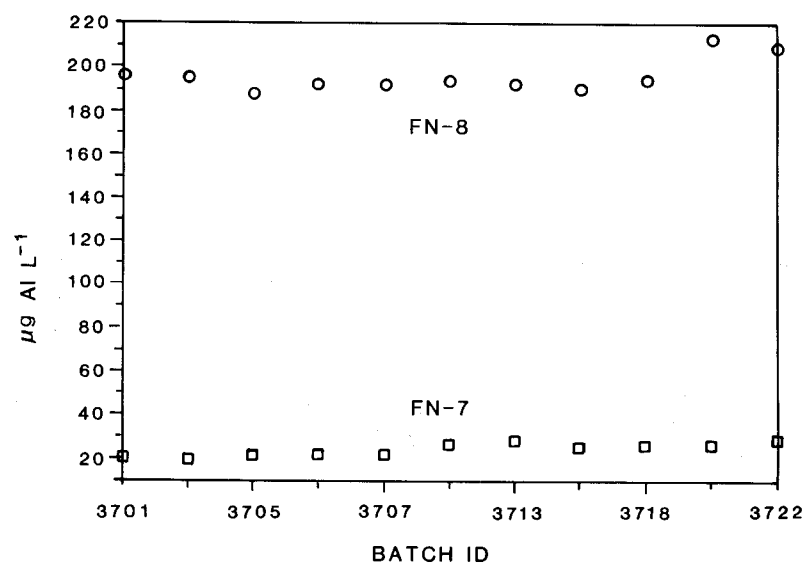
41

Figure 17. Flow Injection analysis-aluminum natural field audit sample results versus batch ID. FN-7 and FN-8 results for the Eastern Lake Survey-Phase II (fall).

Upper: Total monomeric aluminum (channel 1)

Lower: Organic monomeric aluminum (channel 2)

Table 15. Natural Field Audit Sample Results

| | | pH | Flow injection analysis-aluminum | | Dissolved inorganic carbon |
		All surveys except Snowpack	ELS-II (fall) μg/L Al total monomeric	ELS-II (fall) μg/L Al organic monomeric	All surveys except Snowpack mg/L C
FN-7	$\bar{X}$	6.83	24.6	15.3	2.023
	Two Standard Deviations	0.22	6.84	6.74	0.410
	n	33	11	11	37
FN-8	$\bar{X}$	5.13	196.3	52.5	0.551
	Two Standard Deviations	0.12	16.16	16.00	0.110
	n	68	11	11	68

NOTE: These results have been calculated from the raw data which were input directly from the processing laboratory Batch/QC data forms (Appendix D, Figure D-1).
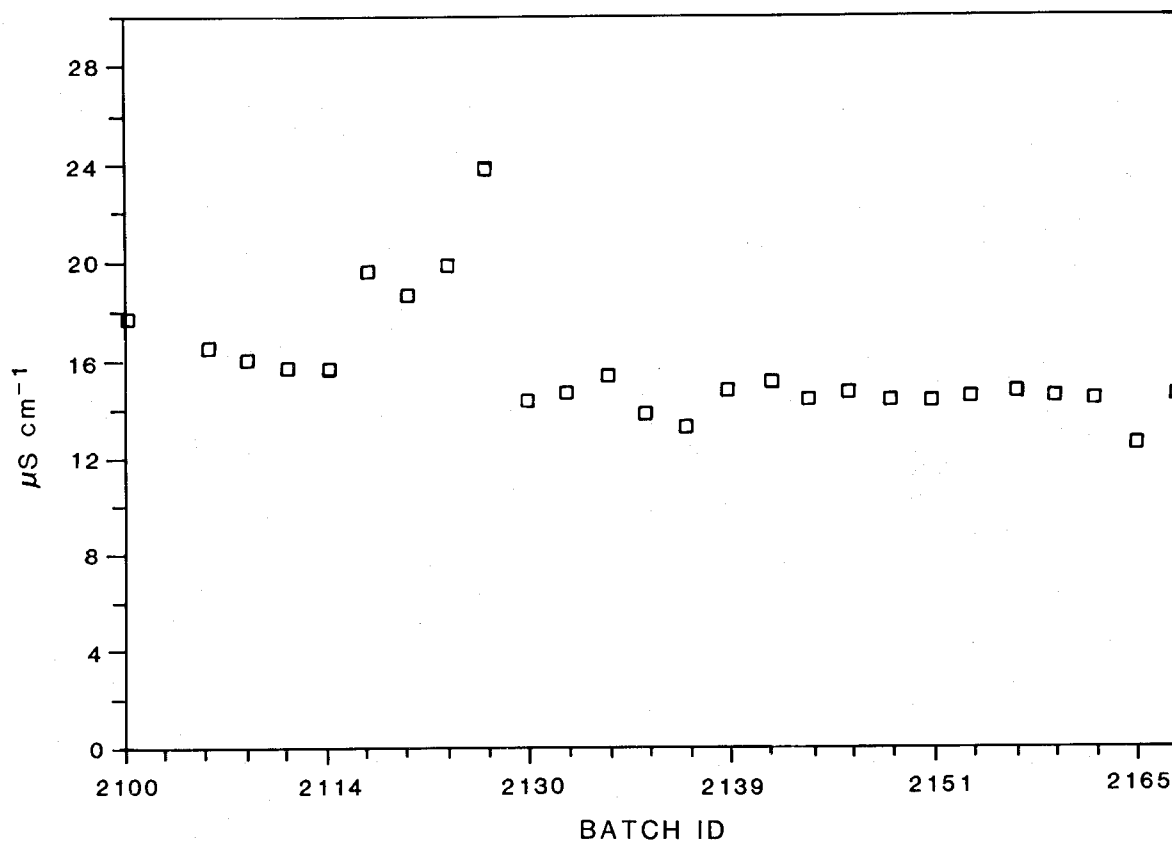

Figure 18. Conductivity natural field audit sample results versus batch ID. FN-6 results for the National Stream Survey-Phase I. (Values corrected to 25 °C.)

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Section 6

Conclusions and Recommendations

The NSWS processing laboratory located in Las Vegas, Nevada, successfully prepared and analyzed 3,377 lake, stream, snowpack, and special interest samples for the following 1986 surveys: Spring Variability Pilot Study (SVS-P), Snowpack Study, National Stream Survey-Phase I (NSS-I), and Eastern Lake Survey-Phase II (ELS-II) spring, summer, and fall seasonal studies. Samples were prepared for shipment to the contracted analytical laboratories within the specified sample holding time in all cases. No personal safety incidents occurred during the laboratory operations.

It was difficult to maintain high quality in the training programs while processing samples at the same time. We recommend that a specific block of time be identified for training only. Certification in first aid and CPR as a prerequisite for employment would facilitate the training program.

The mean of 485 pH QCCS measurements during the spring was 4.06 ± 0.05 (mean $\pm$ two standard deviations), which differs from the established value of 4.00 ± 0.1 pH units for a 1×10^{-4} N H_2SO_4 solution (Metcalf, 1987). We recommend that the acceptable value of the QCCS be changed to reflect the apparent pH of the standard using the system described. The simultaneous use of two pH meters for sample batches with more than 20 samples was required in order to analyze the samples within the allowable holding time. A new pH protocol that utilized an additional standard was developed to check the comparability of the results obtained from different pH meters. The use of this protocol should be continued.

For NSS-I samples, the determination of conductivity was added as a processing laboratory measurement. Modification of the method included the addition of a temperature correction factor and a low concentration QCCS. These additions to the protocol proved successful and we suggest that they be incorporated in future studies.

Aluminum concentrations were determined by extraction into MIBK followed by atomic absorption spectrophotometry and by FIA. With the development of a reliable FIA-aluminum method, we recommend that the hazardous-waste-producing extraction method using MIBK be discontinued. A series of QC checks were developed for the FIA-aluminum protocol, including the use of a natural sample used to monitor the status of the instrument. The development of additional QC checks provided valuable information during sample analysis and these guidelines should be continued for future surveys.

The large sample loads in the spring (30 to 90 per day) required up to seven aliquot preparation analysts. To increase efficiency, a two-stage filtration apparatus which employs a coarse prefilter is recommended, especially for stream samples. Many NSS-I samples had high turbidity or color values. This required the development of high concentration measurement procedures for turbidity and true color.

A day scheduled each week for instrument maintenance only is recommended. In the spring, instrument maintenance was performed concurrently with sample processing as time permitted. This was necessary due to various changes in field sampling schedules. For the summer and fall seasonal studies, a day for instrument maintenance was available. This significantly reduced the number of analytical instrument malfunctions. This practice should be adopted for any future efforts of this type.

The efficiency and quality of sample processing was increased by conscientious laboratory maintenance procedures and careful checks on data reporting. The coordinator reviewed the data forms each day. Preliminary review of the processing laboratory QC solution and audit data results during the laboratory operations indicate that the data are of acceptable quality. The development of daily data review procedures for each method reduced the chances of omissions and recording errors.

Section 7

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Appendix A

Instrumentation, Equipment, and Supply Lists

Table A-1. Instrumentation

Parameter	Instrument	Manufacturer	Model
pH	pH/millivolt meter Combination electrode	Orion Orion Ross	611 8104BN, 8104
Dissolved inorganic carbon	Carbon analyzer Infrared gas analyzer	Dohrman/Xertex Horiba	DC-80 PIR-2000
Flow injection analysis-aluminum	Flow injection analyzer	LaChat Quick Chem	System IV Colorimeter
Turbidity	Nephelometer	Monitek	21
True color	Color test kit	Hach	CO-1
Conductivity	Conductivity meter Conductivity cell	Yellow Springs Instruments	32 3401, 3417

Table A-2. Equipment and Supplies

Chemicals-Dry

Aquasorb
Baking soda
Hexamethylene tetramine
Hydroxylamine hydrochloride
8-hydroxyquinoline-99% purity
Ion-exchange resin (Amberlite IR-120 14-50 mesh)
Mallcosorb
1,10-phenantholine monohydrochloride
Potassium chloride (ultrapure)
Pyrocatechol violet
Sodium acetate (anhydrous, ultrapure)
Sodium carbonate (American Chemical Society [ACS] Primary Standard Grade)
Sodium chloride (ACS reagent grade)
Sodium hydroxide pellets
Tin metal

Chemicals-Liquid

Acetic acid, glacial (Baker Instra-analyzed, Ultrex)
Aluminum Stock Solution-1000 mg/L
Ammonium hydroxide-5M (Baker Instra-analyzed, Ultrex)
Bleach
Formalin
Hydrochloric acid-12 M (Baker Instra-analyzed)
Isopropyl alcohol

(continued)

Table A-2. Continued

Chemicals-Liquid (continued)

    Methyl isobutyl ketone (high performance liquid chromatography)
    NBS traceable buffers: pH 4, pH 7
    Nitric acid-12 M (Baker Instra-analyzed, Ultrex)
    Phenol red-0.04% w/v
    Phosphoric acid-85%
    Potassium chloride-3 M
    Sulfuric acid-18 M (Ultrex)
    Sulfuric acid-0.1 N
    Turbidity standards: 5, 10, 20, 50, 100, 200 NTU

Equipment and Supplies

    Accessory part kits for carbon and flow injection analyzers
    Analytical balance (Ohaus)
    Centrifuge (Dynac)
    Chemical refrigerant packs
    Color viewing tubes (Hach)
    Copier
    Electric and water inputs
    Emergency shower
    Emergency spill kits (J. T. Baker)
    Eye-wash station (Lab-Line)
    Filtration units (Fisher Filtrator)
    Fire extinguishers
    Freezer
    Hazardous waste containers: 1, 5-gallon
    Heating/cooling system
    Laminar flow hood-Class 100 air (Forma Scientific)
    MIBK gas tank for calibration of the organic vapor meter
    NBS thermometers
    Nitrogen gas tanks (analytical grade)
    Optical cuvettes
    Organic vapor meter
    Pipettes: 40-200, 200-1000 μL; 1-5 mL (Finnpipette)
    Refrigerator
    pH chambers-8-mL polyethylene
    Portable pumps (Millipore)
    Reagent bottles with 3-valve caps
    Repipettes: 2, 5, 10-mL (Labindustries)
    Respirators and cartridges (Survivair)
    Reverse osmosis water purification system (Millipore)
    Smoke detectors
    Solvent storage cabinets
    Vacuum pump
    Water output
    Weight set
    Wet-dry vacuum

Water System Cartridges (Millipore)

    Carbon
    Ion-exchange
    Millistak filter
    Organic
    Prefilter
    Reverse osmosis membrane

Consumable Products

    Aliquot labels
    Ampules-10-mL
    Beakers: 50-, 250-mL
    BenchKote
    Bottles-Nalgene amber wide-mouth: 125-, 250-mL (acid leached); 250-, 500-mL (deionized water leached)
   (I-Chem)

Table A-2. Continued

Consumable Products (continued)

Capillary tubes
Centrifuge tubes: 15-, 50-mL (I-Chem)
Cubitainers: 1-, 5-gallon (I-Chem)
Data forms
Diskettes
Filters: glass fiber filters, 1.2-μm pore size (Whatman GFC); 25-mm diameter, 0.4-μm pore size (Nucleopore); 47-mm, 0.45-μm pore size (Gelman); syringe filters, 0.45-μm pore size (Acrodisc)
Filter holders-25-mm (Nucleopore)
Forceps-Teflon or plastic
Gloves-powder-free
Kimwipes
Laboratory coats and safety glasses
Laboratory glass and plasticware
Nitrogen gas (zero-grade)
Office supplies
Parafilm
pH paper-ranges: 1.8-3.8, 8.1-9.4 pH units
Pipette tips: 40-200, 200-1000-μL; 1-5-mL
Plastic bags: sandwich, trash, Ziploc
Shipping coolers: plastic, Styrofoam
Spatulas
Syringes-60-mL
Syringe valves (Luer-Lok)
Tape: duct, electrical, cellophane, strapping
Tubing: peristaltic pump, Teflon, Tygon
Wash bottles
Weighboats

Appendix B

Warehouse and Trailer Floor Plans
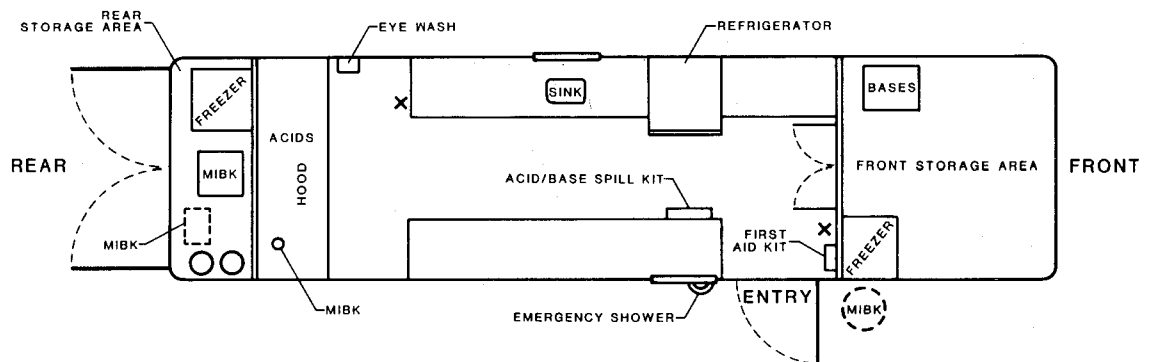
ACIDS – STORED BELOW HOOD AREA IN LAB
BASES – STORED IN COOLER IN FRONT STORAGE AREA OF LAB
MIBK – 1-GALLON BOTTLE STORED IN HOOD IN LAB
        1-GALLON BOTTLE STORED IN CHEMICAL LOCKER IN REAR STORAGE AREA
× – FIRE EXTINGUISHER
O – N_2 & CO_2 COMPRESSED AIR TANKS
( ) – TEMPORARY STORAGE OF SOLID WASTE
[ ] – TEMPORARY STORAGE OF LIQUID WASTE

Figure B-1. Trailer floor plan.

Figure B-2. Warehouse floor plan.

M – TRAILER MAIN CIRCUIT BREAKER
FL – LARGE FIRE EXTINGUISHER
FS – SMALL FIRE EXTINGUISHER

VI

FS
V
FL
M

FL
IV
FS   M

M
FL
III
FS

M   FS
II
FL

ACID AND BASE
STORAGE CABINETS

MIBK
WASTE
AND
GAS
CYLINDER
STORAGE

4677

FL
I
M
FS

WC

WC

4675

FRONT OFFICE
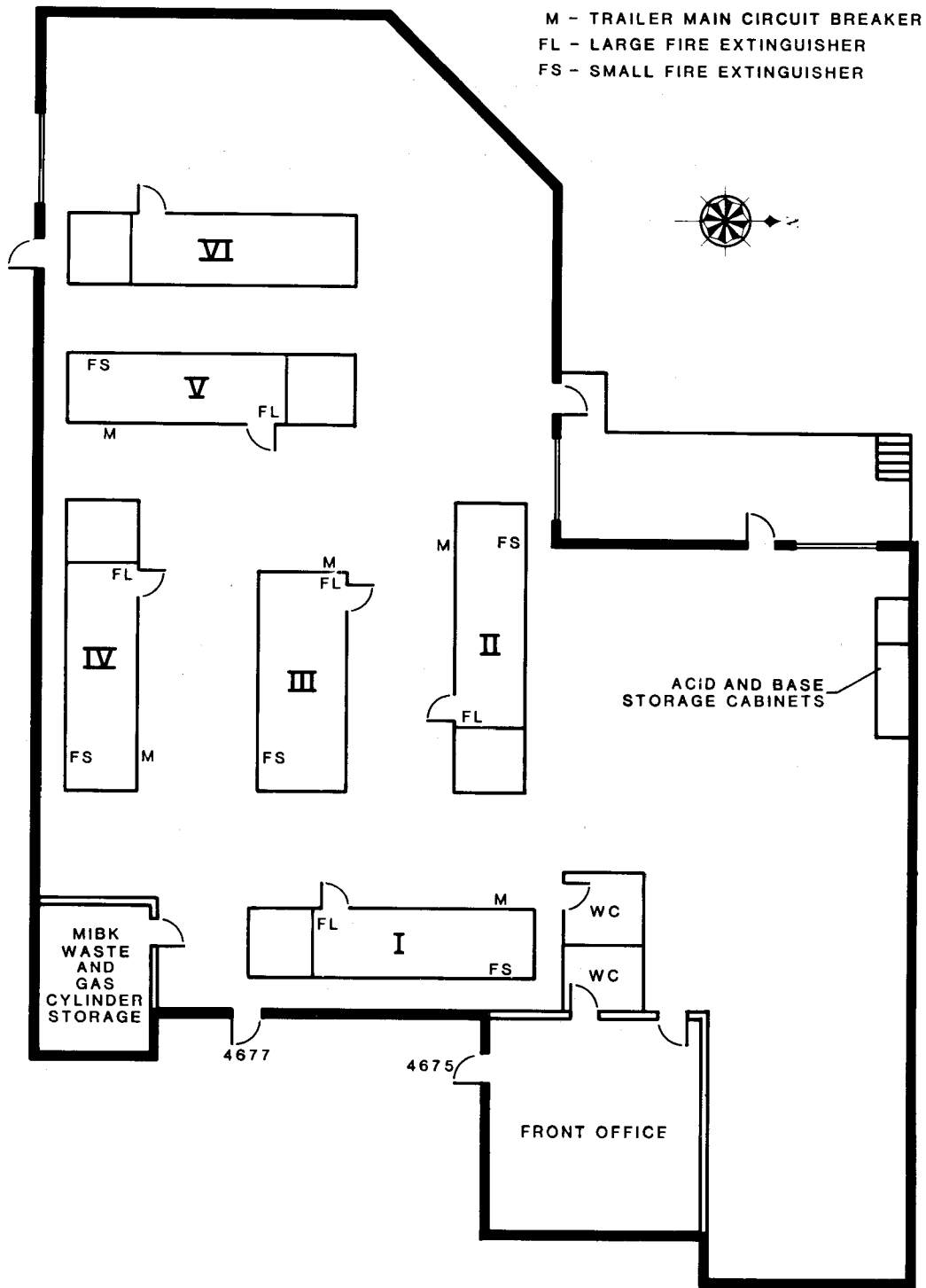
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Appendix C

Personnel List

Table C-1. List of Personnel and Positions Held for the National Surface Water Survey Processing Laboratory Operations

Season	Position Held	Name
Spring 1986	Communications	Jerry Dugas John Nicholson Valerie Sheppe
	Warehouse manager Warehouse assistant	Jeffrey Love Mark Sweeney
	Laboratory coordinator	Deb Chaloud
	Supervisor/analyst	Betsy Dickes Molly Morison
	Analyst	Barney Akuna John Alston Lori Arent Mary Balogh Christina Borror Hal Coleman Robert Heine Herb Herpolsheimer Robert Hughes Valerie Miller James Nitterauer Roxanne Parks James Pendleton Carla Schuman Sally Snell Carl Soong Brenda Whitfield Jeffrey Wolfe
Summer 1986	Communications	Jerry Dugas Dave Peck
	Warehouse manager	Jeffrey Love
	Laboratory coordinator	Deb Chaloud
	Supervisor/analyst	Lori Arent Betsy Dickes
	Analyst	Christina Borror Elizabeth Hill James Nitterauer Carl Soong Brenda Whitfield

(continued)

Table C-1. Continued

Season	Position Held	Name
Fall 1986	Communications	Jerry Dugas
	Warehouse manager	Daron Perez
	Laboratory coordinator/supervisor	Lori Arent
	Analyst	Linda Drewes Elizabeth Hill Molly Morison Dave Peck Carl Soong Brenda Whitfield

Appendix D

Processing Laboratory Data Forms, Aliquot Labels, and Sample Codes

Figure D-1. Forms 2 and 5 laboratory batch/QC field data form.

**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	DATE RECEIVED
			_____	_____ AIR-BILL NO _____	_____

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										
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38										
39										
40										

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
GILL'S (702) 362-2100

Figure D-2. Form 3 Sample shipping/receiving form.

ALIQUOT 1
Filtered - 250 mL

Batch ID _____
Sample ID _____
Date
Sampled _____

Preservative:
    HNO_3, 4 °C
Amount:_____mL
Parameters:
    Ca, Mg, K, Na, Mn, Fe

ALIQUOT 2
Filtered - 10 mL

Batch ID _____
Sample ID _____
Date
Sampled _____

Preservative:
    MIBK - HQ, 4 °C
Amount:_____mL
Parameters:
    Extractable Al

ALIQUOT 3
Filtered - 250 mL

Batch ID _____
Sample ID _____
Date
Sampled _____

Preservative:
    4 °C
Parameters:
    Cl, F⁻, SO_4^{2-}, NO_3^-, SiO_2

ALIQUOT 4
Filtered - 125 mL

Batch ID _____
Sample ID _____
Date
Sampled _____

Preservative:
    H_2SO_4, 4 °C
Amount_____mL
Parameters:
    DOC, NH_4^+

ALIQUOT 5
Unfiltered - 500 mL

Batch ID _____
Sample ID _____
Date
Sampled _____

Preservative:
    4 °C
Parameters: pH, Acidity,
    Alkalinity, DIC,
    Conductivity

ALIQUOT 6
Unfiltered - 125 mL

Batch ID _____
Sample ID _____
Date
Sampled _____

Preservative:
    H_2SO_4, 4 °C
Amount_____mL
Parameters:
    Total P

ALIQUOT 6
Filtered - 125 mL

Batch ID _____
Sample ID _____
Date
Sampled _____

Preservative:
    H_2SO_4, 4 °C
Amount_____mL
Parameters:
    Total Soluble P

ALIQUOT 7
Unfiltered - 125 mL

Batch ID _____
Sample ID _____
Date
Sampled _____

Preservative:
    HNO_3, 4 °C
Amount_____mL
Parameters:
    Total Al

**INDIANA
UNIVERSITY
LAKE SPLIT**

Batch ID _____
Sample ID _____
Date
Sampled _____

Preservative:
    HNO_3, 4 °C
Amount_____mL
Parameters:
    Metals

Figure D-3. Standard sample aliquot labels.

SNOW SPLIT
Filtered - 50 mL

Batch ID:

_____

Sample ID:

_____

Date Processed:

_____

Preservative:
        HNO_3
Amount:

_____mL
Parameters:
        Metals

Lake ID _____

Crew _____

_____

Date Sampled _____

Time Sampled _____

Depth _____meters

Tow No. _____of_____

_____

Batch ID _____

Sample ID _____

Preservative: Formalin

Parameters: Zooplankton

EMSL SPLIT
Unfiltered - 125 mL

Batch ID _____
Sample ID _____
Date
Processed _____

Preservative:
        H_2SO_4, 4 °C
Amount _____mL
Parameters:
        Total N and P

Lake ID _____
Crew _____Sample Type _____

_____

_____

EMSL ANOXIC SPLIT
Aliquot 1A - Filtered - 125 mL

Date Sampled _____
Time   Time
Sampled _____Filtered _____

Batch ID _____
Sample ID _____

Preservative: HNO_3, 4 °C
Amount: _____mL
Parameters: Fe, Mn

Lake ID _____
Crew _____
Sample Type _____

Date Sampled | Time

Volume Filtered

_____mL

Batch ID _____

Sample ID _____

Preservative: -20 °C
Parameter: Chlorophyll

Figure D-4. Special project aliquot labels.

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Table D-1. Sample Codes for Eastern Lake Survey-Phase II Summer Seasonal Study

Code	Sample Type
R	Routine lake sample
D	Duplicate lake sample
B	Field blank sample
TB	Trailer blank sample
TD	Trailer duplicate sample
S	Triplicate sample
	Radian Audit Sample
FN #-#	Field natural audit
LN #-#	Laboratory natural audit
FL #-#	Field low synthetic audit
LL #-#	Laboratory low synthetic audit

```
       |  |_____ Radian ID number
       |_____ Concentration lot number
```

EMSL-LV Audit Samples Eastern Lake Survey-Phase II (fall)

```
#LS# _____ Concentration (1-6)

   |_____ Laboratory tracking number (1-34)
```

NBS-Traceable Rainwater Audit Samples
Eastern Lake Survey-Phase II (fall)

```
RWXX _____ Laboratory tracking letter (A-F)

   |_____ Concentration (L or H)
```

Table D-2. Sample Codes for Eastern Lake Survey-Phase II Summer Seasonal Study

Split Codes	Sample Type
A	Preserved hypolimnetic (anoxic) sample
G	Chlorophyll sample
P	Total nitrogen and phosphorus split
S	Triplicate sample
W	White split
#Z	Zooplankton tows

SUBREGIONS OF THE NATIONAL STREAM SURVEY – PHASE I

Northern Appalachians (2Cn)

Valley and Ridge (2Bn)

Poconos/Catskills (1D)

Southern Blue Ridge (2As)
(Pilot Study)

Ozarks/Ouachitas (2D)

Mid-Atlantic
Coastal Plain (3B)

Piedmont
(3A)

Florida (3C)

Southern Appalachians (2X)