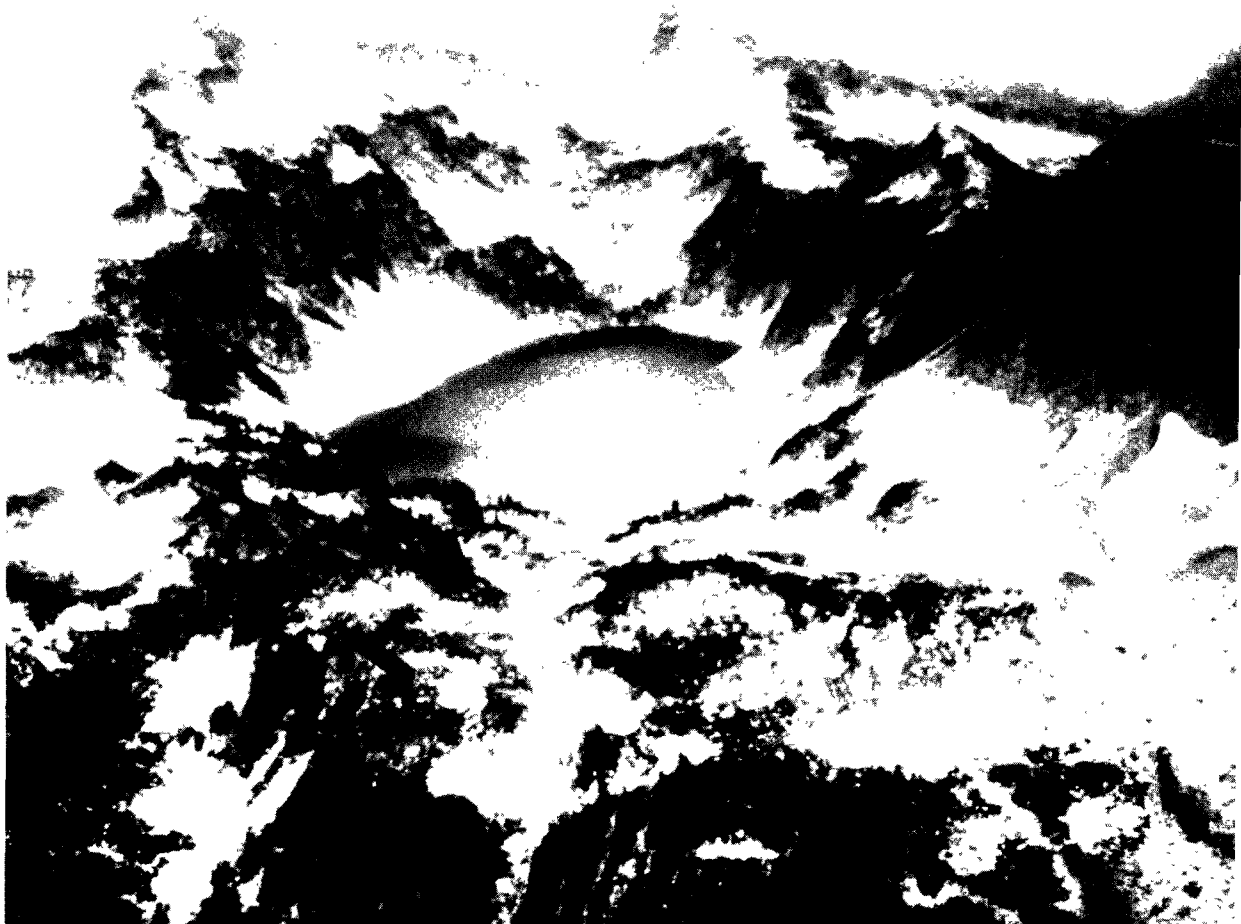


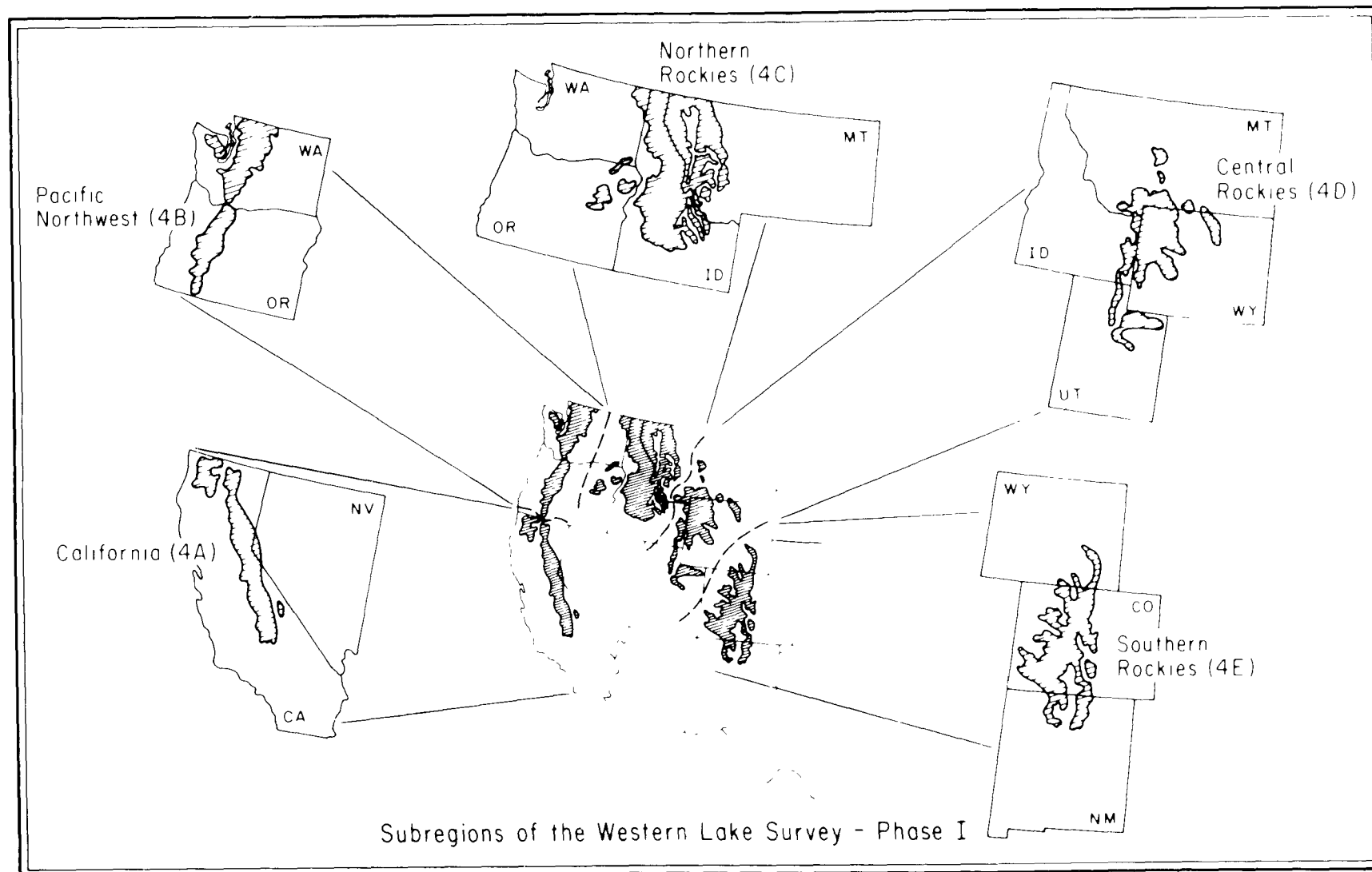
Research and Development



Western Lake Survey Phase I

Quality Assurance Plan





Western Lake Survey Phase I

Quality Assurance Plan

A Contribution to the
National Acid Precitation Assessment Program



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

Environmental Monitoring Systems Laboratory - Las Vegas, NV 89119
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Notice

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This document is one volume of a set which fully describes the Western Lake Survey-Phase I. The complete document set includes the major data report (2 volumes), quality assurance plan, analytical methods manual, field operations report, and quality assurance report. Similar sets are being produced for each Aquatic Effects Research Program component project. Colored covers, artwork, and use of the project name in the document title serve to identify each companion document set.

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Abstract

The purpose of the National Surface Water Survey of the National Acid Precipitation Assessment Program is to evaluate the present water chemistry of lakes and streams, to determine the status of certain biotic resources, and to select regionally representative surface waters for a long-term monitoring program to study changes in aquatic resources. The Western Lake Survey is part of the National Surface Water Survey.

The U.S. Environmental Protection Agency requires that data collection activities be based on a program which ensures that the resulting data are of known quality and are suitable for their intended purpose. In addition, it is necessary that the data obtained be consistent and comparable. For these reasons, all analysts participating in the study must use the same reliable, detailed analytical methodology.

The quality assurance plan and the analytical methods used during Phase I of the Western Lake Survey are based on those used during Phase I of the Eastern Lake Survey; analytical laboratory methods are identical for the two surveys, but some of the field laboratory methods were modified for the Western Lake Survey. Sampling protocols are significantly different in that ground access as well as helicopter access was used to collect samples for the Western Lake Survey.

This quality assurance plan describes in detail the quality assurance requirements and procedures that are unique to the Western Lake Survey - Phase I. Quality assurance requirements and procedures that were adopted verbatim from the Eastern Lake Survey - Phase I are referenced here and are discussed in detail in the quality assurance plan prepared for that survey.

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Abbreviations^a

AA	--	atomic absorption spectroscopy
ANC	--	acid-neutralizing capacity
APHA	--	American Public Health Association
ASA	--	American Statistical Association
ASTM	--	American Society for Testing and Materials
BNC	--	base-neutralizing capacity
CD	--	conductance difference
CI	--	confidence interval
CRDL	--	contract-required detection limit
DIC	--	dissolved inorganic carbon
DL QCCS	--	detection limit quality control check sample
DOC	--	dissolved organic carbon
DQO	--	data quality objective
ELS-I	--	Eastern Lake Survey - Phase I
EMSL-LV	--	Environmental Monitoring Systems Laboratory - Las Vegas
EPA	--	Environmental Protection Agency
ERL-C	--	Environmental Research Laboratory - Corvallis
IBD	--	ion balance difference
ICP	--	inductively coupled plasma atomic emission spectroscopy
ID	--	identification
IDL	--	instrument detection limit
IFB	--	Invitation for Bid
IR	--	infrared
Lockheed-EMSCO	--	Lockheed Engineering and Management Services Company, Inc.
MIBK	--	methyl isobutyl ketone
NAPAP	--	National Acid Precipitation Assessment Program
NBS	--	National Bureau of Standards
NCC	--	National Computer Center
NLS	--	National Lake Survey
NSWS	--	National Surface Water Survey
NTU	--	nephelometric turbidity unit
ORNL	--	Oak Ridge National Laboratory
PE	--	performance evaluation
QA	--	quality assurance
QC	--	quality control
QCCS	--	quality control check sample
RSD	--	relative standard deviation
RTP	--	Research Triangle Park
SAS	--	Statistical Analysis System

^aThis list does not include units of measurement or chemical symbols.

Abbreviations (continued)

SMO	--	Sample Management Office
SOW	--	Statement of Work
USGS	--	United States Geological Survey
UV	--	ultraviolet
WLS-I	--	Western Lake Survey - Phase I

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1.0 Introduction

The National Acid Precipitation Assessment Program (NAPAP) was initiated at the request of the Administrator of the U.S. Environmental Protection Agency (EPA) to evaluate the extent of the effects of acidic deposition on aquatic resources within the United States. When it became apparent that existing data could not be used to assess quantitatively the present chemical and biological status of surface waters in the United States, the National Surface Water Survey (NSWS) program was incorporated as part of NAPAP to obtain that information. The National Lake Survey (NLS) component of NSWS comprises Phase I - Eastern Lake Survey (ELS-I), Phase I - Western Lake Survey (WLS-I), and Phase II - Temporal Variability (see Figure 1-1).

Data published in earlier studies are consistent with the hypothesis that certain surface waters within the United States have decreased in pH or alkalinity over time. Acidic deposition has been suggested as a contributor to such decreases. Also, numerous studies have led to the conclusion that the effects of acidic deposition on surface-water chemistry are influenced by variations among lake, stream, and associated watershed characteristics. Existing data were compiled largely from numerous individual studies. Extrapolating these data to the regional or national scale was difficult because the studies often were biased in terms of site selection. Additionally, many previous studies were incomplete with respect to the chemical variables of interest, were inconsistent relative to sampling and analytical methodologies, or were highly variable in terms of data quality.

ELS-I, a synoptic survey of the chemistry of 1,612 lakes in the Eastern United States, was conducted to obtain a regional and national data base of water quality parameters that are pertinent to evaluating the effects of acidic deposition. To provide a base of information that is complete and consistent in terms of the variables measured and the sampling and analytical procedures used, ELS-I was carried out on representative lakes in the Southeastern, Northeastern, and Upper Midwestern regions of the United States. Detailed sampling procedures (Morris et al., 1986), standardized analytical protocols (Hillman et al., 1986), and a rigorous quality

assurance (QA) program (Drou   et al., 1986) were implemented. The purposes of WLS-I, a synoptic survey of the chemistry of 757 lakes in the Western United States, are parallel to those of ELS-I.

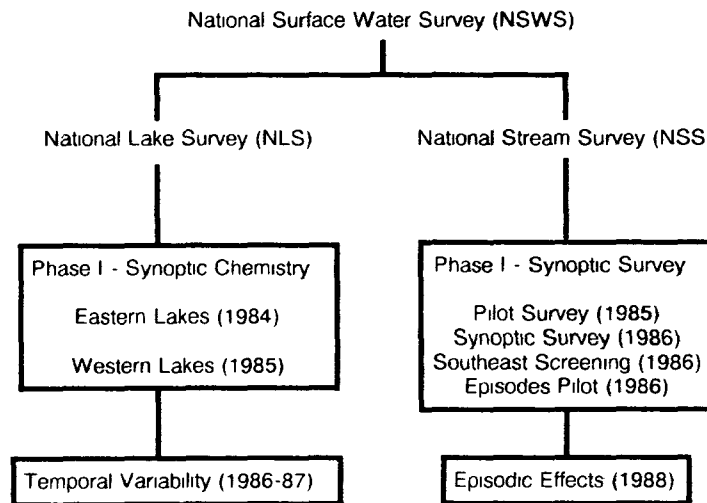
WLS-I was designed to minimize uncertainty in making regional assessments based on existing data. The five major design elements were as follows:

- Provide data from a subset of lakes that are characteristic of the overall population of lakes within a region.
- Use standardized methods to collect chemical data.
- Measure a complete set of variables thought to influence or to be influenced by surface-water acidification.
- Provide data that can be used to investigate statistical relationships among chemical variables on a regional basis.
- Provide reliable estimates of the chemical status of lakes within a region of interest.

The goals in designing WLS-I were to identify objectives, develop an overall conceptual and practical approach to meeting the objectives, identify intended uses and users of the data, identify the quality of data needed, develop an appropriate survey design, develop analytical protocols and quality assurance/ quality control (QA/QC) procedures, and revise and modify approaches and methods as needed. Thus, WLS-I was designed to provide statistically comparable data that could be extrapolated, with a known degree of confidence, to a regional or national scale. The conceptual approach emphasized that the data would not be used to ascribe observed effects to acidic deposition phenomena; rather, through comprehensive monitoring activities, WLS-I would provide information that could be used to develop correlative, not cause-and-effect, relationships.

The conceptual approach to the program was developed by EPA personnel and cooperating

Figure 1-1 Timetable for field activities of the National Surface Water Survey.



scientists. Planning for WLS-I began in October 1983. The research plan for Phase I of the NLS was initially reviewed late in 1983 by a large number of scientists who have expertise in the areas of study. Fifty scientists discussed the plan during a workshop held in December; suggested modifications were incorporated by March 1984. The research plan was submitted to members of the American Statistical Association (ASA) for review in June 1984; a final ASA review was conducted in October 1984.

The QA plan and the analytical methods for WLS-I are based on those used during ELS-I. The analytical laboratory methods are identical for the two surveys, but some field laboratory methods were modified for WLS-I on the basis of ELS-I experience and on the basis of constraints that resulted from the special geographic limitations associated with the high-altitude lakes in the West. New field laboratory protocols also were added to accommodate changes between ELS-I and WLS-I field sampling methods. Sampling protocols are significantly different in that ground access as well as helicopter access is used to collect samples for WLS-I (Bonoff and Groeger, 1987). The sampling protocols differ from those used during ELS-I because 400 of the WLS-I lakes are within designated wilderness areas that are closed to helicopter access. The ground sampling protocol developed for use in sampling the restricted-access lakes was first evaluated in a WLS pilot study conducted by EPA Region VIII office in the autumn of 1984.

A specialized calibration study is included in WLS-I to compare the effects of the two different sampling

methods on analytical results. The purpose of the comparison is to derive calibration factors, if necessary, that can be applied to data for samples collected by ground crews so that these data will be equivalent to data for samples collected by helicopter crews.

EPA requires that data collection activities be based on a program that ensures that the resulting data are of known quality and are suitable for their intended purpose. The purpose of a QA plan is to provide that assurance. Therefore, EPA policy requires that every monitoring and measurement project have a written and approved QA project plan (Costle, 1979a and 1979b). This requirement applies to all environmental monitoring and measurement efforts authorized or supported by EPA through regulations, grants, contracts, or other formal means. The QA project plan should specify the policies, organization, objectives, functional activities, and QA/QC activities designed to achieve the data quality goals of the project. All project personnel should be familiar with the policies and objectives outlined in the QA project plan to ensure proper interactions among the field operations, laboratory operations, and data management.

EPA guidance states that the 16 items shown in Table 1-1 should be addressed in the QA project plan (U.S. EPA, 1980). Some of these items are addressed extensively in other manuals (Hillman et al., 1986; Kerfoot and Faber, 1987; Morris et al., 1985); therefore, as allowed by the guidelines, these specific discussions are not repeated in this document.

Table 1-1. Cross-References to Quality Assurance Subjects, Western Lake Survey - Phase I^a

Subject	Quality Assurance Plan	Field Operations Report ^b	Methods Manual ^c
Title Page			
Table of Contents	Contents		
Project Description	2		
Project Organization and Responsibility	3		
QA Objectives	4		1
Sampling Procedures	6	Field Sampling Operations	2
Sample Custody	6	Field Sampling Operations	2, 3
Calibration Procedures	6	Field Sampling Operations	2
Analytical Procedures	8	Field Laboratory Operations	4 to 13
Data Analysis, Validation, and Reporting	6, 9, 12, 13, 14		3
Internal QC Checks	7,9		3
Performance and System Audits	10		
Preventive Maintenance	6		2, 3
Assessment of Precision, Accuracy, and Completeness	4,11		
Corrective Actions	9,11		3
QA Reports to Management	9,10		

^a The requirement to address these 16 QA subjects is stated in U S EPA (1980).

^b Bonoff and Groeger (1987).

^c Hillman et al. (1986). Summary in Kerfoot and Faber (1987)

Quality assurance requirements and procedures that were adopted verbatim from ELS-I are referenced here and are described in detail in the ELS-I QA plan (Drou   et al., 1986). ELS-I recommendations that led to WLS-I protocol changes are discussed in the ELS-I QA report (Best et al., 1987). The sections that follow describe in detail only those QA requirements and procedures that are specific to WLS-I.

2.0 Project Description

The WLS-I portion of NSWS is a synoptic survey of 757 lakes in the Western United States that will be conducted during fall overturn. During this overturn period, chemical variability within a lake is expected to be minimal as a result of circulation within the water column. WLS-I is designed to meet the following objectives for designated regions of the Western United States:

- Determine the percentage (by number and area) and location of lakes that are potentially susceptible to change as a result of acidic deposition and that have low acid-neutralizing capacity (ANC).
- Investigate the relationships among water chemistry, regional acidic deposition patterns, land use, physiographic features, lake morphology, and basin geometry within and among regions.
- Identify smaller subsets of representative lakes for more intensive sampling in future surveys.

Of the lakes to be sampled during WLS-I, 455 lie within designated wilderness areas. In order to observe the guidelines and regulations set forth in the Wilderness Act, almost all lakes located within wilderness areas that have been selected for sampling must be sampled by ground crews of the U.S. Department of Agriculture - Forest Service. The ground crews travel to lakes by foot or on horseback. The lakes that are not in wilderness areas are sampled by helicopter crews under the direction of EPA.

Selected wilderness-area lakes that have been determined to be inaccessible by ground crews are sampled by helicopter crews during periods when disturbance to wildlife or hikers is minimal. In addition, 45 wilderness-area lakes are sampled by ground crews and by helicopter crews. The results for samples collected from these 45 calibration lakes will be used to evaluate the comparability of ground crew and helicopter crew sampling protocols for collecting and handling water samples.

This calibration study is designed to meet three goals:

- Quantify the differences between the two sampling methods (helicopter and ground access).
- Quantify the effects of holding samples for different lengths of time prior to processing, preservation, and analysis.
- Quantify any significant interlaboratory bias between the two analytical laboratories that analyze WLS-I samples.

Data derived from the chemical analyses conducted during the study will be used to establish calibration factors that can be applied to analytical values reported for all WLS-I samples. The calibration factors are intended to eliminate value differences that result from variations in sampling protocol, sample holding time, or laboratory bias.

Two other studies are being conducted as part of WLS-I. The purpose of one study, the nitrate/sulfate stability study, is to compare sample preservation methods and to study the effects of holding samples for different lengths of time before preserving them. The nitrate/sulfate sample is an extra aliquot taken from the Van Dorn sampling unit, preserved with HgCl_2 , and analyzed at the U.S. EPA Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV). The purpose of the second study, the Corvallis study, is to compare results for splits of the same sample when the splits have been analyzed by different methods. The analytical laboratories use NSWS protocols for atomic absorption spectroscopy (AA), inductively coupled plasma emission spectroscopy (ICP), automated colorimetry, and ion chromatography, according to the analyte; the Environmental Research Laboratory at Corvallis, Oregon (ERL-C), used ICP only and is not restricted to the NSWS protocols and detection limits. A further purpose of the Corvallis study is to determine if the ICP data can be substituted in the data base if problems arise with the standard analysis. Both studies can provide checks on sampling, processing, and analytical performance.

To ensure that WLS-I procedures are performed consistently and that the quality of the data generated can be determined, the QA project plan for WLS-I specifies the following measures:

the survey and the effectiveness of this QA plan will be issued after these factors have been evaluated.

- Provide detailed, written sampling methodology (Morris et al., 1985, and Peck et al., 1985; summarized in Bonoff and Groeger, 1987).
- Simultaneously train and test all personnel participating in field activities.
- Conduct on-site visits to each field operations base and remote site soon after sampling begins, and maintain daily telephone contact throughout the sampling period to ensure that all methods are being performed properly.
- Perform extensive evaluation of analytical laboratories throughout their participation.
- Assess variability introduced at each level of activity in field and analytical laboratories by processing audit samples (synthetic and natural lake samples), duplicate samples, and blank samples along with routine samples. (Field laboratory refers to the on-site mobile laboratory that performs preliminary analyses and aliquot preparation; analytical laboratory refers to the off-site contract laboratory that performs the more sophisticated analyses.)
- Provide detailed, written analytical methodology (Hillman et al., 1986; summarized in Kerfoot and Faber, 1987).
- Use internal QC procedures at the analytical laboratory to detect potential contamination and to verify established detection limits.
- Enforce holding-time requirements.
- Use protocols in the field and in the analytical laboratory to confirm that reported data are correct.
- Enter data from standardized data reporting forms into the data base twice, and scan for outlying values to eliminate effects of transcription errors.
- Verify data by means of range checks, internal consistency checks, and QA evaluations.
- Validate verified data by identifying values that are not typical of values observed for the group of lakes (e.g., stratum) from which the sample or samples were drawn.

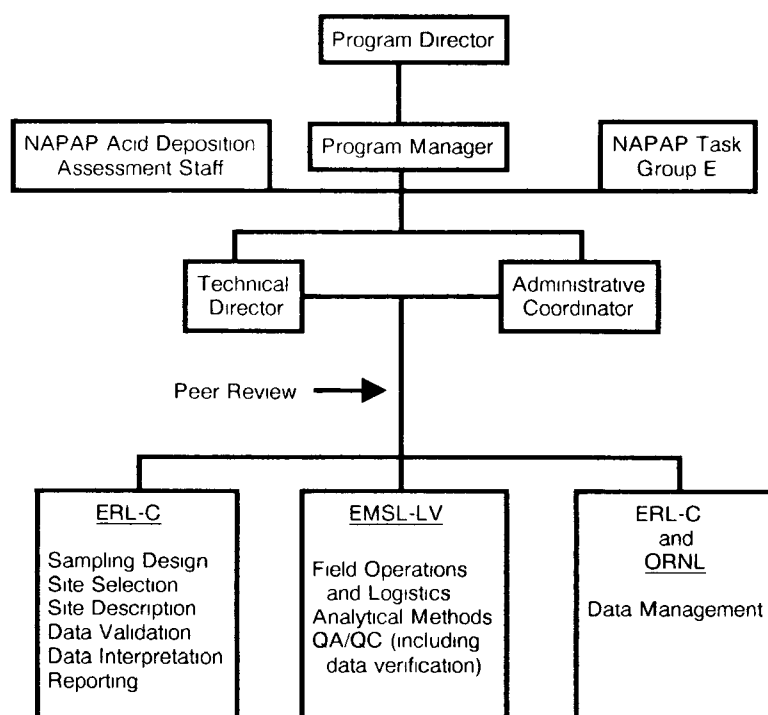
This QA plan is the final version of the draft plans that were written before and were modified during WLS-I activities. A QA report that describes the findings of

3.0 Project Organization

Figure 3-1 illustrates the NSWS management structure. The program director is the EPA official who has overall responsibility for the program. The responsibilities of the program manager, technical director, and administrative coordinator are discussed in detail in Drou   et al. (1986) as are the roles of the

Environmental Research Laboratory at Corvallis, Oregon (ERL-C), the Environmental Monitoring Systems Laboratory at Las Vegas, Nevada (EMSL-LV), and the Oak Ridge National Laboratory (ORNL) at Oak Ridge, Tennessee.

Figure 3-1. National Surface Water Survey internal management structure.



4.0 Quality Assurance Objectives

The statistical design, sampling and analytical methods, and QA activities for WLS-I are structured to meet specific data quality objectives (DQOs) for the measurement of sampling, field laboratory, and analytical laboratory performance. These DQOs are designed to facilitate checking for chemical variability and to provide confidence levels for reporting population estimates.

4.1 Precision, Accuracy, and Detectability

The primary DQOs are measures of precision (expressed as relative standard deviation), accuracy (expressed as maximum absolute bias), and detectability (expressed as an expected value range and a required detection limit). These DQOs are applied to each parameter measured at the lake sampling site, in the field laboratory, and in the analytical laboratory. Appropriate values and ranges were established for each DQO (for each parameter and measurement site) during ELS-I (Drou   et al., 1986). The values and ranges used for WLS-I are based on experience gained during ELS-I and on standard laboratory QA/QC requirements. Table 4-1 summarizes the primary DQOs used for WLS-I; further discussion can be found in Drou   et al. (1986).

4.2 Completeness and Comparability

Certain other DQOs also have been considered in the survey design. Completeness (the quantity of acceptable data actually collected in relation to the total quantity that is expected to be collected) is set at 90 percent or better for all variables, on the basis of experience gained during ELS-I. Comparability (a measure of the confidence with which one data set can be compared to another) is ensured by requiring that standard procedures be used for laboratory analyses and that a uniform set of units be used for reporting data. The calibration study was performed to ensure that differences in the sampling and on-site analytical procedures used by helicopter crews and ground crews did not reduce data comparability.

4.3 Representativeness

Representativeness (the degree to which data accurately and precisely represent a characteristic of

a population) is an important concern of NSWS. The sampling scheme for WLS-I was designed to maximize representativeness. A systematic random sample drawn within strata ensured good geographical coverage without bias (Landers et al., 1987).

WLS-I is not intended to characterize the chemistry of any given lake spatially or temporally. Therefore, achieving WLS-I objectives does not require that the only sample taken from a lake be completely representative of the lake. In most cases (except for the lakes to be sampled during the calibration study) only one sample per lake is taken during WLS-I. A determination of whether one sample per lake is sufficient to achieve the general objectives of NSWS Phase I, however, can be made from estimates of "within-lake" and "among-lakes" variances. Although some estimates of these variances will be made for WLS-I lakes in accordance with the statistical sampling design, future, more intensive studies of individual lakes will provide more complete data on representativeness.

Although the individual sample is not necessarily representative of the lake, the subset of lakes sampled should be representative of the sub-regional or regional population of lakes. The systematic sampling design that was adopted for this survey is intended to ensure representativeness at this level.

4.4 Samples Used to Monitor Data Quality

Several types of QA and QC samples are used to ensure that sampling and analytical methods are performed according to the NSWS Statement of Work (SOW) and this QA plan (Figure 4-1). QA samples are used by the QA staff to evaluate overall method performance for field sampling, field laboratory procedures, and analytical laboratory procedures and to evaluate overall data quality for the survey. QC samples allow field samplers and personnel at the field and analytical laboratories to identify and correct local problems (e.g., providing the analyst with immediate feedback on reagent contamination or questionable instrument performance). The use of QC samples in the field is discussed in Section 7 of this document; QC samples and procedures for the

Table 4-1. Data Quality Objectives for Precision, Accuracy, and Detectability, Western Lake Survey - Phase I

Site ^a	Parameter ^b	Method	Units	Expected Range ^c	Required Detection Limits	Precision Relative Standard Deviation (RSD) Upper Limit (%) ^d	Accuracy Max. Absolute Bias (%)
2, 3	Al, Extractable	Extraction with 8- hydroxyquinoline into MIBK followed by AA ^e (furnace)	mg/L	0.005 - 1.0	0.005	10 (Al conc. > 0.01) 20 (Al conc ≤ 0.01)	10 20
2, 3	Al, Total	AA ^e (furnace)	mg/L	0.005 - 1.0	0.005	10 (Al conc > 0.01) 20 (Al conc ≤ 0.01)	10 20
3	ANC	Titration and Gran analysis	µeq/L	-100 - 1,000	^f	10	10
3	BNC	Titration and Gran analysis	µeq/L	-10 - 150	^f	10	10
3	Ca	AA ^e (flame) or ICP ^g	mg/L	0.5 - 20	0.01	5	10
3	Cl ⁻	Ion chromatography	mg/L	0.2 - 10	0.01	5	10
1, 3	Conductance	Conductivity cell and meter	µS/cm	5 - 1,000	^h	2	5
2, 3	DIC	Instrumental (acidification, CO ₂ generation, IR detection)	mg/L	0.05 - 15	0.05	10	10
3	DOC	Instrumental (UV- promoted oxidation, CO ₂ generation, IR detection)	mg/L	0.1 - 50	0.1	5 (DOC conc > 5) 10 (DOC conc ≤ 5)	10
3	F ⁻ , Total dissolved	Ion-selective electrode and meter	mg/L	0.01 - 0.2	0.005	5	10
3	Fe	AA ^e (flame) or ICP ^g	mg/L	0.01 - 5	0.01	10	10
3	K	AA ^e (flame)	mg/L	0.1 - 1	0.01	5	10
3	Mg	AA ^e (flame) or ICP ^g	mg/L	0.1 - 7	0.01	5	10
3	Mn	AA ^e (flame) or ICP ^g	mg/L	0.01 - 5	0.01	10	10
3	Na	AA ^e (flame)	mg/L	0.5 - 7	0.01	5	10
3	NH ₄ ⁺	Automated colorimetry (phenate)	mg/L	0.01 - 2	0.01	5	10
3	NO ₃	Ion chromatography	mg/L	0.01 - 5	0.005	10	10

(continued)

analytical laboratories are discussed in Section 9 of Drou   et al. (1986). The types of QA and QC samples to be used during WLS-I are described in subsections 4.4.1 and 4.4.2.

4.4.1 Quality Assurance Samples

QA samples that are introduced in the field or at the field laboratory are analyzed at the field laboratory and at the analytical laboratory. These samples are used to judge the overall performance of WLS-I sampling and analytical activities and to establish data quality. The QA samples are "double blind" to the

analytical laboratories (i.e., the laboratories do not know the origin, identity, or composition of the samples). Consequently, the analytical laboratories process QA samples as they would any other routinely analyzed sample. The QA samples used are (1) field blanks, (2) trailer blanks, (3) field duplicates, and (4) field audits.

- Field Blank -

A field blank, which is prepared at the field laboratory, is a deionized water sample that

Table 4-1 (Continued)

Site ^a	Parameter ^b	Method	Units	Expected Range ^c	Required Detection Limits	Precision Relative Standard Deviation (RSD) Upper Limit (%) ^d	Accuracy Max. Absolute Bias (%)
1, 2	pH, Field	pH electrode and meter	pH units	3 - 8	--	± 0.1 ^f	± 0.1 ^f
3	pH, Analytical laboratory	pH electrode and meter	pH units	3 - 8	--	± 0.05 ^f	± 0.05 ^f
3	P, Total	Automated colorimetry (phospho-molybdate)	mg/L	0.005 - 0.07	0.002	10 (P conc. > 0.01) 20 (P conc. ≤ 0.01)	10 20
3	SiO ₂	Automated colorimetry (molybdate blue)	mg/L	0.1 - 25	0.05	5	10
3	SO ₄ ²⁻	Ion chromatography	mg/L	1 - 20	0.05	5	10
2	True color	Comparison to platinum-cobalt color standards	PCU ^g	0 - 200	0	± 5 ^f	--
2	Turbidity	Instrument (nephelometer)	NTU ^k	2 - 15	2	10	10

^a 1 = lake site, 2 = field laboratory, 3 = analytical laboratory

^b Dissolved ions and metals are being determined, except where noted

^c Ranges are for lake waters.

^d Unless otherwise noted, this is the %RSD at concentrations greater than 10 times required detection limits

^e AA = atomic absorption spectroscopy

^f Absolute blank value must be ≤ 10.

^g ICP = inductively coupled plasma atomic emission spectroscopy

^h Blank must be ≤ 0.9 µS/cm

ⁱ Absolute precision goal in terms of applicable units.

American Public Health Association platinum-cobalt units.

^k Nephelometric turbidity units

meets specifications of the American Society for Testing and Materials (ASTM) for Type 1 reagent-grade water (ASTM, 1984). The sampling crew transports the blank water to the lake in Cubitainers and processes the blank through the Van Dorn sampler as if the blank were a lake sample. Because the action of pouring the blank water through the Van Dorn sampler creates the possibility of changing the CO₂ concentration in the sample, which would affect the pH and DIC field measurements, pH and DIC syringe samples are not taken for the field blanks. True color and turbidity, however, are determined for each field blank at the field laboratory. Each helicopter crew collects one field blank on each operating day; each ground crew collects two field blanks during the course of the survey.

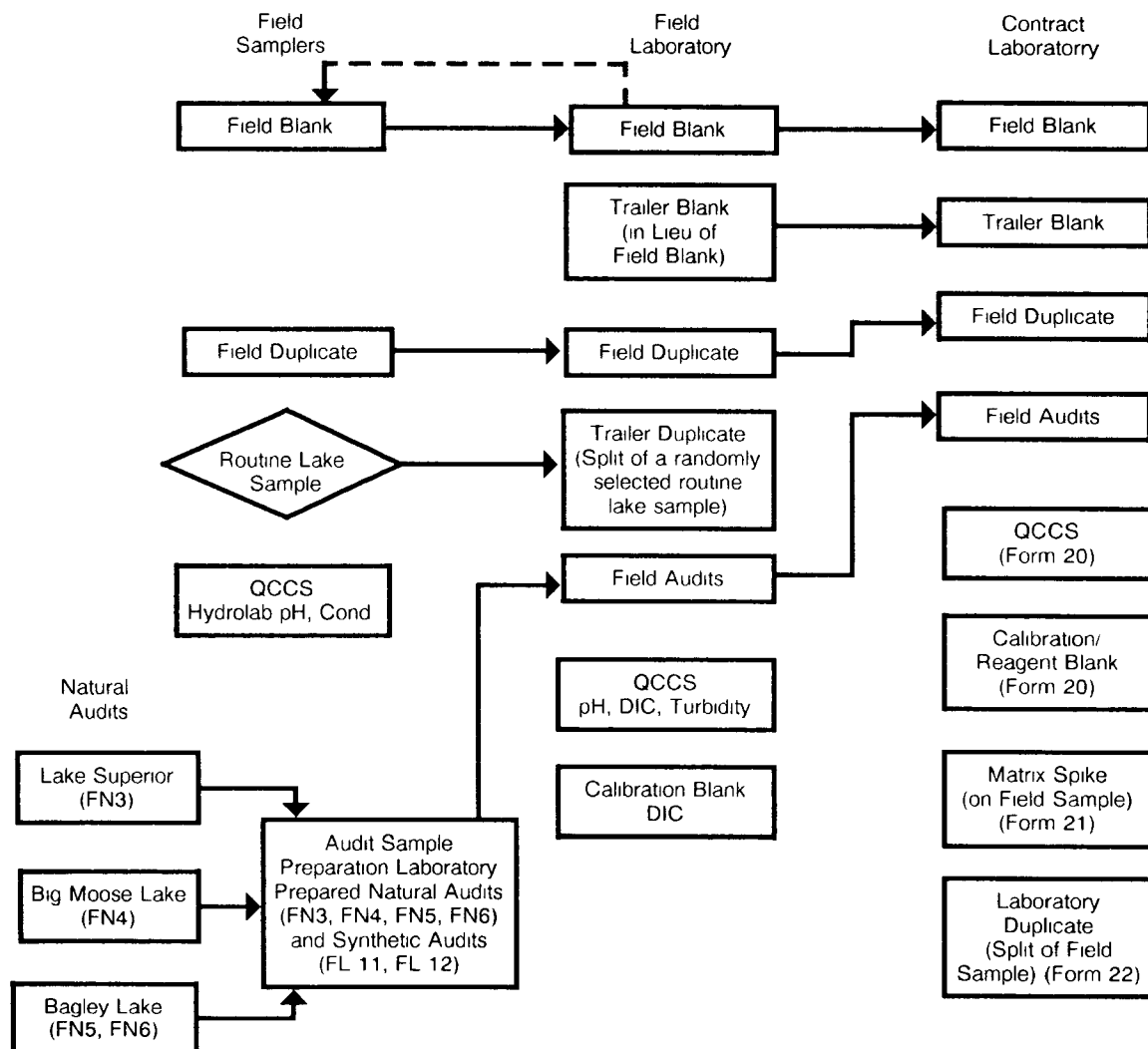
Field blanks are inserted in the sample batches that are sent to the analytical laboratories. They are used to identify contamination problems that

may occur during the sampling and analytical processes and to provide data that are used to establish the estimated system decision limit, quantitation limit, and background levels that could be expected for each variable. For data interpretation, any data point above the expected value for the blank is considered to be a positive response for a given analyte.

• Trailer Blank -

The trailer blank is used instead of a field blank when a field blank is not collected for a particular sample batch. The sampling design of WLS-I occasionally results in situations in which a field blank is not scheduled to be processed at any lake site for a particular sampling day. When this situation occurs, a deionized water sample is processed in the field laboratory as if it were a field blank that has been delivered to the field laboratory by the sampling crew. The chief difference between the

Figure 4-1. Flow of quality assurance and quality control samples, Western Lake Survey - Phase I.



two types of blanks is that the trailer blank is never processed through the Van Dorn sampler. The trailer blank is then inserted (in place of a field blank) in the sample batch that is sent to the analytical laboratory.

- Field Duplicate -

A field duplicate is a second sample collected at the lake site immediately after the routine sample is collected. The field duplicate is collected by the same sampling crew that collects the routine sample; the same procedure is used to collect both samples. For each field base, one helicopter crew collects a field duplicate on each sampling day. Each ground crew collects two field duplicates during the course of the survey. Field duplicates are processed by the field laboratory and are inserted as double-blind samples in the sample

batches that are sent to the analytical laboratories.

Field routine/duplicate pairs are used to determine the precision of the field samplers' technique in sampling, the precision of the field laboratory in analyzing and processing samples, and the precision of the analytical laboratory in analyzing samples. The routine/duplicate pair is also used to determine the homogeneity of the lake sample.

NOTE: Duplicate samples that are collected for the calibration lake study are not used as QA samples because sampling methods, holding times, and batches differ for the five comparable samples collected from one lake (routine and duplicate collected by the ground crew and routine, duplicate, and triplicate

collected by the helicopter crew). See Section 6 for a discussion of calibration study procedures.

- **Field Audits -**

Two types of audit samples (field natural audit samples and field synthetic audit samples) are used to establish overall field and analytical laboratory performance. A third type of audit sample, a laboratory audit, which was used for ELS-I, is not being used for WLS-I. ELS-I results showed that the practical significance of the difference in precision between laboratory audits and field audits was negligible; therefore, the use of laboratory audits was determined not to be cost effective.

Field natural audit samples are composed of natural lake water; field synthetic audit samples, which are prepared to simulate natural lake water, are reagent-grade water that contains the analytes of interest at specified theoretical concentrations.

Field audit samples are used (1) to determine the relative bias between analytical laboratories, so that measurements made by the two laboratories can be compared and (2) to indicate precision of those measurements through repeated analysis of the same sample type.

Both types of field audit samples are received in 2-L portions from a central source; at the field laboratory, the samples are filtered and preserved. Aliquots are taken from the filtered audit samples as from routine lake samples, and these aliquots are shipped to the analytical laboratory as double-blind samples.

Only low-concentration synthetic audit samples are used for this survey. High-concentration synthetic samples are not utilized because concentrations of analytes in WLS-I lakes are anticipated to be low.

4.4.2 Quality Control Samples

4.4.2.1 Hydrolab Quality Control Samples--

Quality control check samples (QCCSs) are used by the helicopter crews to check Hydrolab pH and conductance measurements in the morning (prior to sampling activity) and in the evening (after sampling activity is completed for the day). The morning QCCSs are used to check the calibration of the Hydrolab; the evening QCCSs indicate instrument drift over time.

4.4.2.2 Field Laboratory Quality Control Samples--

Three types of QC samples are used by the field laboratory staff to ensure that instruments and data collection are within specified control limits. The QC samples are (1) calibration blanks, (2) QCCSs, and (3) trailer duplicates.

- **Calibration Blank -** A calibration blank (deionized water drawn directly from the water purification unit located in the field laboratory) is used to check for baseline drift of the carbon analyzer and to check for contamination. The calibration blank is analyzed prior to sample analysis for dissolved inorganic carbon (DIC).
- **Quality Control Check Sample -** QCCSs are prepared in the field laboratory or are purchased. They are used to check initial instrument calibration and, during sample analysis, to check at specified regular intervals for instrumental drift. QCCSs are analyzed for pH, DIC, and turbidity. The QCCS for pH is a 0.0001 N H₂SO₄ solution with a pH of 4.0; for DIC, QCCSs of 2 mg/L and 20 mg/L Na₂CO₃ are prepared; for turbidity, the QCCSs are turbidity standards of 10.00, 20.00, 100.00, and 200.00 nephelometric turbidity units (NTU).
- **Trailer Duplicate -** The trailer duplicate, a second measurement of a routine sample, is used to check the precision of measurements made in the field laboratory. The field laboratory supervisor randomly selects one lake sample per trailer operating day; this sample is analyzed in duplicate for pH, DIC, true color, and turbidity.

4.4.2.3 Analytical Laboratory Quality Control Samples--

Six types of QC samples are used by the analytical laboratories to ensure that instruments and data collection are within control limits. These six sample types are (1) calibration blanks, (2) reagent blanks, (3) detection limit QCCSs, (4) low-concentration and high-concentration QCCSs, (5) matrix spikes, and (6) laboratory duplicates. The sources, compositions, and concentration ranges of these QC samples are described in Hillman et al. (1986).

- **Calibration Blank -** For each sample batch, the analytical laboratory must analyze one calibration blank for each required analyte. For each analytical procedure, the calibration blank, which is a 0-mg/L standard, is analyzed after the initial instrument calibration to check for drift in the measured signal and to check for potential contamination during the analytical process. The observed analyte concentration for the calibration blank must not exceed twice the

contract-required detection limit (CRDL) for that analyte.

intralaboratory precision limits established for these variables (see Table 4-1).

- **Reagent Blank** - A reagent blank is required for dissolved SiO_2 and total aluminum analyses because additional reagents are added during a digestion step prior to analysis. The reagent blank comprises all the reagents (in the same volumes) used in preparing a lake sample for analysis. The reagent blank and lake samples are carried through the same preparation steps (e.g., digestions) prior to analysis. Values obtained for the reagent blank must not exceed twice the CRDL for the analyte.
- **Detection Limit Quality Control Check Sample** - A detection limit QCCS (DL QCCS) is also analyzed for required variables. The DL QCCS is used to determine and verify the low end of the calibration curve and the values for the low-level samples that are near the detection limits. The DL QCCS concentration must be between 2 and 3 times the CRDL. The DL QCCS is analyzed once, prior to regular sample analysis.
- **Low-Concentration and High-Concentration Quality Control Check Samples** - The analytical laboratory QCCS is a commercially or laboratory-prepared sample that is prepared from a stock solution different from the one that is used to prepare the calibration standards. The QCCS is analyzed to verify calibration at the beginning of sample analysis, after each specified number of sample analyses, and after the final sample in the batch is analyzed. The observed concentrations must be within the specified control limits.
- **Matrix Spike** - A matrix spike, which is analyzed for specified analytes in each sample batch, is a check to determine the level of analytical interference that is caused by the matrix of the water sample on a particular analyte. The analyst "spikes" (i.e., enriches) an aliquot of sample with a known quantity of an analyte and then analyzes the spiked and unspiked samples. The percentage of spiked analyte recovered (percent recovery) is then calculated to determine whether or not there is a matrix effect on the analytical value of the original sample.
- **Laboratory Duplicate** - An analytical laboratory duplicate is required for each batch of samples. A duplicate analysis is performed on one sample for each required variable in each batch to establish within-laboratory precision. The observed precision must meet the required

5.0 Sampling Strategy

5.1 Overall Sampling Strategy

The sampling strategy for selecting NSWS lakes is discussed in detail in Landers et al. (1987) and is summarized in Drou   et al. (1986).

The lakes are selected by means of a systematic, stratified design. There are three stratification factors: regions, subregions, and alkalinity classes (see Table 5-1). Each stratum is an alkalinity class within a sub-region within a region. In the Western United States (defined as NLS Region 4) all three alkalinity classes are found within each of the five subregions designated 4A through 4E, so the total number of strata in WLS-I is fifteen. Figures 5-1 through 5-6 depict the region, subregions, and alkalinity classes the strata comprise.

Table 5-1. Variables Selected for Lake Classification, Western Lake Survey - Phase I

Level	Divisions within Levels
Region	Western United States
Subregion	4A, California 4B, Pacific Northwest 4C, Northern Rocky Mountains 4D, Central Rocky Mountains 4E, Southern Rocky Mountains
Alkalinity Class	1. Alkalinity < 100 µeq/L 2. Alkalinity 100 to 200 µeq/L 3. Alkalinity > 200 µeq/L

5.2 Sampling Strategy for the Calibration Study

As a part of the overall WLS-I sampling and analytical strategy, 45 of the 455 wilderness-area lakes being studied are included in a calibration study.

Legislation restricts activities that jeopardize the pristine character of wilderness areas, and considerable precedent has been established to limit helicopter and other motorized access to such areas. However, because information obtained from WLS-I might be of great help in long-term maintenance of wilderness characteristics, the Forest Service approved helicopter access to the 45 lakes so that

the established sampling method (by helicopter) could be compared to the new method (ground access). Each calibration lake is sampled by one helicopter crew and by one ground crew. The two crews collect samples from approximately the same location (the deepest spot) on the lake. The ground crew samples the lake from a boat, then the helicopter crew samples the lake as soon as possible thereafter (optimally, within 1 hour). The ground crew collects a routine sample and a duplicate sample; the helicopter crew collects a routine sample, a duplicate sample, and a triplicate sample. Both types of sampling crews use standard WLS-I sample collection techniques.

Because collecting samples by ground access is a new protocol, it is important to be certain that this protocol is applied uniformly to all WLS-I lakes. To ensure that each ground crew's sampling procedure is representative of the sampling done at all WLS-I lakes, the ground crews are not told (i.e., they are "blind" to) which lakes are calibration lakes. The helicopter sample collection procedure is a proven protocol that was tested during ELS-I; therefore, it is not necessary for the WLS-I helicopter crews to be blind to the identity of calibration lakes.

The logistics of the sampling design raised the possibility that the ground samples might arrive at the field laboratory 1 to 5 days after they were collected. Therefore, the possible effects of delayed sample preservation (or "holding time") are of interest. Three processing procedures have been developed to allow for possible delays in delivering samples from the lake site to the field laboratory and to allow the effects of different holding times to be observed. Each procedure assumes a different relationship between the sampling and arrival times of the helicopter crew's samples and the ground crew's samples.

For each of the three processing procedures, the field laboratory preserves the ground crew's samples on the collection date (or on the date the samples arrive at the field laboratory) and preserves two of the helicopter crew's samples on the collection date. The third sample collected by the helicopter crew is not preserved on the collection date. Instead, this sample, which is randomly selected from among the three samples collected by the helicopter crew, is held at the field laboratory for a specified length of time

Figure 5-1. Subregions of the Western United States that are potentially susceptible to acidic deposition, Western Lake Survey - Phase I.

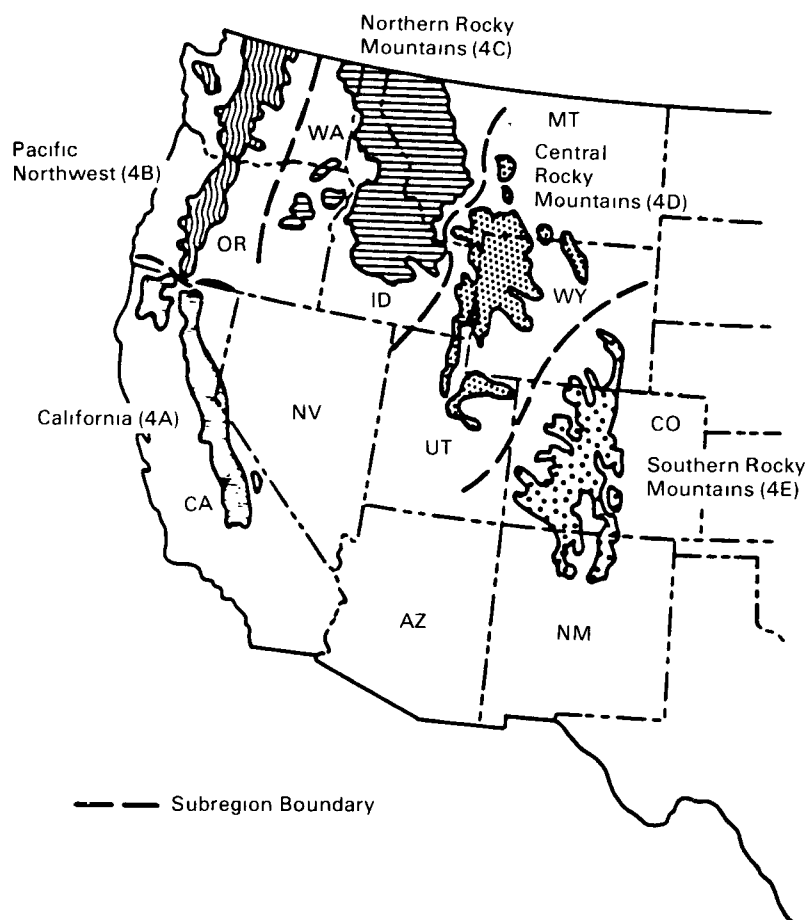


Figure 5-2. Alkalinity map of the California subregion, Western Lake Survey - Phase I.

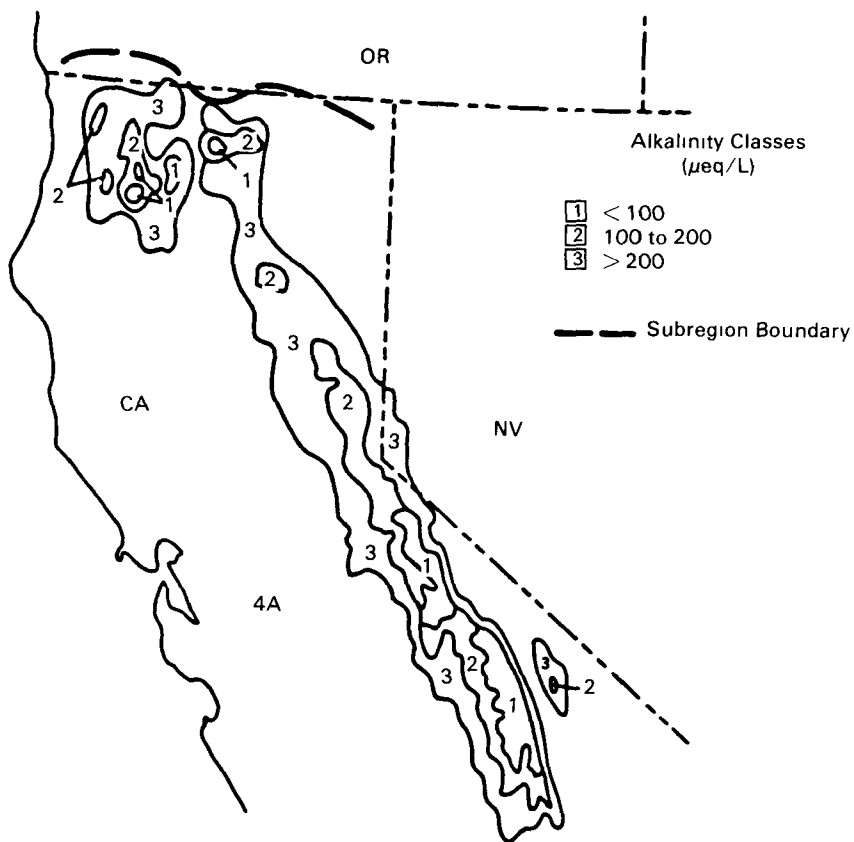


Figure 5-3. Alkalinity map of the Pacific Northwest subregion, Western Lake Survey - Phase I.

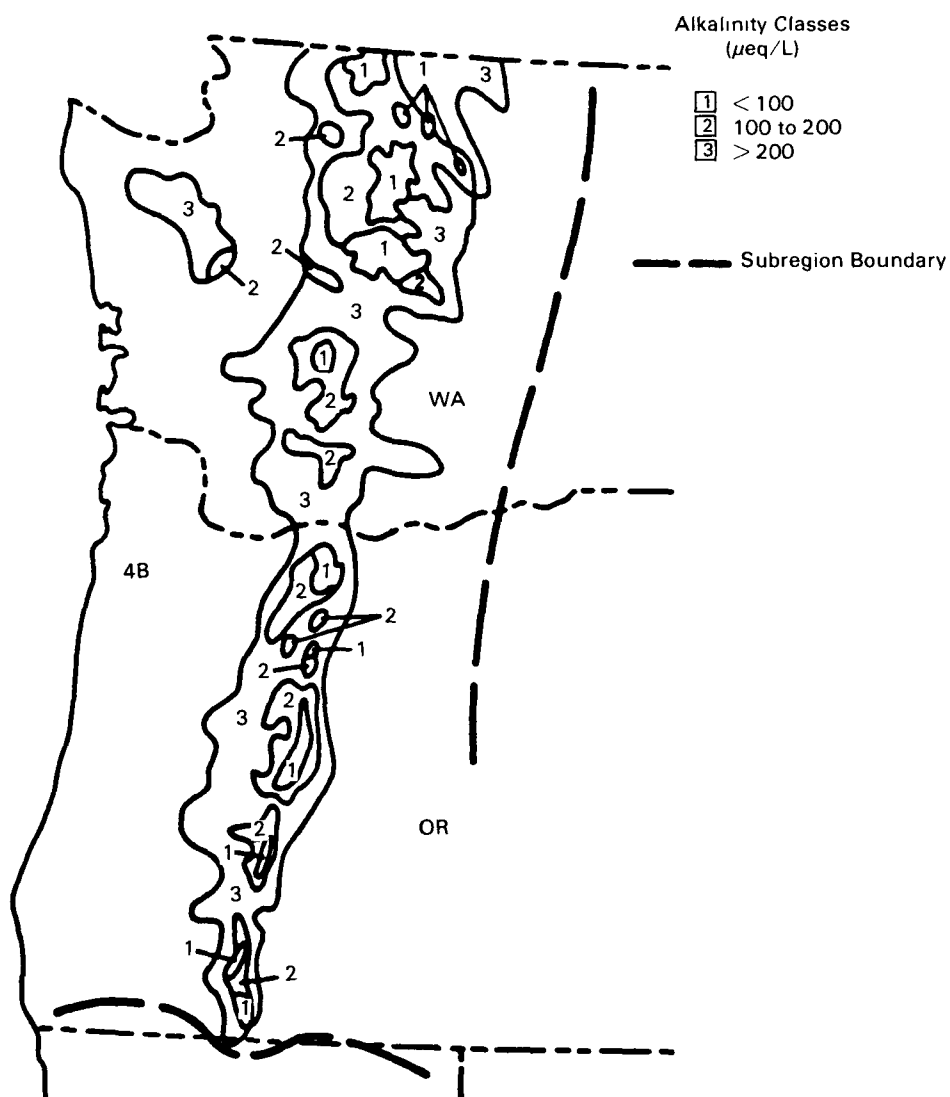


Figure 5-4. Alkalinity map of the Northern Rocky Mountain subregion, Western Lake Survey - Phase I.

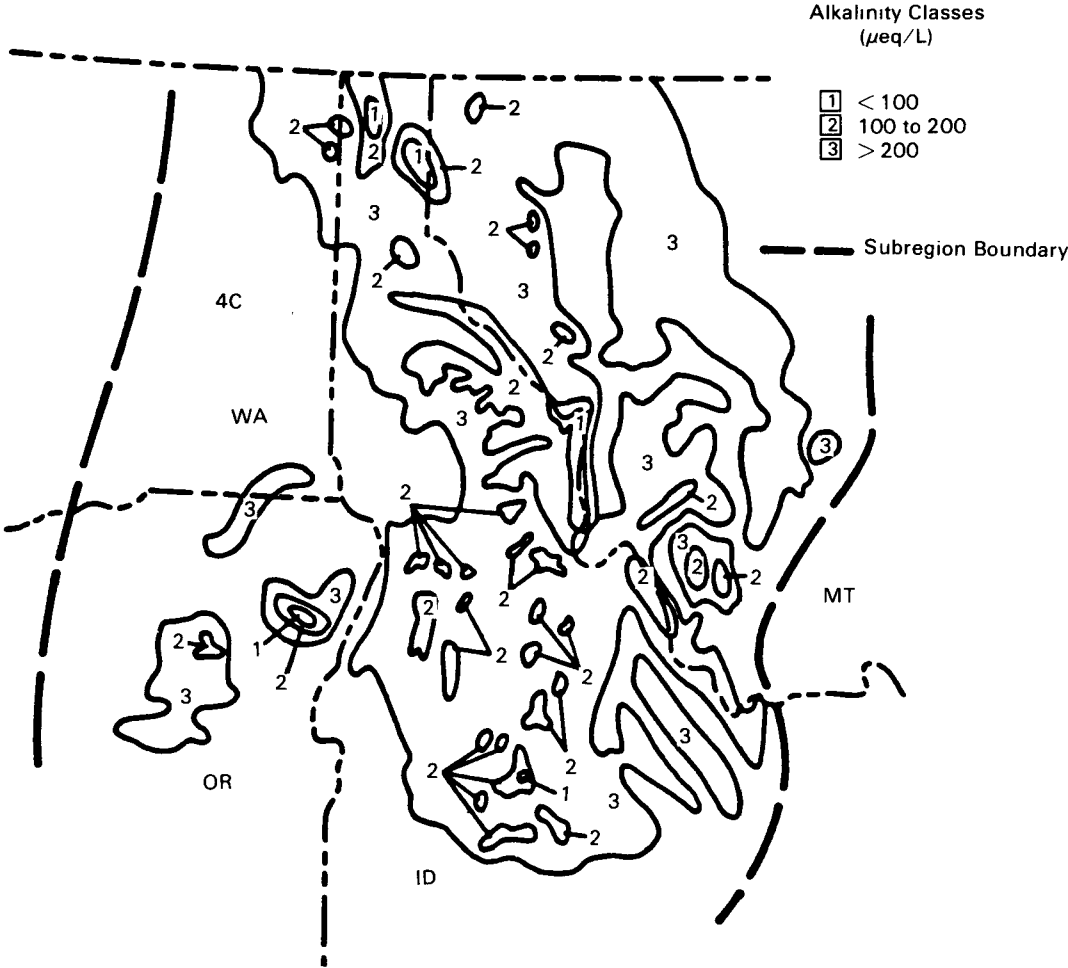


Figure 5-5. Alkalinity map of the Central Rocky Mountain subregion, Western Lake Survey - Phase I.

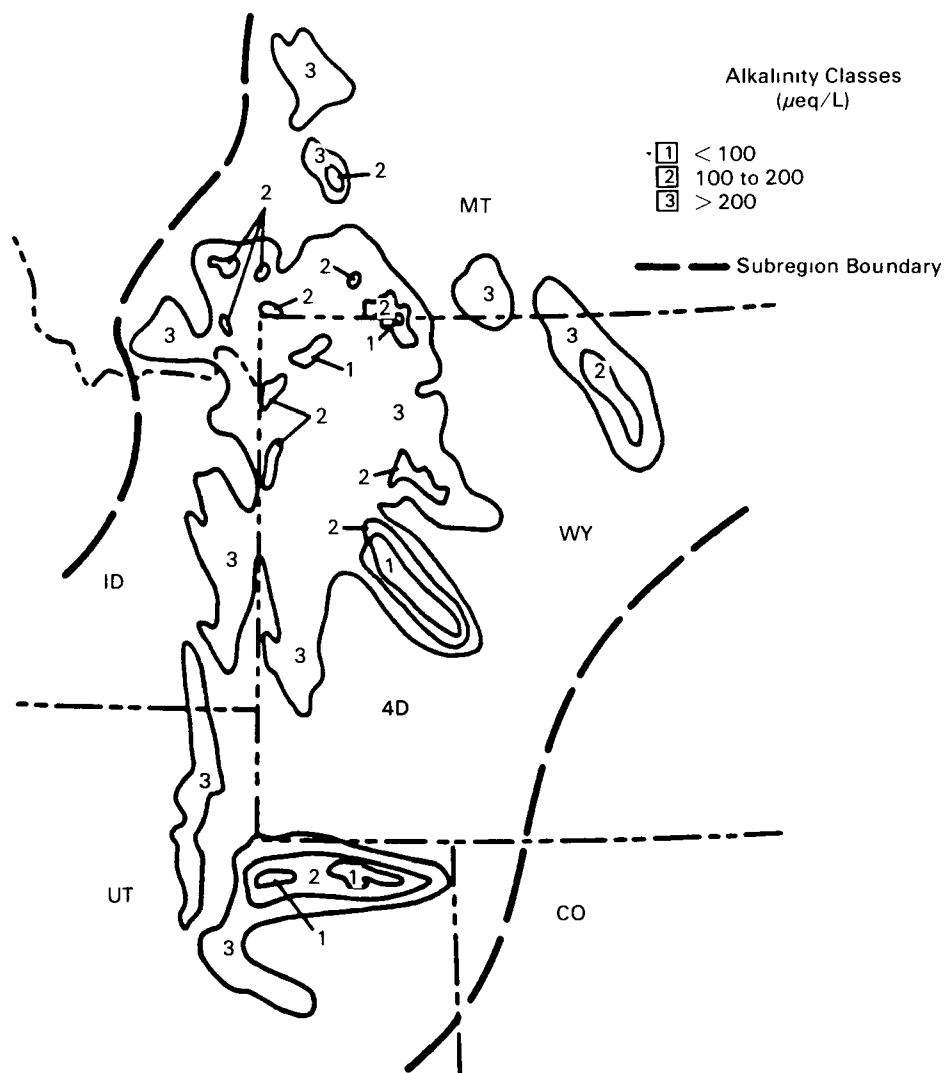
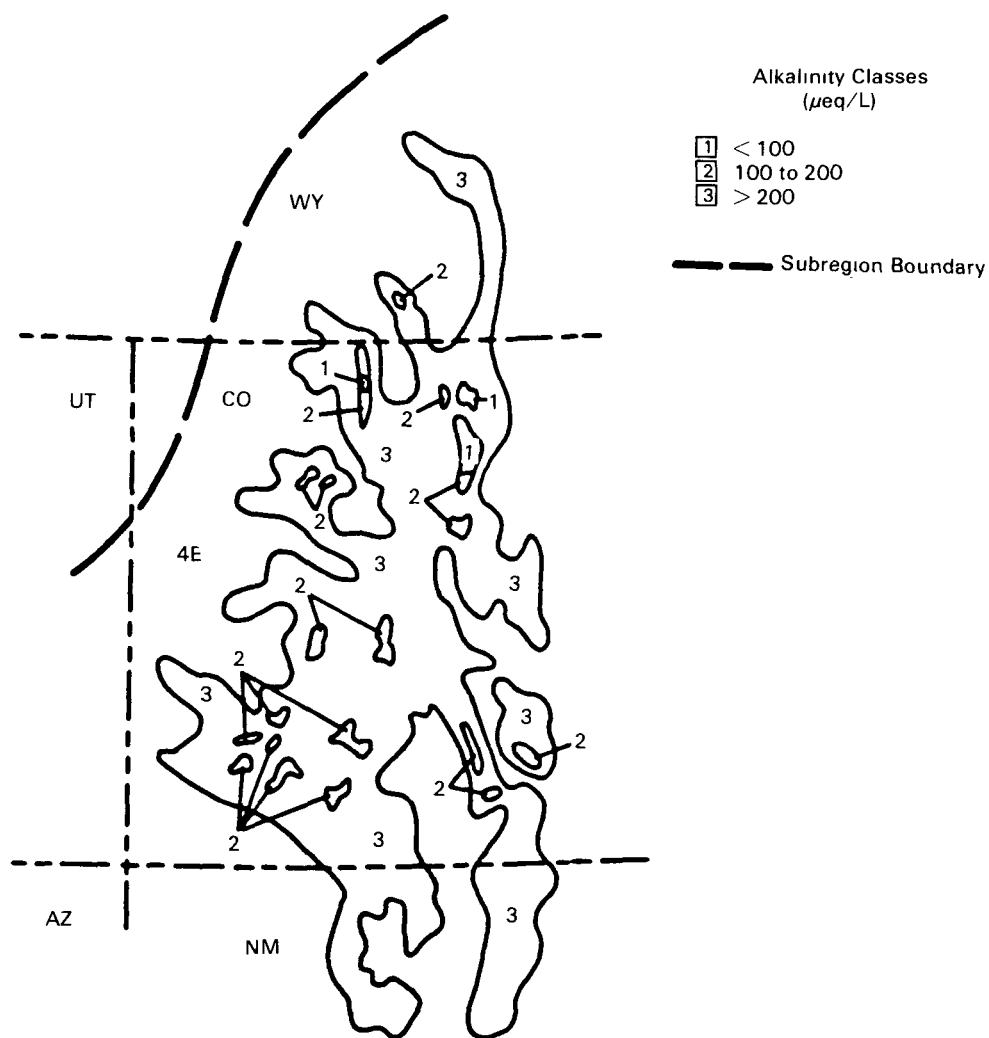


Figure 5-6. Alkalinity map of the Southern Rocky Mountain subregion, Western Lake Survey - Phase I.



before it is preserved. The holding time imposed on the withheld sample depends on which of the three processing procedures is applied.

The calibration study has also been designed to provide data that can be used to evaluate interlaboratory bias. To meet this goal, the field laboratory sends one sample from each routine/duplicate pair collected by a ground crew and one sample from each routine/duplicate triplicate set collected by a helicopter crew to each analytical laboratory.

The remaining sample from each set collected by helicopter is the one that is withheld at the field laboratory for later processing and preserving; the assignment of a sample (routine, duplicate, or triplicate) to a particular analytical laboratory is made randomly and individually for every pair or set of samples. Figure 5-7 illustrates the sample assignment procedure that is used.

Specific sample codes are recorded on NSWS Form 2 - Batch/QC Field Data, Figure 5-8, (1) to distinguish the calibration lake samples from the routine lake samples, (2) to distinguish samples collected by the helicopter crews from samples collected by the ground crews, and (3) to distinguish helicopter samples withheld for later processing from samples processed on the day of sample collection.

Samples collected by the ground crews are coded RGC (routine ground calibration) and DGC (duplicate ground calibration). The samples collected by the helicopter crews are coded RHC (routine helicopter calibration), DHC (duplicate helicopter calibration), and THC (triplicate helicopter calibration) on the batch/QC form. A "W" is added after the last letter of one of the helicopter sample codes to indicate that the sample is being withheld (e.g., if the RHC sample is withheld, it is coded RHCW on the batch form).

When the calibration lake samples collected by the helicopter crew arrive at the field laboratory, they are separated into batches, are assigned identification (ID) numbers, and are shipped to the analytical laboratory. This process is shown in Figure 5-9. The laboratory coordinator uses the random selection procedure mentioned above to determine (1) which sample to withhold at the field laboratory (at 4 °C in the dark), (2) which samples to process with the corresponding samples collected by the ground crew, and (3) which analytical laboratory analyzes each sample.

Thus, the five samples collected from a single calibration lake are processed in three different batches: one sample collected by the helicopter crew and one sample collected by the ground crew are

incorporated in the sample batch that is sent to the "regular" analytical laboratory (the laboratory to which the field base ships its usual, daily sample batch). One sample collected by each crew is incorporated into the sample batch that is sent to the "alternate" analytical laboratory (the laboratory used regularly by another field base). The last sample (the withheld sample designated from among the samples collected by the helicopter crew) is kept at the field base for incorporation into a sample batch shipped on a different day.

Calibration lake samples that are incorporated in the daily sample batch to be shipped to the regular analytical laboratory receive appropriate batch and sample ID numbers. A complex batch and sample numbering scheme is necessary to enable calibration samples to be associated with their QA samples in the data verification step. For the two or three calibration lake samples that constitute a batch that will be sent to the alternate laboratory, the laboratory coordinator obtains batch and sample ID numbers from the laboratory coordinator at a second field base; these numbers correspond to the batch that the second field laboratory is processing that day. This second field laboratory is called the "reference" field laboratory, and it, in turn, uses the alternate analytical laboratory of the first field laboratory as its regular analytical laboratory.

This cross-laboratory procedure allows the two or three samples destined for the alternate analytical laboratory to be incorporated into the larger daily sample batch from the reference field laboratory when the shipments from the two field laboratories are received. In this way, the two or three samples do not constitute a separate batch and, thus, do not have to be accompanied by a separate set of field blank and audit samples.

To obtain the batch and sample ID numbers for the calibration lake samples that are to be sent to the alternate analytical laboratory, the field laboratory coordinator calls the laboratory coordinator at the appropriate reference field laboratory. The reference laboratory coordinator assigns the sample ID numbers in order, according to the order of phone calls received from the requesting field laboratories.

The laboratory coordinator who is preparing the samples for shipment fills out a separate batch/QC form for the calibration samples that will be shipped to the alternate analytical laboratory. This form shows the batch ID assigned by the reference laboratory. Field laboratory data for each calibration sample are entered on the line of the batch/QC form that corresponds to the assigned sample ID. The reference field laboratory coordinator should note in the comment section on the batch/QC form which

Figure 5-7. Sample flow for the calibration study, Western Lake Survey - Phase I.

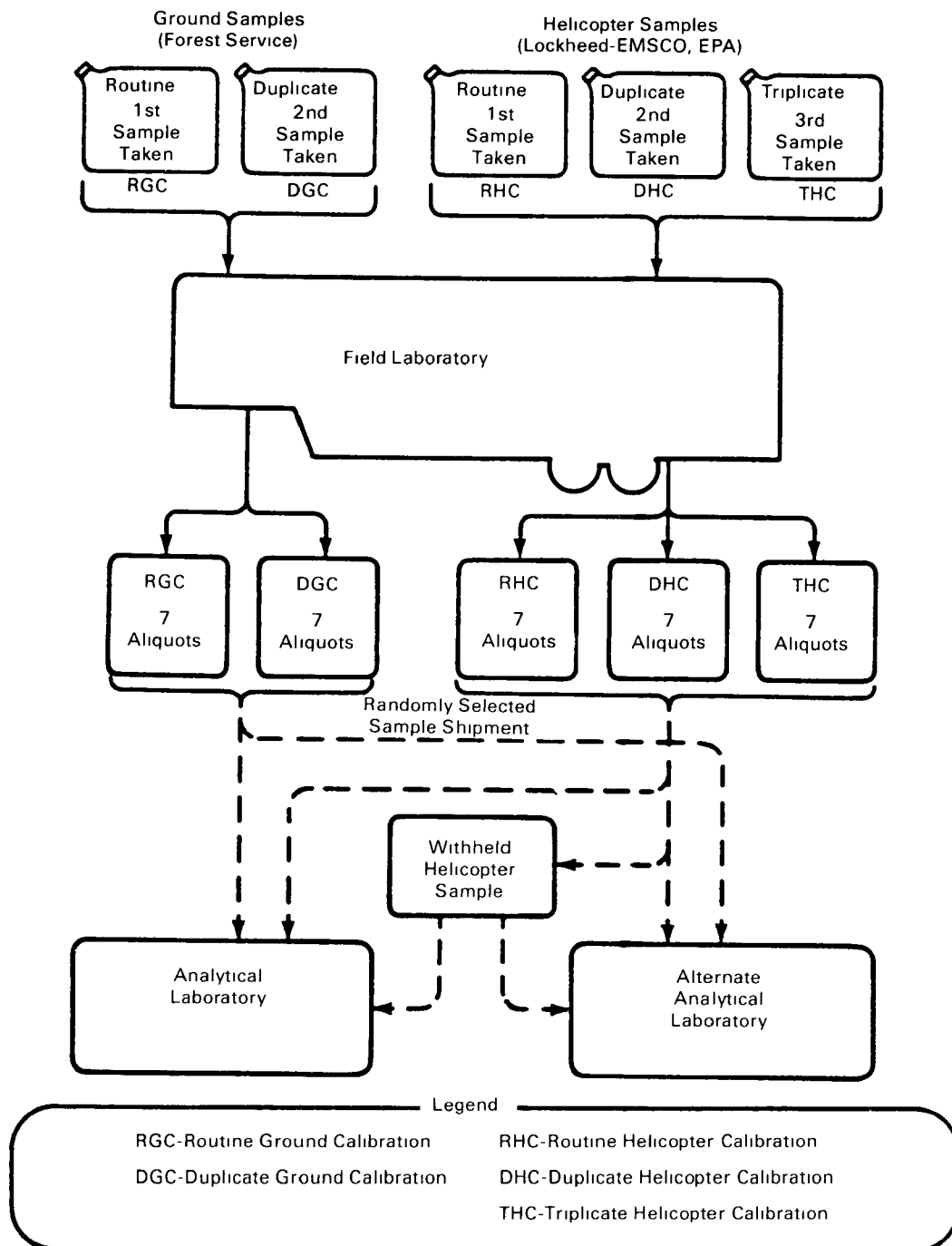


Figure 5-8. National Surface Water Survey Form 2 - Batch/QC Field Data.

National Surface Water Survey
Form 2
Batch/QC Field Data

Date Received _____
By Data Mgt _____
Entered _____
Re-Entered _____

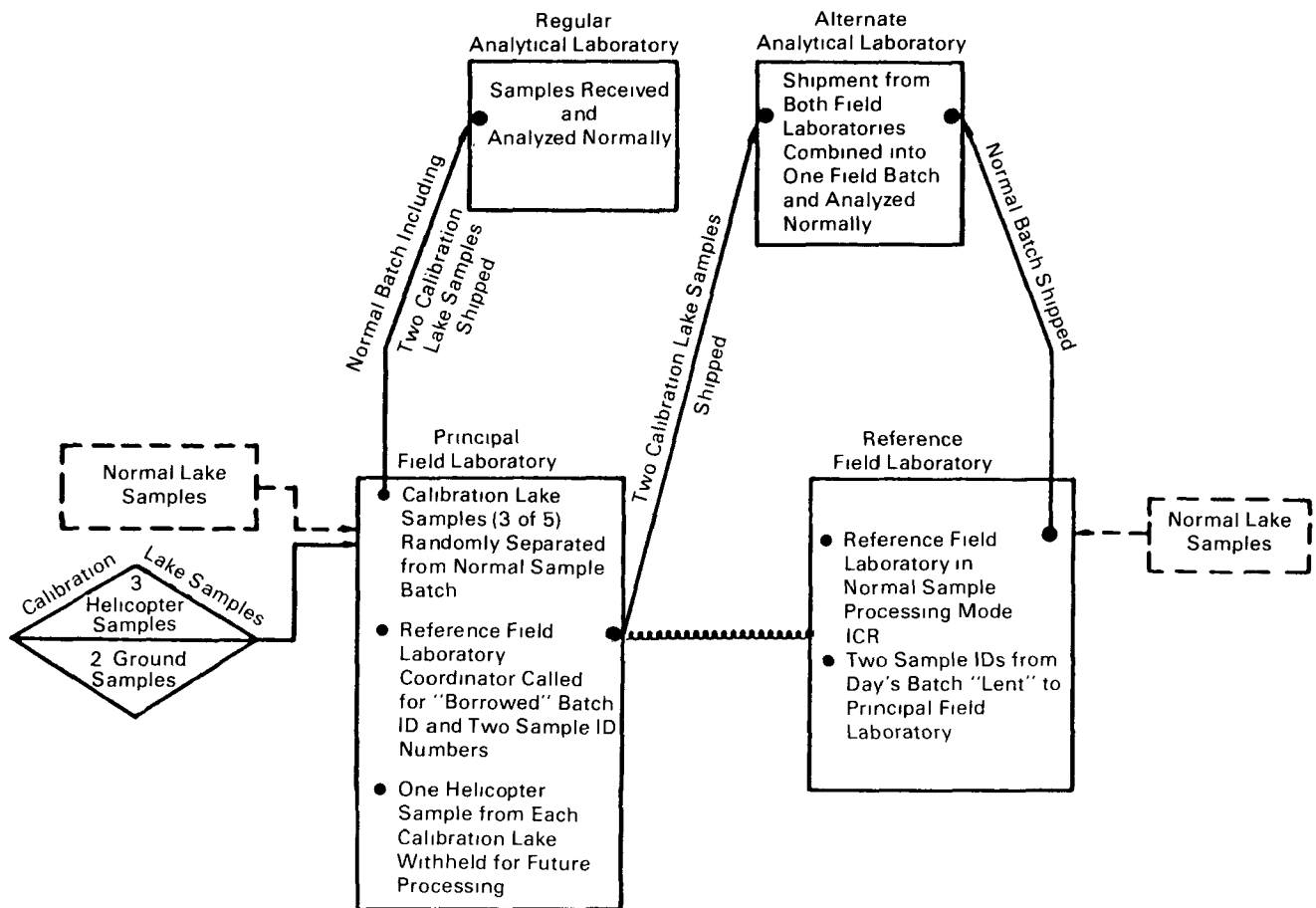
Batch ID _____		Lab to Which Batch Sent _____		Date Processed _____	
No. Samples in Batch _____		Date Shipped _____		Air-Bill No. _____	
Base Site ID _____		Lab Crew ID _____		Field Laboratory Supervisor _____	

Sample ID	Field Crew ID	Lake ID (XXX-XXX)	Sample Code	DIC (mg/L) QCCS Limits UCL--2.2 LCL--1.8		Statoin pH QCCS Limits UCL--4.1 LCL--3.9		Turbidity (NTU) QCCS Limits UCL--5.5 LCL--4.5		Color (APHA Units)	Split Codes (E L)
				Value	QCCS	Value	QCCS	Value	QCCS		
01											
02											
03											
04											
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Comments

White—ORNL Copy Yellow—Field Copy Pink—EMSL-LV Copy

Figure 5-9. Preparation, identification, and shipment of sample batches for the calibration study, Western Lake Survey - Phase I.



sample ID numbers were assigned to the other field laboratories for calibration samples. Explanation of the qualifier should be in the comments section of the batch/QC form.

6.0 Field Operations

Field operations are coordinated at field bases under the supervision of an EPA field base coordinator. Each field base contains a mobile field laboratory that is operated by a five-person crew. One or two helicopter crews operate from each field base through an EPA duty officer. Each helicopter crew makes one or more excursions to lake sites each day. Ten to fifteen ground crews operate from each base site through a Forest Service field manager. Each helicopter crew samples as many as 10 lakes per day, and each ground crew samples 1 or 2 lakes per day (or per excursion). The field base coordinator and the field manager coordinate lake sampling so that no more than 30 field samples are processed at a field base on any day to prevent an overload of samples arriving at the analytical laboratories.

Sections 6.1 through 6.3 describe the activities of the helicopter crews, the ground crews, and field base crews. Bonoff and Groeger (1987) provide a further description of field operations. Section 6.4 of this QA project plan refers to the field personnel training. Quality control checks for field measurements are presented in Section 7. Figure 6-1 depicts the flow of samples and data forms for WLS-I.

6.1 Activities of the Helicopter Sampling Crews

Activities that are conducted by the helicopter crews during WLS-I are similar to those conducted during ELS-I. Each helicopter crew consists of a pilot, an observer, a sampler, and a support person who remains at the field base. The observer's responsibility is to ensure that all measurements and sampling operations are performed correctly and that data are recorded accurately. The sampler must be qualified to operate all equipment and must follow prescribed procedures. For each excursion, the activities of each helicopter crew are divided into three sections: (1) activities at the field base prior to sampling, (2) activities en route to or at the lake site, and (3) activities at the field base after the sampling day is completed. These activities are described in the following three subsections. A flowchart of helicopter field crew activities is shown on page 29 (Figure 6-2).

6.1.1 Field Base Activities Conducted Prior to Sampling

Before leaving the field base, the helicopter crew must perform the following tasks:

- Prepare a detailed navigation sheet that gives courses and distances for the excursion and the navigational coordinates of each lake to be sampled. Preliminary information about a lake, such as latitude, longitude, and name, is supplied by ERL-C and local authorities. If possible, the location of the deepest part of each lake is predetermined (i.e., interpolated from topographic maps) and is indicated on a map as the preferred sampling site.
- File a flight plan with the field base coordinator so that sample arrival time can be predicted and so that safety requirements can be met. (Any deviations from the flight plan that occur during an excursion are relayed immediately to the field base coordinator.)
- Calibrate the Hydrolab unit, which is used to obtain pH, conductance, and temperature profiles of each lake. Hydrolab calibration data are recorded on the Hydrolab calibration form.
- Using a checklist, ensure that all the required supplies are on hand. The crew packs the supplies and loads the helicopter.

While the helicopter crew performs these operations, the pilot must carry out the following activities:

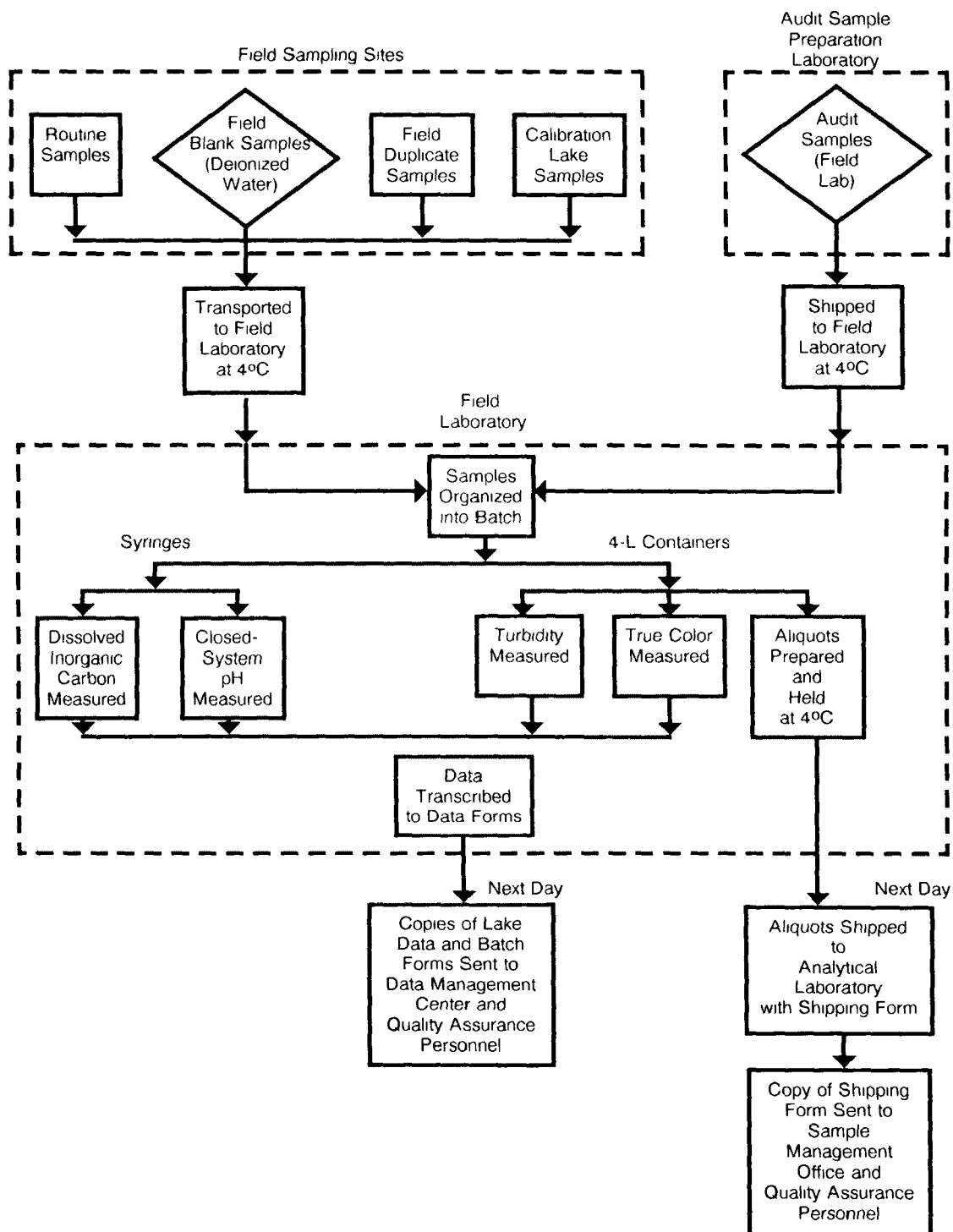
- Calibrate and program the Ioran-C.
- Confer with the mechanic about maintenance checks and possible refueling stops.

Once these steps are performed, the helicopter proceeds to the lake.

6.1.2 Lake Site Activities

As the helicopter approaches a lake, one crew member takes photographs of the area. Preceding each set of lake photographs, a photograph is taken

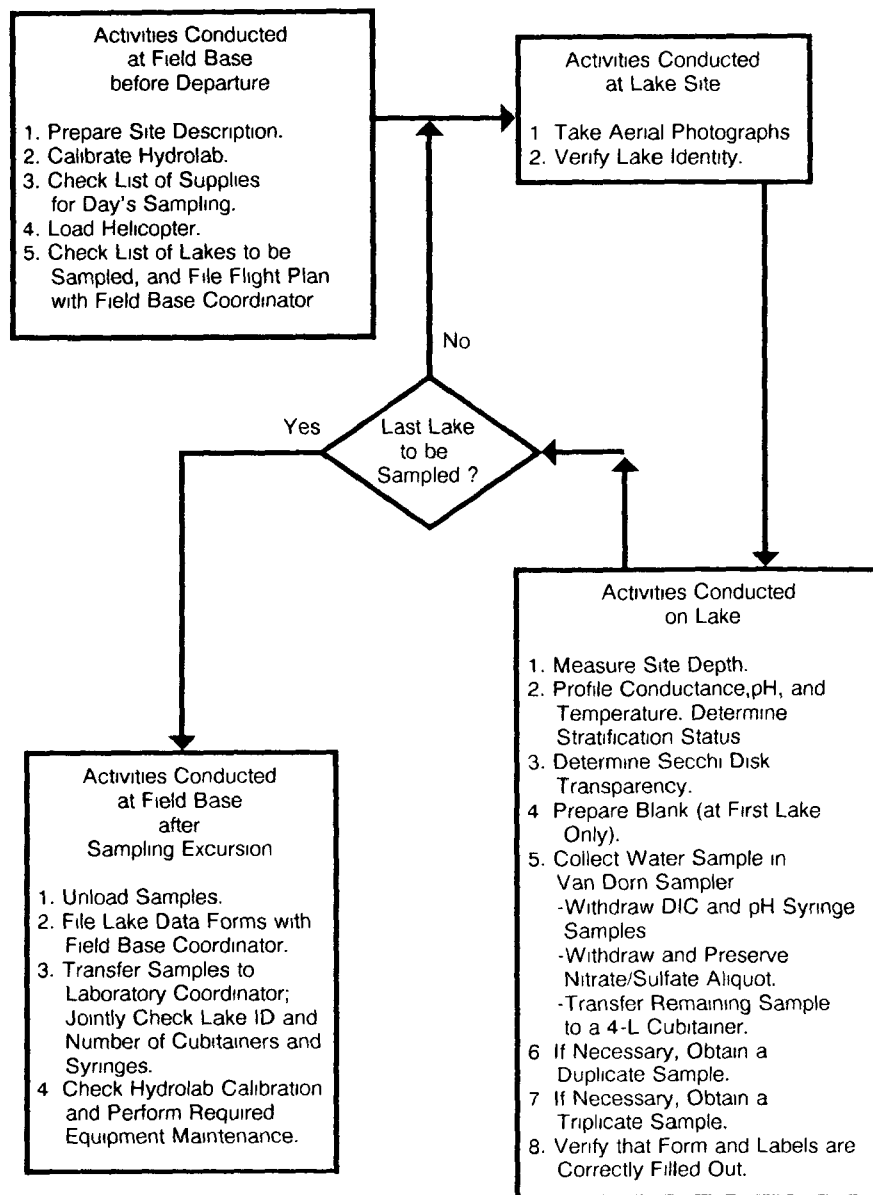
Figure 6-1. Flowchart of sampling activities, Western Lake Survey - Phase I.



of a card (lap card) that shows the date, the lake ID number, the lake name, and the crew ID. These photographs are useful as an additional check in

verifying that the correct lake was sampled. After the photographs are taken, the photograph frame numbers are written on Form 1 - Lake Data, which

Figure 6-2. Flowchart of helicopter crew activities, Western Lake Survey - Phase I.



is shown in Figure 6-3. (Table 6-1 lists the data forms and labels used in the field.) The observer notes watershed characteristics (e.g., inlets, outlets, dams, and local disturbances) that can be determined from the air. The lake data form contains an outline of the lake, sketched previously from U.S. Geological Survey (USGS) or equivalent topographic maps. The sampling location is marked on the sketch with an "X." The pilot then lands at or near the deepest part of the lake. This point is determined by using a combination of visual observations from the air and the electronic depth recorder.

When the helicopter crew arrives at the given coordinates, the members may find conditions that require special procedures. No sample is taken if there is found to be: (1) no lake, (2) more than one lake, (3) a stream or other flowing water, (4) a lake too shallow (<0.75 m) to allow a debris-free water sample to be obtained, (5) an inaccessible lake, (6) a lake with high conductance ($>1500 \mu\text{S}\cdot\text{cm}$), (7) a frozen lake, (8) an urban or industrial site, (9) a stock pond (i.e., agricultural watering pond), or (10) no permission for access. For a multilobed or dendritic lake, the observer determines the location of the best

Figure 6-3. National Surface Water Survey Form 1 - Lake Data.

National Surface Water Survey Form 1 Lake Data				Date _ _ . _ _ . _ _ D M M Y																																											
<input type="checkbox"/> Helicopter <input type="checkbox"/> Ground Team				Sampling Time _ _ : _ _ h Meter ID: _ _ _																																											
State _ _		Lake ID _ _		Lake Name _ _ _ _ _		Initial _ _ _ _ pH Final _ _ _ _ pH Initial _ _ _ _ μ S Final _ _ _ _ μ S																																									
Map Coordinates _ _		Loran Readings _ _		Altimeter _ _ _ _																																											
Lat _ _		Lat _ _																																													
Long _ _		Long _ _																																													
Photographs _ _		Disturbances Within 100 Meters of Shore																																													
Frame ID _ _		<input type="checkbox"/> Roads <input type="checkbox"/> Livestock <input type="checkbox"/> Mines/Quarries <input type="checkbox"/> Fire <input type="checkbox"/> Dwellings <input type="checkbox"/> Industry <input type="checkbox"/> Logging <input type="checkbox"/> Other																																													
Azimuth _ _		Secchi Depth Disappear _ _ m Reappear _ _ m																																													
Lap Card _ _		Site Depth _ _ ft Site Depth (ft) \times 0.3048 m/ft = _ _ m Air Temp _ _ °C																																													
Lake Stratification Data																																															
Depth _ _ T°C _ _ 1 5m _ _ _ _ Bottom-1 5m _ _ _ _ Δ T°C (1 5, B-1 5m) _ _				μ S _ _ pH _ _ If Δ > 4°C Proceed _ _ If Not, Stop Here																																											
Site Depth _ _ T°C _ _ Δ T°C (1 5, 0 6 Depth) _ _				μ S _ _ pH _ _ If Δ T > 4°C Fill In Following Data Block																																											
Lake Diagram (from topographic map) Elevation _ _ ft Outlets () _ _ Inlets () _ _ Reservoir _ _ Verified by _ _ _ _ _				Site Depth Check One T°C <input type="checkbox"/> \leq 20m <input type="checkbox"/> >20m																																											
				<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th>Site Depth</th> <th>Check One</th> <th>T°C</th> <th>μS</th> </tr> </thead> <tbody> <tr><td>4</td><td>5</td><td>_ _</td><td>_ _</td></tr> <tr><td>6</td><td>10</td><td>_ _</td><td>_ _</td></tr> <tr><td>8</td><td>15</td><td>_ _</td><td>_ _</td></tr> <tr><td>10</td><td>20</td><td>_ _</td><td>_ _</td></tr> <tr><td>12</td><td>25</td><td>_ _</td><td>_ _</td></tr> <tr><td>14</td><td>30</td><td>_ _</td><td>_ _</td></tr> <tr><td>16</td><td>35</td><td>_ _</td><td>_ _</td></tr> <tr><td>18</td><td>40</td><td>_ _</td><td>_ _</td></tr> <tr><td>20</td><td>45</td><td>_ _</td><td>_ _</td></tr> <tr><td></td><td>50</td><td>_ _</td><td>_ _</td></tr> </tbody> </table>				Site Depth	Check One	T°C	μ S	4	5	_ _	_ _	6	10	_ _	_ _	8	15	_ _	_ _	10	20	_ _	_ _	12	25	_ _	_ _	14	30	_ _	_ _	16	35	_ _	_ _	18	40	_ _	_ _	20	45	_ _	_ _
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	50	_ _	_ _																																												
Comments <input type="checkbox"/> Not Sampled, See Below				Data Qualifiers (A) Instrument Unstable (B) Redone, First Reading Not Acceptable (C) Instruments, Sampling Gear Not Vertical in Water Column (D) Slow Stabilization (E) Cable Too Short ● Do Not Meet QCC < Sample Collected at 0.5m (X) (Y) (Z) Other (explain in Comments section)																																											
Reason Lake Not Sampled (Check) <input type="checkbox"/> Flowing Water <input type="checkbox"/> Inaccessible <input type="checkbox"/> No Access Permit <input type="checkbox"/> Urban/Industrial <input type="checkbox"/> Frozen <input type="checkbox"/> High Cond. (> 1500 μ S) <input type="checkbox"/> Non-Lake <input type="checkbox"/> Too Shallow <input type="checkbox"/> Stock Pond <input type="checkbox"/> Other _ _ _																																															
Field Lab Use Only				Field Crew Date																																											
Trailer ID _ _ _ _ Batch ID _ _ _ _ Sample ID (Routine) _ _ _ _ Date Received _ _ _ _ Time Received _ _ _ _				Helicopter ID _ _ Crew ID _ _ Observer (Print) _ _ _ _ _ Sampler (Print) _ _ _ _ _ Obs Sign _ _ _ _ Ground Crew Member _ _ _ _ _																																											
				Form Distribution White Copy—ORNL Pink Copy—EMSL-LV Yellow Copy—Field																																											

Table 6-1. Data Forms and Labels Used in the Field, Western Lake Survey - Phase I

Data Form Number	Description	Location of Facsimile
1	Lake Data Form	Figure 6-3
2	Batch QC/Field Data Form	Figure 5-8
3	Shipping Form	Figure 6-11
-	Hydrolab Calibration Form	-
-	Sample Tracking and Custody Form	Figure 6-8
-	Field Sample Label	Figure 6-5
-	Field Audit Sample Label	Figure 6-10
-	Aliquot Label	Figure 6-6

sampling site, following specific guidelines; for small lakes, sampling procedures are modified.

The rotor wash of the helicopter can create a surficial disturbance. The disturbance is normally away from the sampling point and is minimized by the pilot's positioning of the helicopter.

While the pilot maintains position by visual reference to landmarks or an anchored buoy, as conditions dictate, the sampler must perform the following operations in the order given:

1. Measure the lake depth at the sampling site with a calibrated sounding line, then record the result on the lake data form.
2. Use the Hydrolab to profile the pH, conductance, and temperature measured at 1.5 m below the surface and at 1.5 m above the lake bottom. (In shallow lakes, only one set of readings is taken, at 0.75 m.) If the temperature difference exceeds 4°C, the sampler takes a third set of measurements at 60 percent of the lake depth. If the temperature difference between the top and the 60 percent depth is <4°C, the lake is classified as weakly stratified. If the temperature difference exceeds 4°C, the lake is considered to be strongly stratified. In a strongly stratified lake, the sampler obtains a temperature and conductance profile at 5-m intervals for lakes greater than 20 m deep and at 2-m intervals for lakes less than 20 m deep. Figure 6-4 shows how the profile is taken and how the stratification is determined. The sampler records the results on the lake data form.
3. Measure the Secchi disk transparency by lowering a Secchi disk secured on a calibrated line into the water on the shady side of the

helicopter until the disk disappears from view, then raising the disk until it reappears. The observer records both of these depths on the lake data form. Their average is the Secchi disk transparency. If the Secchi disk is still visible when it rests on the bottom of the lake, the observer does not enter a reappearance depth on the lake data form but makes an explanatory notation in the comments section of the form. The observer must not wear sunglasses unless they have photogray prescription lenses. If sunglasses are worn, the observer makes a notation of this in the comments section of the form. In addition, any conditions such as glare, choppy water, or other physical interferences that are hindrances to taking the reading are documented on the lake data form.

4. Collect the sample from the upwind side of the helicopter, where the potential for contamination from engine exhaust is minimal. The sampler rinses the 6.2-L Van Dorn sampling unit with surface water, lowers the unit to 1.5 m below the lake surface, triggers it to collect a sample, raises it to the surface, then sets it on the pontoon platform in a vertical position. This position prevents the sample from leaking out and prevents air from leaking in. It is imperative that air is not introduced before step 5 is performed.
5. Take DIC and pH syringe samples from the Luer-Lok syringe port on the Van Dorn sampling unit. The sampler uses a 60-mL syringe equipped with a valve to withdraw a 20-mL aliquot, rinses the syringe with this aliquot and discards the rinse, then withdraws a 60-mL aliquot and seals the syringe. Repeating the procedure, the sampler obtains a second syringe sample. The sampler fills out field sample labels (see Figure 6-5), excluding "Batch ID" and "Sample ID" which are assigned at the field base, and attaches the labels to the syringes. After labeling the syringes, the sampler places them in a plastic bag and stores them in the cooler (maintained at 4°C).
6. Prepare the Cubitainer sample. The sampler rinses a clean 4-L Cubitainer with three 500-mL portions of sample, fills it with as much sample as possible, compresses it to remove all headspace, then caps it securely. The field sample label is attached and completed. After it is labeled, the Cubitainer is stored with the syringes in the cooler.
7. Collect a duplicate sample. At the first lake sampled each day, one helicopter crew from each field base (as assigned by the field base coordinator) collects a duplicate sample by

Figure 6-4. Determination of temperature stratification class and lake temperature profile, Western Lake Survey - Phase I.

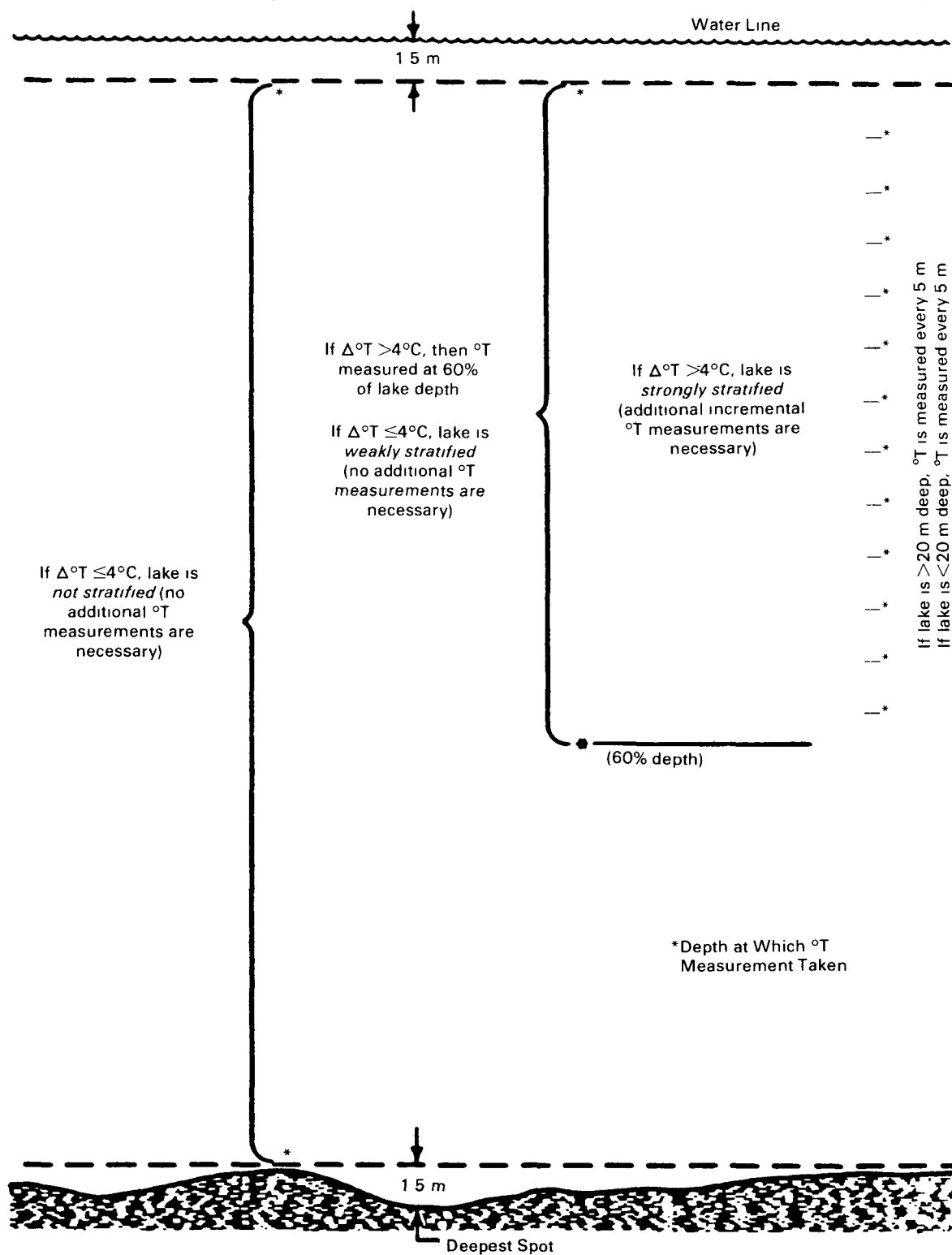


Figure 6-5. Field sample label, Western Lake Survey - Phase I.

Lake ID _____	Crew ID _____
Date Sampled _____	Time Sampled _____
Sample Type (Check One) Routine _____ Duplicate _____ Blank _____	
Batch ID _____	Sample ID _____

repeating steps 4 through 6. On the label, sample type "Duplicate" is checked.

8. Collect a field blank sample. Each helicopter crew prepares one field blank at the first lake sampled each day before collecting the routine sample. In place of step 4, the sampler rinses the Van Dorn sampling unit with three 200-mL portions of deionized water, then fills it with deionized water. Step 5 is omitted, and step 6 is performed as for a lake sample. The sample type "Blank" is checked on the label.
9. Collect and preserve the nitrate/sulfate aliquot (the EMSL-LV split sample). Helicopter crews collect nitrate/sulfate aliquots at calibration lakes only.

The sampler must prepare one 125-mL aliquot as follows:

- Complete and affix an aliquot label (see Figure 6-6) to a 125-mL Nalgene bottle. Fill the bottle to the shoulder with sample from the Van Dorn.
- Using a dropper bottle, add 2 drops (0.1 mL) of a 5 percent solution of reagent-grade mercuric chloride (HgCl_2) to the aliquot bottle, record the amount of preservative used on the aliquot label, cap the aliquot bottle tightly,

and invert the bottle several times to mix the contents.

- Tape the cap on with electrician's tape, and place the bottle in a plastic bag in the cooler for transport.
10. Upon completion of steps 1 through 9, rinse the Hydrolab sonde and the Van Dorn sampler with deionized water, and store them securely in the helicopter. The observer verifies that the lake data form is properly completed and that all sample containers are correctly labeled.
 11. The helicopter proceeds to the next lake, where the same lake site activities are performed. When time or weather conditions necessitate, the helicopter returns to the field base. The helicopter is refueled, when necessary, at remote airports or by fuel truck. In some cases, where sampling sites are more than 150 miles from the field base, remote bases are established. The helicopter and its crew remain at the remote base overnight, but the samples are flown to the field base by fixed-wing aircraft.

6.1.3 Field Base Activities Conducted at the End of the Sampling Day

Upon the return of the helicopter crew to the field base, the field samples are transferred to the laboratory coordinator. The Hydrolab calibration is checked at the end of each day. Any instrumental drift is noted on the calibration form and on the lake data form, and the affected data are qualified appropriately. If a drift problem is significant and a reliable Hydrolab is available, the faulty Hydrolab is not used on the next sampling day. The manufacturer's instructions for care and maintenance of the pH meter and electrode are followed. The rechargeable batteries are charged overnight, and the electrodes are stored in tap water or 3M KCl.

All lake data forms are checked for consistency. After supplies and equipment are checked and are stored for the next sampling day, the helicopter crew, duty officer, and field base coordinator participate in a debriefing to discuss the day's activities and to prepare for the next day's sampling activities.

6.2 Activities of the Ground Sampling Crews

Each ground sampling crew is composed of two samplers. Depending on the circumstances (i.e., lake location and availability of pack animals), as many as three logistics support personnel may aid in carrying equipment to the lake. A local Forest Service expert travels with the samplers to ensure that the proper lake is located. Both samplers must be qualified to

Figure 6-6. Aliquot label, Western Lake Survey - Phase I.

Aliquot	_____
Batch ID	_____
Sample ID	_____
Date Sampled	_____
Preservative	_____
Amount	_____
Parameters	_____

Note. The aliquot number, preservative, and parameters are preprinted on the aliquot labels

operate all equipment and must follow prescribed procedures. For each excursion, the activities are divided into those conducted (1) at the field base (or remote base) prior to sampling, (2) en route to or at the lake site, and (3) after lake-site activities are completed (see Figure 6-7).

6.2.1 Field Base Activities

Before leaving the field base (or remote base), ground crews perform the following tasks:

- Check and calibrate the temperature meter (see Section 7.2.1).
- Check and pack the equipment and supplies necessary for the sampling excursion. Sample containers are prepackaged into kits for each lake. Sampling crews should obtain additional kits as reserves and in case additional QA samples (including field blanks) are required for a given excursion.
- Coordinate the sampling plan with the field manager, and file an appropriate sampling itinerary. The itinerary includes the estimated duration of the excursion, a check-in schedule, and, when applicable, the location of overnight stops and a time and location for samples to be transferred for delivery to the field laboratory.

6.2.2 Lake Site Activities

6.2.2.1 Verification of Lake Location--

The ground crew must verify the map coordinates of the lake as follows:

- Compare the lake shape to that shown on the map (USGS 7.5 minute topographic map or equivalent).
- Determine the position of the lake relative to identifiable topographic features shown on the map.
- Determine the position of the lake by compass triangulation on suitable landmarks.
- Use maps other than USGS topographic maps (e.g., Forest Service maps) to confirm the lake location.
- Obtain assistance from a local person (usually from the Forest Service) who is familiar with the area.

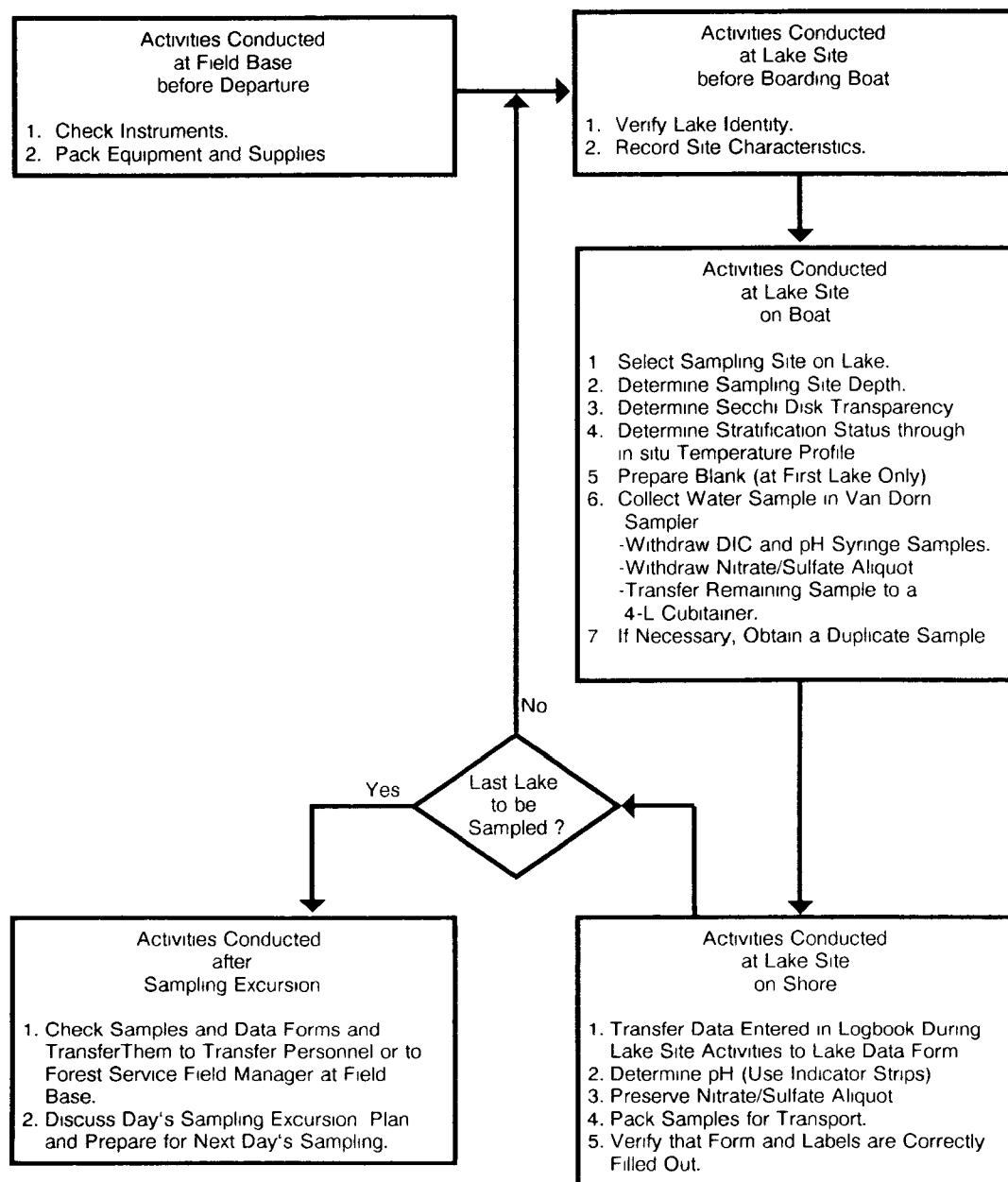
If the lake in question is confirmed as the proper lake to be sampled, the ground crew completes the site description portion of the data in the field logbook. When exceptional conditions are found at the given coordinates, the ground crew follows the same procedures as the helicopter crews follow. These procedures are listed in Section 6.1.2.

6.2.2.2 On-Shore Activities--

The ground crew must perform the following on-shore activities prior to sampling:

- Collect and clean rocks (if available) for use as an anchor.
- Inflate the boat, and load the equipment and supplies.

Figure 6-7. Flowchart of ground crew activities, Western Lake Survey - Phase I.



- Complete field sample and nitrate/sulfate aliquot labels (except for "Batch ID" and "Sample ID") for all samples to be collected.
- Record site description information on the lake data form provided in the field logbook.
- Check the operation of the temperature meter according to the directions in the operations manual for the instrument.
- Check the calibration of the temperature meter and thermistor as described in Section 7.2.1.

6.2.2.3 On-Lake Activities--

On the lake, the ground crew locates the part of the lake that is estimated to be the deepest and, if weather conditions require, anchors the boat. The crew then must perform the following operations:

1. Measure the depth at the sampling site. Use a weighted calibrated sounding line, and record the result on the lake data form in the field logbook.
2. Profile the temperature at 1.5 m below the lake surface and at 1.5 m above the bottom by lowering the thermistor probe to the proper depth, allowing the reading to stabilize, and recording the temperature on the data form in the field logbook. In shallow lakes (less than 3 m deep), the temperature is measured at 0.75 m below the surface.

If the temperature difference between the two depths exceeds 4°C, the crew takes a third measurement at 60 percent of the lake depth. If the temperature difference between the top and the 60-percent depth is less than 4°C, the lake is classified as weakly stratified. If the temperature difference exceeds 4°C, the lake is considered to be strongly stratified. In a strongly stratified lake, a temperature profile is obtained at 5-m intervals for lakes greater than 20 m deep and at 2-m intervals for lakes less than 20 m deep (see Figure 6-3).

3. Measure the Secchi disk transparency of the water on the shady side of the boat. The samplers in boats use the same procedure for this measurement as the samplers in helicopters do; the procedure is described in Section 6.1.2, step 3.
4. Collect samples of the same types as helicopter crews collect (see Section 6.1.2, step 4). The ground crews, however, collect a nitrate/sulfate aliquot for every routine, duplicate, and blank sample they collect. Also, a crew member fills a 10-mL vial with lake water from the Van Dorn sampler for pH determination on shore.

6.2.2.4 On-Shore Activities After Sample Collection--

On shore, following sample collection, the ground crew performs the following activities:

1. Measure the pH of the samples. Because neither pH meters nor Hydrolabs are available to the ground crew, a crew member makes on-site pH determinations with ColorpHast pH indicator strips that cover two pH ranges (4.0 to 7.0 and 6.5 to 10.0). The crew member places a pH indicator strip in the vial, allows the color to develop for 10

minutes, compares the color of the strip to the color chart, and records the pH value on the lake data form in the field logbook.

2. Preserve the nitrate/sulfate aliquot (split) by adding two drops (0.1 mL) of a 5 percent solution of reagent-grade HgCl_2 ; then tape the cap on the aliquot bottle with electrician's tape.
3. Pack the Cubitainers, syringes, and split samples in coolers with frozen gel packs and thermometers for transporting to the field laboratory.
4. Transcribe all field logbook data onto the lake data form. The member of the crew who does not transcribe the data checks the form for transcription errors.
5. Initiate a sample tracking and custody form (see Figure 6-8).

6.2.3 Activities Following Completion of Lake Site Activities

6.2.3.1 Delivery of Samples and Data Forms to the Field Laboratory--

If a ground crew returns to the field base after a sampling excursion, the crew members report to the field manager upon arrival.

- The crew transfers custody of the samples and the data forms to the field manager, who records the time of receipt and signs the custody form.
- The field manager conveys custody of forms and samples to the laboratory coordinator, who measures the temperature of each cooler and records the results on the custody form and on the appropriate lake data form. The laboratory coordinator also records the date and time of receipt of each sample on the corresponding lake data form.

NOTE: The custody form must be signed by the field manager or the field manager's designee before the field laboratory will accept samples. The field base coordinator must also be informed of sample arrivals and of the total number of samples received.

If the ground crews do not return to the field base, they are met at a pick-up point by a transfer crew.

- A member of the ground sampling crew measures the temperature of each 30-qt ice chest (or portable cooler) with a field

Figure 6-8. National Surface Water Survey Sample Tracking and Custody Form.

National Surface Water Survey Western Lake Survey Sample Tracking And Custody Form							
Base Site: _____				Date Out: _____			
Crew ID: _____				Date Returned: _____			
Number of Containers							
Lake ID	4-L Cubitaier	Syringes	Nitrate/Sulfate Aliquot	Completed Lake Data Form	Comments		
_____	_____	_____	_____	_____	_____		
_____	_____	_____	_____	_____	_____		
_____	_____	_____	_____	_____	_____		
_____	_____	_____	_____	_____	_____		
_____	_____	_____	_____	_____	_____		
_____	_____	_____	_____	_____	_____		
_____	_____	_____	_____	_____	_____		
_____	_____	_____	_____	_____	_____		

1. Relinquished by (Sampler)	Date	Time	Temps	2. Received by: (Pick-up Crew)	Date	Time	Temps
3. Received by. (Field Manager)				4. Received by (Lab Coordinator)			

Comments: _____

Copies: Base Coordinator, Field Manager, Field Lab, EMSL-LV (Comm. Ctr.)

- thermometer and records the temperature on the custody form. The field thermometer is placed in a corner of the cooler or is taped to an inner wall so that the temperature of the cooler, not of a gel pack or sample, is measured.

 - The Cubitainers, syringes, and splits are transferred to ice chests or Styrofoam coolers containing new frozen gel packs.

- The samplers give the lake data forms and custody forms to the transfer crew.
 - The transfer crew conveys any necessary supplies or information to the ground sampling crew and obtains information and supply requests from the sampling crew for the field manager.

6.3 Field Base Operations

The field base includes a fully equipped mobile laboratory that is staffed by a field laboratory coordinator, a field laboratory supervisor, and three analysts. The field laboratory coordinator is responsible for the overall operation of the laboratory (sample tracking and logistics, data, forms, safety, etc.). The field laboratory supervisor and the analysts are responsible for sample measurements made at the field base and for sample processing. If necessary, the field laboratory coordinator also assists with sample processing. This section describes the field base activities that are outlined in Figure 6-9. Section 6.3.1 refers to reagent preparation, and Section 6.3.2 describes sample processing.

6.3.1 Reagent Preparation

Reagents for aluminum extraction, DIC determination, and pH determination must be prepared before helicopter crews return with samples. Reagents used for lake-site measurements must be made as required. Detailed procedures for reagent preparations are given in Morris et al. (1985).

6.3.2 Sample Processing

The following steps describe sample processing operations. These operations fit into the sample flow as shown in Figure 6-1. They are performed in the order given.

6.3.2.1 Sample Description and Identification--

Samples are organized into batches that are processed together. A batch consists of all samples (approximately 20 to 30, including routine, duplicate, blank, split, and audit samples) that are processed at a field base on a given day. Each batch is assigned a unique batch ID number, which is recorded on the labels of all samples and of corresponding aliquots. Each sample is then randomly assigned a sample ID number as follows:

- **Routine Samples** - Three sample containers are filled at each lake, namely two 60-mL syringes (for DIC and pH determinations) and a 4-L Cubitainer. One sample ID number is assigned to all three containers and is recorded on each container label.
- **Duplicate, Triplicate, and Blank Samples** - Sample ID numbers are assigned in the same manner as for the routine samples. There are no syringe samples for the blanks.
- **Field Audit Samples** - One or two 2-L field audit samples (received each day from a central source) are included in each day's batch of samples. The label for the field audit container is

shown in Figure 6-10. Two syringes are labeled, filled, and sealed for pH and DIC determinations. The code (Table 6-2) indicates what kind of a sample it is and the concentrate lot number. A field audit sample is assigned a sample ID number in the same manner as a routine sample. The sample ID number is recorded on the label.

After the batch and sample ID numbers are assigned and are recorded on each sample label, the same information is entered on the batch/QC form. Also, the lake ID and the appropriate code for each sample (from Table 6-2) are entered on the batch/QC form.

The sample ID numbers are assigned at random to all samples in a batch, except for certain calibration lake samples (see Section 5.2). Furthermore, sample ID numbers run consecutively from 1 to the number of samples in the batch. Audit samples must not always be assigned the same sample ID number.

NOTE 1: Field audit samples are processed exactly like routine lake samples.

NOTE 2: Seven different aliquots (numbered as in Table 6-3) are prepared from each field sample (routine, duplicate, audit, and blank samples). Each aliquot is assigned the same batch and sample ID numbers as the sample from which it is prepared. (This is not always the case for all calibration lake samples: see Section 5.2). Additional aliquots are taken for split samples.

6.3.2.2 DIC Determination--

Immediately after assignment of batch and sample ID numbers, the laboratory supervisor begins the DIC analyses. DIC is determined in routine, lake duplicate, and field audit samples. The routine and lake duplicate samples are contained in sealed syringes (filled at the lake site) and are kept in refrigerators in the field laboratory at 4°C until analysis. For field audit samples, a syringe sample is taken from the refrigerated 2-L sample prior to analysis. The results are recorded on the batch/QC form. The measurement procedures are discussed in Section 7.2.1 of Drou   et al. (1986). Copies of all raw data are kept in a DIC logbook and must be sent to the QA manager when requested.

6.3.2.3 Sample Filtration, Preservation, and Aliquot Preparation--

The aliquot bottles are pre-labeled and pre-numbered before filtration and aliquot preparation begin. One analyst filters the samples in a laminar-flow hood referred to as the "clean air station"; a

Figure 6-9. Flowchart of daily field base activities, Western Lake Survey - Phase I.

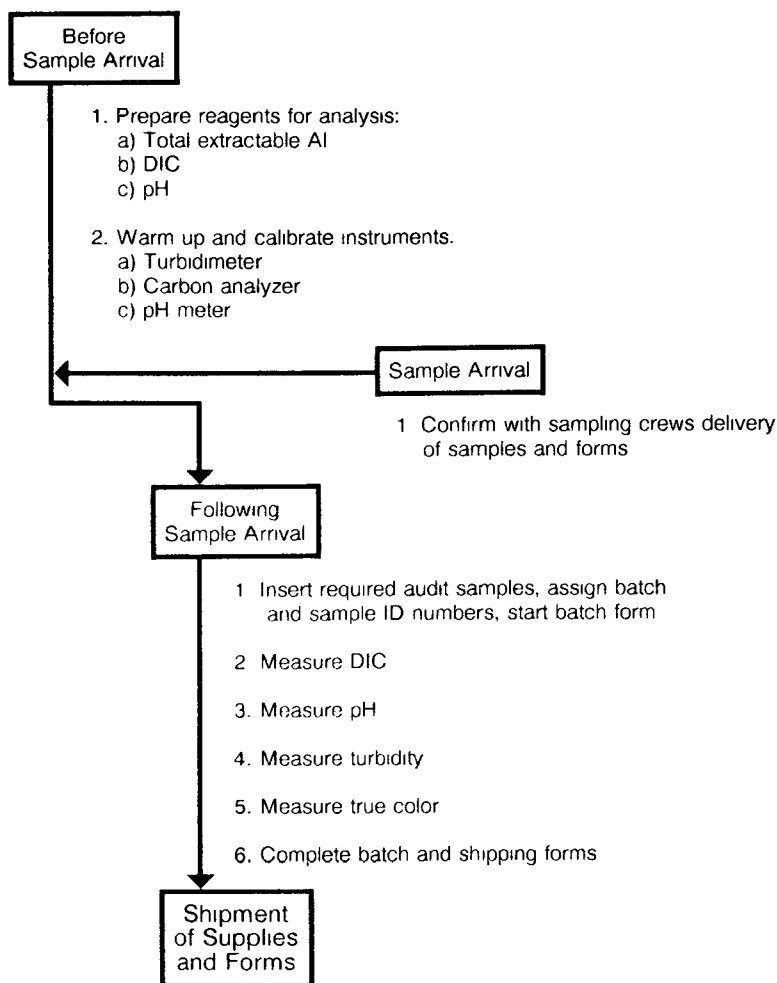


Figure 6-10. Field audit sample label, Western Lake Survey - Phase I.

Field Audit Sample	
Radian ID No	
Date Shipped	Date Received
Code	
Batch	ID

**Table 6-2. Sample Codes Used to Complete Lake Data Forms,
Western Lake Survey - Phase I**

Sample Type	Code	Description
Normal ^a	RH	Routine lake sample - helicopter
	RG	Routine lake sample - ground
	DH	Duplicate lake sample - helicopter
	DG	Duplicate lake sample - ground
	BH	Field blank - helicopter
	BG	Field blank - ground
	TB	Field laboratory (trailer) blank
	TD	Field laboratory (trailer) duplicate
Calibration Study ^a	RHC ^b	Routine calibration - helicopter
	DHC ^b	Duplicate calibration - helicopter
	THC ^b	Triplicate calibration - helicopter
	RGC	Routine calibration - ground
	DGC	Duplicate calibration - ground
Audit	<div><div><div><div>F</div><div>L</div><div>1-001</div></div><div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div></div><div>Radian ID number</div><div>Concentrate (or lake) lot number</div><div>Natural or synthetic (concentration level)</div><div>N = natural L = low synthetic</div><div>Type of audit sample</div><div>F = field (no other type used)</div></div>	
	Split	E
<div>E = ERL-C</div> <div>L = EMSL-LV</div> <div>A split sample is an additional aliquot from a routine, duplicate, audit, or blank sample, and has the same ID number as the original sample. However, the aliquot has an additional sample code. For example, if the original sample is assigned the ID number 4, the split sample also receives the ID number 4, with the letter E (or L) recorded in the Split Code column on the batch/QC form.</div>		

^a Samples require a lake ID, except for TB

^b This sample can have a "W" as a fourth character, indicating that it was withheld as part of the calibration study

second analyst prepares aliquots and split samples and preserves them if necessary. Both analysts wear disposable gloves while performing these tasks. The seven aliquots prepared from each sample are specified in Table 6-3.

There are two types of split samples for WLS-I. Descriptions of both are given below and are summarized in Table 6-4. When a sample is split, the appropriate split code is recorded on the batch/QC form.

- **ERL-C (Corvallis) Split** - An ERL-C split consists of one aliquot that is prepared in the same way as aliquot 1 (Table 6-3), except that the sample volume is 125 mL and a 125-mL container is used. If the volume permits, all samples are split for shipment to Corvallis. When volume limitations exist, routine aliquots and analyses take precedence. At ERL-C, the samples are analyzed by inductively coupled

plasma atomic emission spectroscopy (ICP), which provides checks on the performance of the analytical laboratories as well as additional data that are potentially useful in understanding lake chemistry. This split (annotated by an "E" on the batch/QC form) is shipped to the Corvallis laboratory on a multiple-batch basis (e.g., weekly). This split sample need not be stored at 4°C.

- **EMSL-LV Split** - An EMSL-LV split consists of one 125-mL aliquot that is collected and preserved as described in Sections 6.1.2, 6.2.2.3, and 6.2.2.4. At Las Vegas, the split samples are analyzed by ion chromatography for NO₃⁻ and SO₄²⁻. The purpose of analyzing this split sample is to compare preservation methods, to compare the effects of different holding times before preservation, and to provide an additional check on sampling, processing, and analytical performance. Split samples (indicated by an "L" on the batch/ QC

Table 6-3. Aliquots, Containers, Preservatives, and Corresponding Analyses, Western Lake Survey - Phase I

Aliquot (Container Volume)	Preservative and Description	Analyses
1 (250 mL)	Filtered, preserved with HNO ₃ to pH < 2	Ca, Mg, K, Na, Mn, Fe
2 (10 mL)	Filtered, preserved with MIBK-HQ extract	Extractable Al
3 (250 mL)	Filtered, no preservative	Cl ⁻ , total dissolved F ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , SiO ₂
4 (125 mL)	Filtered, preserved with H ₂ SO ₄ to pH < 2	DOC, NH ₄ ⁺
5 ^a (500 mL)	Unfiltered, no preservative	pH, BNC, ANC, conductance, DIC
6 (125 mL)	Unfiltered, preserved with H ₂ SO ₄ to pH < 2	Total P
7 (125 mL)	Unfiltered, preserved with HNO ₃ to pH < 2	Total Al

^a There must be no headspace in the Aliquot 5 bottle.

^b Aliquots 2, 3, 4, 5, and 6 must be stored at 4°C in the dark

Table 6-4. Split Sample Descriptions, Western Lake Survey - Phase I

Split	Quantity	Number	Description
ERL-C	125 mL	All samples ^a	Filtered sample acidified with HNO ₃ to pH < 2
EMSL-LV	125 mL	All samples collected by ground crews, all calibration lake samples collected by helicopter crews, and all natural audit samples.	Unfiltered sample preserved in field with 0.1 mL 5% HgCl ₂

^a Except when there is insufficient sample as a result of other splits

form) are stored in the dark at 4°C and are shipped to Las Vegas on a daily basis.

6.3.2.4 Extractable Aluminum--

The WLS-I procedure for processing the sample for extractable aluminum is identical to the procedure used during ELS-I. The third analyst begins this procedure when the DIC measurements are begun. The aluminum in the sample is extracted into MIBK, which is transferred to a 10-mL centrifuge tube that is capped tightly. An aliquot label is attached. This is aliquot 2 in Table 6-3. The aliquot is stored at 4°C in the dark until shipment.

6.3.2.5 pH (Field Laboratory)--

The WLS-I procedure for field laboratory pH determination is identical to the procedure used during ELS-I. After determining DIC, the laboratory supervisor determines the pH of the sample in the second syringe, which has been allowed to come to room temperature. The QC procedures are discussed in the ELS-I QA plan (Drouse et al., 1986, Section 7.2.2).

6.3.2.6 Turbidity--

The WLS-I procedure for turbidity determination is identical to the procedure used during ELS-I. The

analyst who prepares the aliquots also measures the turbidity of raw portions of the routine, duplicate, and blank samples. A Monitek Model 21 laboratory nephelometer is used for this procedure. The nephelometer is calibrated directly in nephelometric turbidity units (NTUs). The QC procedures are discussed in the ELS-I QA plan (Drou   et al., 1986, Section 7.2.3).

6.3.2.7 True Color--

The WLS-I procedure for true color determination is identical to the procedure used during ELS-I. The same analyst who performs the turbidity analysis centrifuges raw portions of routine and duplicate samples (as well as audit and blank samples when sample volume permits) and measures the color of the supernatants with the Hach Model CO-1 Color Test Kit, following the manufacturer's instructions. The QC procedures are described in the ELS-I QA plan (Drou   et al., 1986, Section 7.2.4).

6.3.2.8 Sample Shipment--

When a batch is completely processed and is ready for shipment, the samples are assembled into groups according to their shipping destinations. Except for ERL-C splits, all samples are stored at 4  C until they leave the field laboratory. Split samples are shipped to ERL-C and to EMSL-LV. All other samples are shipped to an analytical laboratory (see variations in sample shipment protocol for calibration lake samples in Section 5.2). Before shipping, the cap of each aliquot bottle is taped on, and the bottle is sealed in a plastic bag that is placed in a Styrofoam-lined shipping carton, along with 8 to 12 frozen freeze-gel packs to maintain the aliquots at 4  C. (Approximately eight samples will fit in one shipping carton.) One multicopy set of Form 3 - Shipping (see Figure 6-11) is completed for each carton, and two copies (sealed in a plastic bag) are enclosed in the carton. The carton then is sealed and is shipped by overnight delivery to its destination.

Upon receiving the shipment, the analytical laboratory checks the temperature inside the shipping carton and checks the condition of the shipping carton and the aliquot bottles. The analytical laboratory also verifies that all the aliquot bottles listed on the shipping form are included in the shipment. If there is any discrepancy, the field laboratory coordinator should be notified immediately, and the deviations should be noted in a cover letter to the QA manager.

6.3.2.9 Data Distribution--

The WLS-I procedure for distribution of field data forms is identical to the procedure used during ELS-I. A flowchart of the process is included on page 28 (Figure 6-1).

6.4 Training

The WLS-I procedure for training helicopter sampling and field laboratory personnel is identical to the procedure used during ELS-I. Ground sampling creates new safety and technical considerations, so additional training is provided for ground sampling participants. This training is carried out at Las Vegas and at the field bases and remote sites. Further discussion of training activities can be found in Morris et al. (1985).

Figure 6-11 National Surface Water Survey Form 3 - Shipping.

National Surface Water Survey
Sample Management Office
P.o. Box 818
Alexandria, VA 22314

**NSWS
Form 3
Shipping**

Received by _____
If Incomplete Immediately Notify
Sample Management Office
(703) 567-2490

Page _____ of _____

From (Station ID)	To (lab)	Batch ID	Date Processed -----		Date Shipped ----- Air-Bill No. -----		Date Received -----			
Sample ID	Aliquots Shipped (For Station Use Only)								Splits	Sample Condition Upon Lab Receipt (For Lab Use Only)
	1	2	3	4	5	6	7	8		
01										
02										
03										
04										
05										
06										
07										
08										
09										
10										
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23										
24										
25										
26										
27										
28										
29										
30										

Qualifiers

- X 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

7.0 Field Measurement Quality Control Checks

Field measurements are those made by the helicopter sampling crews, the ground sampling crews, and the field laboratory crews. The QC checks associated with these measurements are described in Sections 7.1, 7.2, and 7.3, respectively.

7.1 Quality Control Checks for Measurements Taken by Helicopter Crews

The lake site measurements taken by helicopter crews consist of three Hydrolab determinations (lake-water temperature, pH, and conductance), Secchi disk transparency, air temperature, and site depth. All measurements are recorded on the lake data form.

7.1.1 Hydrolab

The Hydrolab instrument is used to measure in situ lake-water temperature, pH, and conductance.

The QC procedures consist of calibrating the instrument at a designated clean work station at the base (or remote) site before and after each daily sampling excursion. Any instrumental drift between calibrations is monitored. These procedures are adapted from Hydrolab (1985). The following is a summary of QC procedures for the Hydrolab.

- **Lake-water temperature** - There is no calibration control for temperature. The instrument is calibrated at the factory and should be accurate to 0.2°C. The accuracy is checked each day against a National Bureau of Standards (NBS)-traceable thermometer, and, if an error of 1°C or more is found, the manufacturer should be consulted and the discrepancy should be recorded on the lake data form. An error of this size usually indicates a malfunction of the instrument. If a reserve Hydrolab is available that meets specifications, the faulty Hydrolab is replaced.
- **pH** - Following the daily calibration with commercial standard buffer solutions, a QC check sample (QCCS) of CO₂-saturated deionized water is measured. The QCCS has a

theoretical pH value of 3.91 at standard temperature and pressure. The instrument drift is determined by remeasuring the QCCS after completion of all sample analyses. If either QCCS reading deviates from the theoretical pH by more than ± 0.15 pH unit, the data tag qualifier "Q" (Table 12-1) is recorded on the lake data form.

- **Conductance** - A KCl standard of 147 $\mu\text{S}/\text{cm}$ is used to calibrate the conductance function. The same QCCS used to check the pH function of the Hydrolab is used to check the conductance function. The allowed error on the QCCS, which has a standard specific conductance value of 50 $\mu\text{S}/\text{cm}$, is ± 20 $\mu\text{S}/\text{cm}$. This error is 1 percent of the highest reading on the conductance meter scale used (2,000 $\mu\text{S}/\text{cm}$).

7.1.2 Secchi Disk Transparency

There are no applicable QC checks for this measurement.

7.1.3 Air Temperature

Ambient air temperature is measured by an outdoor thermometer affixed to the outside of the helicopter. The temperature is recorded on the lake data form. There are no applicable QC checks for this measurement.

7.1.4 Site Depth

Ideally, the sampling site should be the deepest part of the lake. This point is located with an electronic depth recorder that is mounted to the helicopter. Once daily, at the first lake to be sampled, the depth recorder is checked against a calibrated sounding line. The depth, which is measured in feet, is recorded on the lake data form, where it is converted to meters by multiplying the measurement in feet by 0.3048.

7.1.5 Elevation

Site elevation is taken from the map reading. This elevation is confirmed by the helicopter altimeter, which is periodically checked by the pilot. The map contour reading and the altimeter reading are recorded on the lake data form.

7.1.6 Lake Location

The lake location is determined from map coordinates (i.e., latitude and longitude) and is confirmed by the loran-C instrument readout and by a comparison of observed and map topographic features. The map coordinates and loran-C readings are recorded on the lake data form.

7.2 Quality Control Checks for Measurements Taken by Ground Crews

Ground crew samplers measure lake-water temperature, pH, Secchi disk transparency, air temperature, and site depth. The ground crew does not use a Hydrolab. All measurements are recorded on the lake data form.

7.2.1 Lake-Water Temperature

A temperature meter is calibrated before the first sampling excursion of the day by measuring the temperature of an ice slurry (4°C) and a water sample (15 to 20°C) with the thermistor and with an NBS-traceable thermometer. If the thermistor readings differ from the thermometer readings by 0.5°C or more, the problem with the meter must be identified and resolved by following the manufacturer's instructions. A calibration check at the lake site is done by comparing the reading of the thermistor with that of a field thermometer in a sample of lake surface water collected in a plastic beaker. If the two readings differ by 2°C or more, the in situ readings are qualified on the lake data form.

7.2.2 pH

No QC checks are available for pH determinations that are made with pH indicator strips.

7.2.3 Secchi Disk Transparency

There are no applicable QC checks for this measurement.

7.2.4 Air Temperature

Ambient air temperature is measured by reading an NBS-traceable thermometer above the ground in the shade. There are no applicable QC checks for this measurement.

7.2.5 Site Depth

The samplers locate the sampling site by observing shoreline topography and by performing a visual inspection of the site while they are on the lake surface. A calibrated, weighted sounding line is used to determine sampling site depth in feet. The measurement is recorded on the lake data form, where it is converted to meters by multiplying by a conversion factor of 0.3048. Ideally, the sampling site should be the deepest part of the lake.

7.2.6 Elevation

Site elevation is taken from the map reading and is recorded on the lake data form. There are no applicable QC checks for this measurement.

7.2.7 Verification of Lake Location

The map coordinates of the lake are verified as described in Section 6.2.2.1.

7.3 Field Laboratory Measurements

See the ELS-I QA plan (Drouse et al., 1986, Section 7.2) for QC checks for DIC, pH, turbidity, and true color determinations.

8.0 Analytical Procedures

WLS-I analytical procedures are identical to those used for ELS-I. The Las Vegas laboratory uses the same procedures for sulfate and nitrate analysis of the EMSL-LV splits as the analytical laboratory does for analysis of the conventional nitrate sulfate aliquot.

These procedures, listed in Table 4-1, are described fully in the ELS-I methods manual (Hillman et al., 1986) and are summarized in the WLS-I methods manual (Kerfoot and Faber, 1987).

9.0 Analytical Internal Quality Control

Analytical internal QC provisions for WLS-I are identical to those for ELS-I. They are discussed fully in Section 9.0 of the ELS-I QA plan (Drou   et al., 1986) and are summarized in Table 9-1.

Table 9-1. Summary of Internal Quality Control Checks for Analytical Methods, Western Lake Survey -Phase I

Parameter	QC Check	Control Limits	Corrective Action ^a
ANC, BNC, pH	1. Titrant Standardization cross-check	1. Relative differences < 5%	1. Restandardized titrants.
	2. Electrode calibration (Nernstian response check)	2. Slope = 1.00 ± 0.05	2. Recalibrate or replace electrode.
	3. pH QCCS (pH 4 and 10) analysis	3. pH 4 = 4.00 ± 0.05 pH 10 = 10.00 ± 0.05	3. Recalibrate electrode.
	4. Blank analysis (salt spike)	4. [Blank] ≤ 10 µeq/L (ANC and BNC)	4. Prepare fresh KCl spike solution.
	5. Duplicate analysis	5. RSD ≤ 10% (ANC and BNC) ± 0.05 pH unit (pH)	5. Refine analytical technique, analyze another duplicate
	6. Protolyte comparison	6. See Hillman et al (1986)	6. See Hillman et al. (1986).
Ions (Cl ⁻ , total dissolved F ⁻ , NH ₄ ⁺ , NO ₃ ⁻ , SO ₄ ²⁻)	1a. Initial QCCS analysis (calibration and verification)	1a,b The lesser of the 99% CI or value given in Table 9-2 of Drou�� et al (1986)	1a. Prepare new standards and recalibrate
Metals (total Al, extractable Al, Ca, Fe, K, Mg, Mn, Na)	1b. Continuing QCCS analysis (every 10 samples)		1b. Recalibrate Reanalyze associated samples.
	2a. Detection limit determination (weekly)	2a. Detection limits given in Table 4-1	2a,b. Optimize instrumentation and technique.
SiO ₂ , total P, DIC, DOC, Conductance	2b. DL QCCS analysis (daily, metals and total P only)	2b. % Recovery = 100 ± 20%	
	3. Blank analysis	3a. Blank ≤ 2 x DL (except conductance) 3b. Blank ≤ 0.9 µS/cm (conductance only)	3a,b. Determine and eliminate contamination source Prepare fresh blank solution Reanalyze associated samples
	4. Duplicate analysis	4. Duplicate precision (%RSD) limits given in Table 4-1	4. Investigate and eliminate source of imprecision. Analyze another duplicate
	5. Matrix spike (except ext. Al, DIC, and conductance)	5. % Recovery = 100 ± 15%	5. Analyze 2 additional spikes. If one or both outside control limits, analyze all samples in that batch by method of standard additions.
Metals (total Al, extractable Al, Ca, Fe, K, Mg, Mn, Na)	6. Resolution test (Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ only)	6. Resolution ≥ 60%	6. clean or replace IC separator column. Recalibrate.
SiO ₂ , total P, DIC, DOC, conductance			

^a To be followed when QC check is outside control limits.

10.0 Performance and System Audits

10.1 Performance Audit Samples

Field audit samples are used as part of the QA activities of WLS-I. The purpose of field audit samples is to identify problems affecting data quality that may occur during sample processing, shipment, or analysis. These problems could include sample contamination, sample degradation, solvent evaporation, and improper or inaccurate sample analysis.

The audit samples are shipped to the analytical laboratories from the field bases as though the audit samples were aliquots of routine lake samples. Every attempt is made to ensure that the analytical laboratory does not recognize the audit samples as different from the routine lake samples. As a result, the audit samples are double blind to the analytical laboratory.

There are two types of field audit samples: field synthetic audit samples and field natural audit samples.

10.1.1 Field Synthetic Audit Samples

The field synthetic audit samples are prepared at a central laboratory and are sent to the field laboratory to be processed through all the filtration and preservation steps and to be labeled as though they were authentic lake samples. Thus, they are single-blind samples to the field laboratory and, concurrently, double-blind samples to the analytical laboratory.

The desired composition of the field synthetic audit samples is shown in Table 10-1 and reflects the low concentrations of analytes expected in actual WLS-I lake samples. Synthetic lots are prepared in bulk as stock solutions. The stock solution is diluted to the desired concentration and the dilute sample is shipped to the field laboratories one day before aliquot processing is scheduled.

10.1.2 Field Natural Audit Samples

Waters collected from Big Moose Lake in the Adirondack Mountains, from Lake Superior at Duluth, Minnesota, and from Bagley Lake in the Cascade Range of Washington State are used as natural audit samples for the survey. The waters of Big Moose

Lake are acidic; the Lake Superior waters represent a buffered system; and Bagley Lake represents a partially buffered system. In bulk, these natural samples are passed in 50- to 200-L increments through a 0.45- μ m filter into 2-L bottles and are maintained at 4°C to minimize changes in composition. These 2-L quantities are the individual natural audit samples that are included in the sample batches.

10.1.3 Application of Field Audit Sample Data

Data are obtained from the analyses of the field audit samples for the following purposes:

- to judge the performance of the field bases in the processing and shipment of samples
- to judge the continued capability of the analytical laboratories to analyze the samples properly
- to establish a statistically valid estimate of the overall bias and precision of the analyses
- to establish a statistically valid estimate of the stability of a typical lake sample when stored at 4°C by evaluating the natural lake sample over the period of the study.

Acceptance windows are established for the measurement of each parameter in the audit samples. A preliminary determination of the size of the windows is based upon the information available for each analytical method at the time the study is initiated; the final determination is made after data verification is completed. If the analytical results for a measurement fall outside the acceptance window, the EMSL-LV QA staff reviews the data to determine the cause of the problem and immediately calls the analytical laboratory or field base, whichever is appropriate, to seek corrective action. Data for routine samples analyzed with the audit samples also are checked to determine if they were affected by the problem. If they were affected, reanalysis of the samples in question may be requested. The establishment of the acceptance windows is summarized in Section 11 of this QA plan and is described in more detail in Drou   et al. (1986, Section 11).

Approximately 75 synthetic audit samples and 150 natural-water audit samples are scheduled to be

Table 10. 1. Desired Composition of Field Synthetic Audit Samples, Western Lake Survey - Phase I

Parameter	Concentration	Units
Acid-Neutralizing Capacity (ANC) ^a	10-50	µeq/L
Al (total and extractable)	0.01-0.10	mg/L
Base-Neutralizing Capacity (BNC) ^a	10-50	µeq/L
Ca	0.1-1	mg/L
Cl ⁻	0.1-1	mg/L
Conductance ^b	1-50	µS/cm
DIC ^a	0.1-1.0	mg/L
DOC	0.1-1.0	mg/L
F ⁻ , total dissolved	0.01-0.05	mg/L
Fe	0.02-1.0	mg/L
K	0.1-1	mg/L
Mg	0.1-1	mg/L
Mn	0.02-1.0	mg/L
Na	0.5-3	mg/L
NH ₄ ⁺	0.01-0.50	mg/L
NO ₃ ⁻	0.01-0.50	mg/L
P, total	0.005-0.03	mg/L
pH ^a	4-5	pH
SiO ₂	1-5	mg/L
SO ₄ ²⁻	1-5	mg/L

^a These parameters are related, and they affect the analytical results of one another.

^b To be determined by concentration of other parameters.

Note: Mass balance (anions versus cations) in the composition of field synthetic audit samples must be maintained. Nitrogen/phosphorus ratio must be reasonable (10:20).

processed during WLS-I. A statistical evaluation of the audit data, including the setting of audit windows, should provide a good estimate of the bias and precision of the analytical methods for each required measurement. Furthermore, any change over time in analytical results for the natural-water audit samples without a corresponding change in results for the other audit samples can be attributed to lack of analyte stability. The findings of a comparative study between audit sample types will provide an estimate of the true maximum holding times allowable for each type of analyte.

10.2 Quality Assurance System Audits (On-Site Evaluations)

The system audits consist of qualitative evaluation of field and analytical laboratory facilities, equipment,

and operations such as record keeping, data reporting, and QC procedures.

10.2.1 Field Operations On-Site Evaluation

Each field base and helicopter sampling crew can expect at least one on-site evaluation during the course of the sampling effort. The purpose of the on-site inspection is to review the sampling procedures, field base operations, and QA efforts; in addition, as many of the 60 ground sampling crews as possible will be evaluated in the field. The on-site evaluation for each field base and its corresponding sampling crews should be conducted as soon as possible after the start of operations. The questionnaire in Appendix A of this document is used to assist in the evaluation of ground sampling crews. The questionnaire given in Appendix C of Drou   et

al. (1986) is used for the evaluation of field base and helicopter crews.

The field auditor conducts an in-depth review of all field operations. This includes, but is not limited to, (1) interviewing the field base coordinator, the Forest Service field manager, and the field laboratory supervisor; (2) observing the field base operations (including field laboratory operations); (3) interviewing sampling crews; (4) accompanying one or more of the sampling crews during a sampling excursion; and (5) writing a summary report that includes results, observations, and recommendations. If there are any problems, the evaluator must either have the individuals involved correct them or must bring them to the attention of the field base coordinator for resolution.

10.2.2 Analytical Laboratory On-Site Evaluation

Each analytical laboratory participating in WLS-I can expect a minimum of two in-depth, on-site evaluations conducted by the EPA QA manager or his authorized representative. The questionnaire in Appendix D of Drou   et al. (1986) is used to assist in the on-site laboratory evaluation.

The first on-site laboratory evaluation is performed after the laboratory has successfully analyzed a set of preaward Performance Evaluation (PE) samples for the contract-required analyses and before the actual survey analytical work begins. The PE samples contain up to the maximum number of analytes for which measurement is required, in the expected concentration ranges. The PE sample results are scored using the ELS-I Preaward Score Sheet given in Appendix E of Drou   et al. (1986). Grading emphasizes analytical accuracy, but a substantial portion of the grade depends on meeting the QA, internal QC, reporting, and deliverable requirements.

The auditor summarizes all observations in an on-site laboratory evaluation report and brings all problems to the attention of the laboratory manager for corrective action.

The second on-site laboratory evaluation is conducted after approximately one-third of the WLS-I analyses have been completed. During the second on-site evaluation, QA sample (audit, duplicate, and blank) data and QC data received to date are reviewed. The laboratory questionnaire is updated, if necessary, and all changes since the first on-site evaluation are noted. An on-site laboratory evaluation report is written for this and for each additional on-site laboratory evaluation.

11.0 Acceptance Criteria

Acceptance criteria for audit sample values are the same for WLS-I as for ELS-I. These criteria are discussed fully in Section 11 of the ELS-I QA plan (Drou   et al., 1986). The limits of the windows are determined by using a t-statistic (t).

$$t = \frac{Z}{\sqrt{\frac{\mu}{r}}} \text{ is a Student's } t$$

where:

Z is the standard normal variate, having a normal distribution with a mean of 0 and a variance of 1.

μ is a variable that has a chi-square distribution with r degrees of freedom, and Z and μ are independent.

12.0 Data Management System

The purpose of the data base management system is to assemble, store, and edit data generated during WLS-I and during other NSWS surveys. The data base management system also is used to provide basic reports of the survey results, to perform certain statistical analyses, and to provide data security. The relationship of data base management to other survey activities is shown in Figure 12-1.

The data are stored in four major data sets: Data Set 1 - the raw data set, Data Set 2 - the verified data set, Data Set 3 - the validated data set, and Data Set 4 - the final data set. These four data sets make up the WLS-I data base and are discussed in the following subsections. Individual, system, and file passwords protect all data sets from unauthorized or accidental access.

12.1 Data Set 1 - The Raw Data Set

At Oak Ridge National Laboratory (ORNL), the field data, which are reported on the lake data and batch/QC forms (forms 1 and 2, respectively), and the analytical laboratory data, which are reported on analytical data forms 11, 13, 18, 19, 20, 21, 22, and 23 (see Drou   et al., 1986, Appendix A), are entered into the raw data base. Data entry operators use the Statistical Analysis System (SAS) for this purpose. Analytical data from form 26, which is used only by the QA staff for confirmation/reanalysis procedures, are not entered into the raw data set (see Section 12.2). The raw data set includes all analytical results and data qualifiers (see Table 12-1).

The SAS full-screen editor procedure is used to provide gross error checking as data are entered. All data are entered into two separate data sets by two different operators. For the NSWS data base, a program (COMPARE) has been developed in SAS to compare the two data sets and to identify any inconsistencies. The advantage of this double entry and comparison process is that entry errors are removed from the system. The field personnel and the analytical laboratories also send copies of the field forms and data packages, respectively, to the EMSL-LV QA staff for concurrent data analysis. Thus, receipt of the field and analytical data forms by the QA staff verifies that all forms have been received by the data base management personnel.

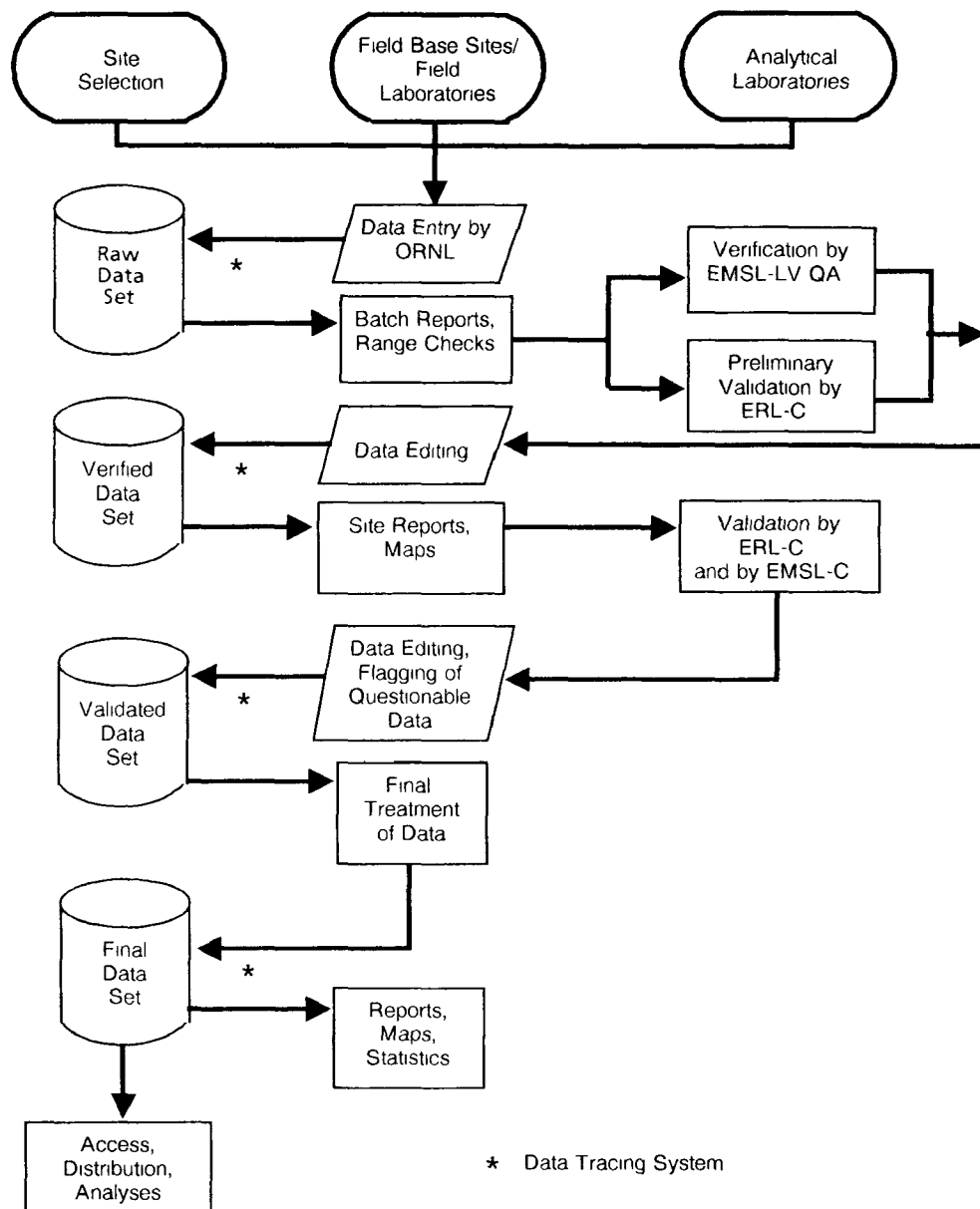
Changes must be made in the field data if errors are identified through the daily QA communication with the field personnel. The checks for identifying errors are given in Sections 13.1.1 and 13.1.2. If the data in question have not been entered yet by ORNL, the changes are included in the raw data set. If the data have been entered already, the changes are included in subsequent data sets.

12.2 Data Set 2 - Verified Data Set

When the field and analytical laboratory data are transmitted through magnetic tapes and the raw data are made available to the EMSL-LV QA group, all data are evaluated and verified as described in Section 13.0. The data are processed by "Automated Quality Assurance Review, Interactive Users System" (AQUARIUS), an on-line QA system developed by the EMSL-LV QA staff. Reports generated by AQUARIUS range in subject from a complex protolyte analysis to simple external/internal blank checks for QA purposes. AQUARIUS generates "tuples" that direct ORNL to mark problem data with flags (given in Table 12-2), as deemed necessary by the EMSL-LV QA staff. Tuples are defined as SAS observations generated by an exception program or manually created by an auditor, which are intended either to change or to annotate a value in a copy of Data Set 1 (the raw data set). Because the raw data set is never changed, a revised data set (the verified data set) is generated. Tuples have a fixed number of fields that specify the batch, the sample, and the variable to be flagged, modified, or verified. The tuples are sent to ORNL via magnetic tape and are entered into the verified data set. Tuples should only have to be transferred twice, once for initial verification and once for final verification. The originally reported data values are maintained in Data Set 1 (the raw data set) for a historical record.

In addition to the standard QA analyses, AQUARIUS is used to generate numerous printouts that are supplied to the QA manager to indicate intra-laboratory, field interlaboratory, and analytical interlaboratory bias, as well as discrepancies in blanks, duplicates, audits, and other QA/QC samples. The overall outcome is a verified data set in which any suspicious values or observations are qualified with a flag (listed in Table 12-2). When a datum is not reported, the missing value code "." is assigned

Figure 12-1. Data management, Western Lake Survey - Phase I.



(in *numeric* fields only) with an accompanying data qualifier for explanation. The QA personnel coordinate with the field bases and with the analytical laboratories to make all appropriate corrections in the data.

12.3 Data Set 3 - The Validated Data Set

The validation process begins in tandem with the verification process. When ORNL provides the ERL-

C staff with a computerized version of the verified data set through the computing facility at Research Triangle Park (RTP), North Carolina, the validation process can be completed. The validation process increases the overall integrity of the data base by using all the QA/QC information available to evaluate all data for internal and regional consistency.

In the validation process, known relationships in aquatic chemistry and limnology are used to identify intrasite sample inconsistencies within data for a set

Table 12-1. National Surface Water Survey Laboratory/Field Data Qualifiers (TAGS), Western Lake Survey - Phase I

Qualifier	Indicates
A	Instrument unstable
B	Redone, first reading not acceptable
C	Instruments, sampling gear not vertical in water column
D	Slow stabilization
E	Hydrolab cable too short
F	Result outside QA criteria (with consent of QA manager)
G	Result obtained from method of standard additions
H	Holding time exceeded criteria
J	Result not available; insufficient sample volume shipped to laboratory from the field
K	Result not available; entire aliquot not shipped
L	Not analyzed because of interference
M	Result not available; sample lost or destroyed by laboratory
N	Not required
P	Result outside QA criteria, but insufficient volume for reanalysis
Q	Result outside QA/QC criteria
R	Result from reanalysis
S	Contamination suspected
T	Leaking container
U	Result not required by procedure; unnecessary
V	Anion/cation balance outside criteria because of high DOC
W	% Difference (%D) calculation (Form 14) outside criteria because of high DOC
X	Available for miscellaneous comments in the field only
Y	Available for miscellaneous comments in the field only
Z	Available for miscellaneous comments in the field only
<	Measurements taken at < 1.5 m (in situ lake measurement only)

of variables. Intersite validation consists of comparing single site values with values for adjacent sites within a region. Data for groups of sites are compared and mapped to check for consistency. The validation process is summarized further in Section 14.0. After undergoing this reviewing process, the data, lake by lake, are transferred to the validated data base.

12.4 Data Set 4 - The Final Data Set

The calculation of population estimates is difficult if the data set contains missing values (Linthurst et al., 1986). To resolve the problems in the validated data set that result from missing values, a final data set (Data Set 4) is prepared. This data set is modified by averaging the field routine/duplicate pair values that are within desired precision limits and by replacing analytical values determined to be in error during validation. The values used for substitution are determined in one of several ways, as described in Section 15.0.

Table 12-2. Data Qualifiers (FLAGS) for the Verified Data Set, Western Lake Survey - Phase I

A0	Anion/cation percent ion balance difference (%IBD) is outside criteria for <i>unknown cause</i> .
A1	Anion/cation percent ion balance difference (%IBD) is outside criteria because of <i>nitrate contamination</i>
A2	Anion/cation percent ion balance difference (%IBD) is outside criteria because of <i>anion (other than nitrate) contamination</i> .
A3	Anion/cation percent ion balance difference (%IBD) is outside criteria because of <i>cation contamination</i> .
A4	Anion/cation percent ion balance difference (%IBD) is outside criteria because of <i>unmeasured organic protolytes (fits Oliver Model)</i> .
A5	Anion/cation percent ion balance difference (%IBD) is outside criteria because of <i>possible analytical error - anion concentration too high (flag suspect anion)</i>
A6	Anion/cation percent ion balance difference (%IBD) is outside criteria because of <i>possible analytical error - cation concentration too low (flag suspect cation)</i>
A7	Anion/cation percent ion balance difference (%IBD) is outside criteria because of <i>possible analytical error - anion concentration too low (flag suspect anion)</i> .
A8	Anion/cation percent ion balance difference (%IBD) is outside criteria because of <i>possible analytical error - cation concentration too high (flag suspect cation)</i>
B0	External (field) blank is above expected criteria for pH, DIC, DOC, conductance, ANC, and BNC determinations
B1	Internal (laboratory) blank is > 2 x CRDL for pH, DIC, DOC, conductance ANC, and BNC determinations.
B2	External (field) blank is above expected criteria and contributed > 20% to sample values (This flag is not used for pH, DIC, DOC, ANC, or BNC determinations)
B3	Internal (laboratory) blank is > 2 x CRDL and contributes > 10% to the sample concentrations (This flag is not used for pH, DIC, DOC, ANC, or BNC determinations)
B4	Potential negative sample bias based on internal (laboratory) blank data
B5	Potential negative sample bias based on external (field) blank data.
C0	Percent conductance difference (%CD) is outside criteria for <i>unknown cause</i> (possible analytical error - ion concentration too high)
C1	Percent conductance difference (%CD) is outside criteria because of <i>possible analytical error - anion concentration too high (flag suspect anion)</i>
C2	Percent conductance difference (%CD) is outside criteria because of <i>anion contamination</i>
C3	Percent conductance difference (%CD) is outside criteria because of <i>cation contamination</i> .
C4	Percent conductance difference (%CD) is outside criteria because of <i>unmeasured organic ions</i> (fits Oliver Model).
C5	Percent conductance difference (%CD) is outside criteria because of <i>possible analytical error in conductance measurement</i> .
C6	Percent conductance difference (%CD) is outside criteria because of <i>possible analytical error - anion concentration too low (flag suspect anion)</i>
C7	Percent conductance difference (%CD) is outside criteria because of <i>unmeasured protolyte ions</i> (does not fit Oliver Model)
C8	Percent conductance difference (%CD) is outside criteria because of <i>possible analytical error - cation concentration too low (flag suspect cation)</i>
C9	Percent conductance difference (%CD) is outside criteria because of <i>possible analytical error - cation concentration too high (flag suspect cation)</i> .
D2	External (field) duplicate precision exceeded the maximum expected percent relative standard deviation (%RSD), and the routine and duplicate sample concentrations both were $\geq 10 \times$ CRDL
D3	Internal (laboratory) duplicate precision exceeded the maximum contract-required percent relative standard deviation (%RSD), and the routine and duplicate sample concentrations both were $\geq 10 \times$ CRDL
F0	Percent conductance difference (%CD) exceeded criteria when Hydrolab conductance value was substituted.
F1	Hillman/Kramer protolyte analysis program indicates <i>field (Hydrolab) pH problem</i> when Hydrolab pH value is substituted for field laboratory pH
F2	Hillman/Kramer protolyte analysis program indicates <i>unexplained field pH or DIC problem</i> when Hydrolab pH value is substituted for field laboratory pH.

(continued)

Table 12-2 (Continued)

F3	Hillman/Kramer protolyte analysis program indicates <i>field problem - field laboratory pH</i>
F4	Hillman/Kramer protolyte analysis program indicates <i>field problem - field laboratory DIC</i>
F5	Hillman/Kramer protolyte analysis program indicates <i>unexplained field problem - pH or DIC</i>
H0	The maximum holding time criteria were not met.
L1	Instrumental detection limit (IDL) exceeded CRDL and sample concentration was $< 10 \times$ IDL.
M0	The method used to obtain the value is not acceptable according to the IFB contract.
N0	Audit sample value exceeded upper control limit.
N1	Audit sample value was below lower control limit.
P0	Hillman/Kramer protolyte analysis program indicates <i>laboratory problem - initial pH (ANC)</i>
P1	Hillman/Kramer protolyte analysis program indicates <i>laboratory problem - initial pH (BNC)</i> .
P2	Hillman/Kramer protolyte analysis program indicates <i>laboratory problem - unexplained - initial pH (ANC or BNC)</i>
P3	Hillman/Kramer protolyte analysis program indicates <i>laboratory problem - initial DIC</i> .
P4	Hillman/Kramer protolyte analysis program indicates <i>laboratory problem - air-equilibrated pH or DIC</i>
P5	Hillman/Kramer protolyte analysis program indicates <i>laboratory problem - unexplained - initial pH or DIC</i>
P6	Hillman/Kramer protolyte analysis program indicates <i>laboratory problem - ANC determination</i>
P7	Hillman/Kramer protolyte analysis program indicates <i>laboratory problem - BNC determination</i>
Q1	QCCS value was above contractual criteria.
Q2	QCCS value was below contractual criteria
Q3	Insufficient number of QCCSs were measured
Q4	No QCCS analysis was performed
Q5	Detection limit QCCS was not 2 to 3 times the CRDL, and measured value differed more than 20 percent from theoretical concentration.
S0	Matrix spike percent recovery (%REC) was above contractual criteria
S1	Matrix spike percent recovery (%REC) was below contractual criteria.
X0	Questionable data point. Recommendation is to remove point from subsequent data sets and from any statistical analyses.
X1	Extractable aluminum (ALEX) $>$ Total aluminum (ALTL) by 0.01 mg/L or more (ALEX $>$ 3 X CRDL and ALEX $>$ ALTL by 0.01 mg/L or more)

13.0 Data Evaluation and Verification

Data review begins with the daily telephone calls made to each field laboratory and analytical laboratory (1) to ensure that QA/QC guidelines are being followed, (2) to ensure that samples are being handled and analyzed properly, (3) to obtain current sample data, and (4) to discuss problems that may occur during analyses. The primary objective of these calls is to identify and resolve issues quickly, before they affect data quality or interfere with the completion of the survey.

Preliminary sample data are obtained verbally, by computer, or by TELEFAX from the different laboratories. The preliminary data are evaluated by comparing the QA sample data to acceptance criteria.

Responsible parties are notified of problems, and all interactions are recorded in bound notebooks. If necessary, a letter of documentation is sent.

As the field and analytical laboratory data are received by the EMSL-LV QA staff, all data are evaluated on the basis of the available QA/QC information. The established and organized review process described here is used for this process. The objective of the data verification process is to identify data of unacceptable quality and to correct them, flag them, or target them for possible sample reanalysis or for elimination of the data from future data sets. Computer programs have been developed to automate this process as much as possible. Each batch of data is evaluated on a sample-by-sample basis, as described in the following subsections.

13.1 Field Data Review

As a result of the complexities involved in this survey, such as the calibration study, the WLS-I data require more extensive review than did the ELS-I data. The two data forms filled out by field personnel are reviewed individually for completeness of data, and then the two forms are compared.

13.1.1 Lake Data Form

The following checks are required on data on the lake data form:

- Hydrolab Calibration Data - Compare pH and conductance calibration data on the lake data

form to data on the Hydrolab calibration forms to ensure that initial calibration, initial QCCS, and final QCCS criteria are met; if the criteria are not met, insert appropriate data qualifiers.

- Stratification - Check that stratification data were collected if the temperature at the surface of the lake minus the temperature at the bottom was greater than 4°C.
- Map Coordinates - Check that the Ioran-C readings match the map coordinates.
- Site Drawing - Check that the lake outline is drawn, that the sample site and any inlets or outlets are marked, and that the map elevation and altimeter readings are noted.
- Signatures - Check that all required signatures are present.
- Secchi Disk Transparency - Check that the Secchi disappearance depth is greater than or equal to the Secchi reappearance depth.
- Conversion Factors - Check that the site depth has been converted correctly from feet to meters.
- Comments - Check if any comments noted by the sampling crew need additional explanations or if data qualifiers need to be applied to the data.

13.1.2 Batch/QC Form

The following checks must be completed on the batch/QC form:

- Trailer Duplicate - Check that this sample is recorded on the bottom of the batch/QC form and that it has a sample code of TD with a sample ID of Dup. This sample should have a lake ID that matches a routine lake sample ID within that batch.
- Field Laboratory QA Samples - Evaluate results of DIC, pH, turbidity, and true color measurements of field routine/duplicate pairs in accordance with associated acceptance criteria for precision; evaluate field audit samples in accordance with associated acceptance criteria; check results of turbidity and true color

measurements of field and trailer blanks for indications of contamination.

- Field Laboratory QCCS - Evaluate results of DIC, pH, turbidity, and true color measurements of QCCSs in accordance with QCCS criteria.
- Split Codes - Split samples go to ERL-C and to EMSL-LV. Check that split codes are correct.
- Dates - Check that date processed and date shipped are correct. Date shipped is one day after date processed, except on weekends.
- Analytical Laboratory - Check that the analytical laboratory to which the batch is scheduled to be shipped is the correct one. This is especially important for tracking calibration study samples.
- Lake ID and Sample Code - Check for consistency (i.e., that a field duplicate has a field routine with the same lake ID; that audit samples are coded properly).
- Signature of Field Laboratory Supervisor - Check that the form is signed.
- Comments - Check if any comments noted by the sampling crew need additional explanations or if data qualifiers need to be applied to the data.

13.1.3 Comparison of Lake Data Form to Batch/QC Form

- Identification Numbers and Codes - Check that the lake IDs, batch IDs, sample IDs, and sample codes on both forms match.
- Hydrolab pH - Compare the pH reading taken at 1.5 m (recorded on the lake data form) to the field laboratory pH reading on the batch form.
- Calibration Study Lakes - Check batch IDs, sample IDs, lake IDs, and sample codes for calibration lake samples. Because samples with the same lake ID are included in more than one batch, sample codes must be checked carefully; therefore, an extensive tracking system is required. The calibration study is discussed in Section 5.2.
- Data Qualifiers and Comments - Check that comments are reasonable and that they are consistent between forms.
- Crew ID - Check for correct transcription of crew ID from the lake data form to the batch/QC form.

Data anomalies are reported to the field laboratory coordinator for review, and data-reporting errors are transmitted to ORNL to be corrected before the improper data are entered into the raw data set. All

telephone communications are recorded in bound notebooks, and data corrections are annotated on the appropriate forms.

13.2 Analytical Data Review

13.2.1 Preliminary Review of Sample Data Package

The sample data packages are reviewed for completeness, internal QC compliance, and appropriate use of data qualifiers. The Data Package Completeness Checklist (like that shown in Appendix F of Drou   et al. (1986) but with an appropriate title change) is used to ensure consistency in the review of all data packages. Any discrepancies related to analytical data are reported to the appropriate analytical laboratory manager for corrective action. If discrepancies affect billing or data entry, then the Sample Management Office (SMO) or ORNL is notified. Comments provided in the cover letter also are reviewed to determine their effect on data quality and the need for any follow-up action by the laboratory. This data review process is also important in verifying that the contractual requirements have been met for the purpose of payment.

13.2.2 Review of QA/QC Data

The analytical data reported on data forms are entered into the raw data set by ORNL as the data packages are received. A magnetic tape containing raw data is sent to the EPA for the IBM 3081 at the National Computer Center (NCC) at RTP. Each tape received by the NCC tape library is given a volume serial number and a BIN number that indicates the physical location of the tape. The tape is loaded remotely by the EMSL-LV QA staff, and the exception-generating programs listed in Table 13-1 are run.

The WLS-I Verification Report (like that shown in Appendix G of Drou   et al. (1986) but with an appropriate title change) is completed. Outputs from exception reports, original data, and field notebooks are used in this process. The verification report is a worksheet designed to guide the auditor systematically through the verification process. It explains how to flag data, tracks data resubmissions and reanalysis and confirmation requests, lists the steps used to help explain the QA exceptions, summarizes all modifications (e.g., value changes) to the raw data base, and lists all verified sample data.

One hundred percent of the analytical data are verified, sample by sample and for the batch as a whole. A routine lake sample has to meet the anion/cation percent ion balance difference (%IBD) and the percent conductance difference (%CD) criteria in order to be verified, unless the discrepancy can be explained by the presence of organic species

Table 13-1. Exception-Generating and Data Review Programs, Western Lake Survey - Phase I

Program	Type
Exception-Generating Programs:	
1 = Audit Sample Summary	(FL,FN)
2 = Laboratory/Field Blank Summary	(BH,BG,TB)
3 = Field Duplicate Precision Summary	(R/D Pairs)
4 = Instrumental Detection Limit Summary	(All Species)
5 = Holding Time Summary	(All Species)
6 = Percent Conductance Difference Calculations	(All Species)
7 = Anion/Cation Balance Calculations	(All Species)
8 = Internal Laboratory Duplicates	
9 = Matrix Spike Summary	
10 = Protolyte Analysis (DIC, DOC, pH, ANC, and BNC Data Evaluation)	
11 = Reagent/Calibration Blanks and QCCS	
12 = Comparison of Total Aluminum to Extractable Aluminum	
Data Review Programs:	
1 = Raw Data Listing - Format for QA Manager	
2 = Complete Raw Data Listing - Format for Audit Staff	
3 = Comparison of Form 1 and Form 2	(pH and DIC)
4 = Comparison of Form 2 and Form 11	(pH and DIC)
5 = QA/QC Flag Summary	
6 = Modified Gran Analysis Program	

(as indicated by the protolyte analysis program) or by an obvious correctable reporting error.

Additional flags are applied to a given parameter for all the samples within the batch when the batch QA sample data do not meet the acceptance criteria for QA samples such as field blanks, field duplicates, or field audit samples. Each sample in the batch is also flagged by parameter if internal QC checks such as matrix spike recovery, calibration and reagent blank analytical results, internal (analytical laboratory) duplicate precision, instrumental detection limits, QCCS analytical results, and holding times do not meet specifications. The final source of flags is the protolyte analysis program. A detailed description of the evaluation of DIC, DOC, pH, ANC, and BNC data by the protolyte analysis program is given in Section 13.2.4. In all cases, the flags that are generated by the computer programs are reviewed by the auditor for reasonableness and consistency before the flags are entered into the data base.

13.2.3 Computer Evaluation of DIC, DOC, pH, ANC, and BNC Data

An evaluative computer program performs data checks and uses carbonate equilibria and DOC data to identify analytical error and the source of protolytes (acidic or basic species) in the sample. The DIC, pH, ANC, and BNC data are rigorously evaluated in light

of known characteristics of carbonate equilibria. DOC data are introduced to the evaluation with the use of a theoretical model (the Oliver model--see Section 13.2.3 2) to predict characteristics of the more complex system. The overall process of data evaluation based on carbonate equilibria is summarized below.

13.2.3.1 Redundant Alkalinity Checks for pH and DIC --

Evaluations of carbonate equilibria indicate that alkalinity is not affected by changes in dissolved CO₂ concentration. Furthermore, alkalinity can be calculated from carbonate equilibria if the DIC and pH are known. A theoretical alkalinity, C, is calculated from each of the three pH/DIC pairs:

C_1 = pH/DIC of "closed system" syringe samples (field laboratory)

C_2 = pH/DIC of "open system" samples (analytical laboratory)

C_3 = pH/DIC of "air-equilibrated system" samples (analytical laboratory)

The third data pair (C_3) is obtained on an aliquot that has been equilibrated with standard air (300 ppm CO₂). If there is no analytical error, the three calculated alkalinites should agree within

experimental error. The precision for calculated alkalinity values of less than or equal to 100 $\mu\text{eq/L}$ should be within $\pm 10 \mu\text{eq/L}$ and within ± 10 percent for calculated alkalinity values greater than 100 $\mu\text{eq/L}$. The precision windows are based on the estimated precision of the pH and DIC measurements used in the calculations. If this comparison indicates a potential analytical error (i.e., the precision limit is exceeded), the redundant pH and DIC values are compared to identify the source of error. Further evaluation of the QA/QC information for the individual data pairs usually identifies one of the pH or DIC measurements within the outlier pair as the source of error. Because of the redundancy in measurement, for every sample that is analyzed, an acceptable pH or DIC value from one of the data pairs should be available to the data user.

13.2.3.2 Verification of Measured ANC --

The measured ANC is evaluated by comparing it to the average of the acceptable calculated values for alkalinity determined during the evaluation of pH and DIC.

Carbonate Systems - For a true carbonate system, the measured ANC should equal (within experimental error) the calculated alkalinity. The difference between measured ANC and the calculated alkalinity should be within $\pm 15 \mu\text{eq/L}$ for calculated alkalinities less than or equal to 100 $\mu\text{eq/L}$, and within ± 10 percent for larger values. If the measured ANC differs from the calculated alkalinity, an analytical error is indicated in the titration or in the pH or DIC measurements.

Mixed Systems - Mixed systems are those represented by samples that have significant concentrations of other protolytes in addition to the carbonate species. In natural waters, organic bases derived from humic and fulvic acids often are present and can make a significant contribution to the ANC. The Oliver model is an empirical method of relating DOC, pH, and organic protolytes in two ways (Oliver et al., 1983). The first way relates the total organic protolyte to DOC, and the second relates the mass action quotient (pK_O) of the organics present to the sample pH.

DOC and pH are measured in each sample. The empirical relationships (defined by the Oliver model) and the measured pH and DOC values are used to estimate the contribution of organic protolytes to the measured ANC. The measured ANC should equal, within experimental error, the sum of the calculated alkalinity and the estimated organic protolyte contribution, if it is assumed that significant concentrations of other (non-organic) protolytes are not present and if there is no analytical error. The precision should be within $\pm 15 \mu\text{eq/L}$ for calculated

ANC less than or equal to 100 $\mu\text{eq/L}$ and within ± 10 percent for larger values.

13.2.3.3 Verification of Measured BNC --

BNC, unlike ANC, is affected by changes in dissolved CO_2 concentration. Therefore, evaluation and verification of BNC data cannot utilize as much redundancy as that of ANC data. Only the initial pH and DIC values determined in the analytical laboratory (data pair C₂, see Section 13.2.3.1) can be used to calculate BNC for comparison with the measured value. As with ANC, other protolytes can contribute to the measured BNC. An estimate of CO_2 -acidity is calculated from data pairs and carbonate equilibria. The calculated acidity should equal, within experimental error, the measured BNC, if no other protolytes are present. Precision for calculated acidity values less than or equal to 100 $\mu\text{eq/L}$ should be within $\pm 10 \mu\text{eq/L}$ and within ± 10 percent for larger values. If the calculated acidity is greater than the measured BNC, an analytical error in the pH, DIC, or BNC determination is indicated.

The pH and DIC measurements are verified by the previous tests (QA/QC redundancy and alkalinity checks). If the calculated acidity is less than the measured BNC, the difference may be due to the presence of other protolytes or to an analytical measurement error. The Oliver model is used to evaluate the contribution from organic protolytes.

13.2.3.4 System Check for Total Carbonate --

For a carbonate system, it can be shown that the sum of alkalinity and acidity equals total carbonate concentration in the sample. For a mixed system, it can be shown that the sum of ANC and BNC equals the total protolyte concentration in the sample. Thus, as an additional check of the data, the calculated values of alkalinity and acidity can be combined and can be compared to the sum of the measured ANC and BNC. For a carbonate system, the sum of ANC and BNC should equal, within experimental error, the total carbonate concentration or the sum of calculated acidity and alkalinity. If this sum is less than the calculated total carbonate, an analytical error is indicated because the two titrations must account for all carbonate species present in the sample. Other protolytes or analytical error is indicated if the sum of ANC and BNC exceeds the calculated total carbonate. Again, the Oliver model is used to evaluate the data.

The precision of the total carbonate results should be within $\pm 15 \mu\text{mole/L}$ for total carbonate concentrations less than or equal to 100 $\mu\text{mole/L}$ and within ± 10 percent for higher concentrations.

The protolyte analysis program generates flags (Table 12-2) on the basis of the data checks described above to indicate the source of problems.

13.2.4 Follow-up with Analytical Laboratories

After all data have been reviewed, the analytical laboratories are requested to submit completed copies of data reporting forms that were incomplete when previously submitted, to submit corrections of previously reported data, to confirm previous results, and to reanalyze certain samples that do not meet QA/QC criteria. The analytical laboratories are directed to respond within a reasonable time so that the results can be evaluated in time for them to be useful to the survey.

13.2.5 Preparation and Delivery of Verification Tapes

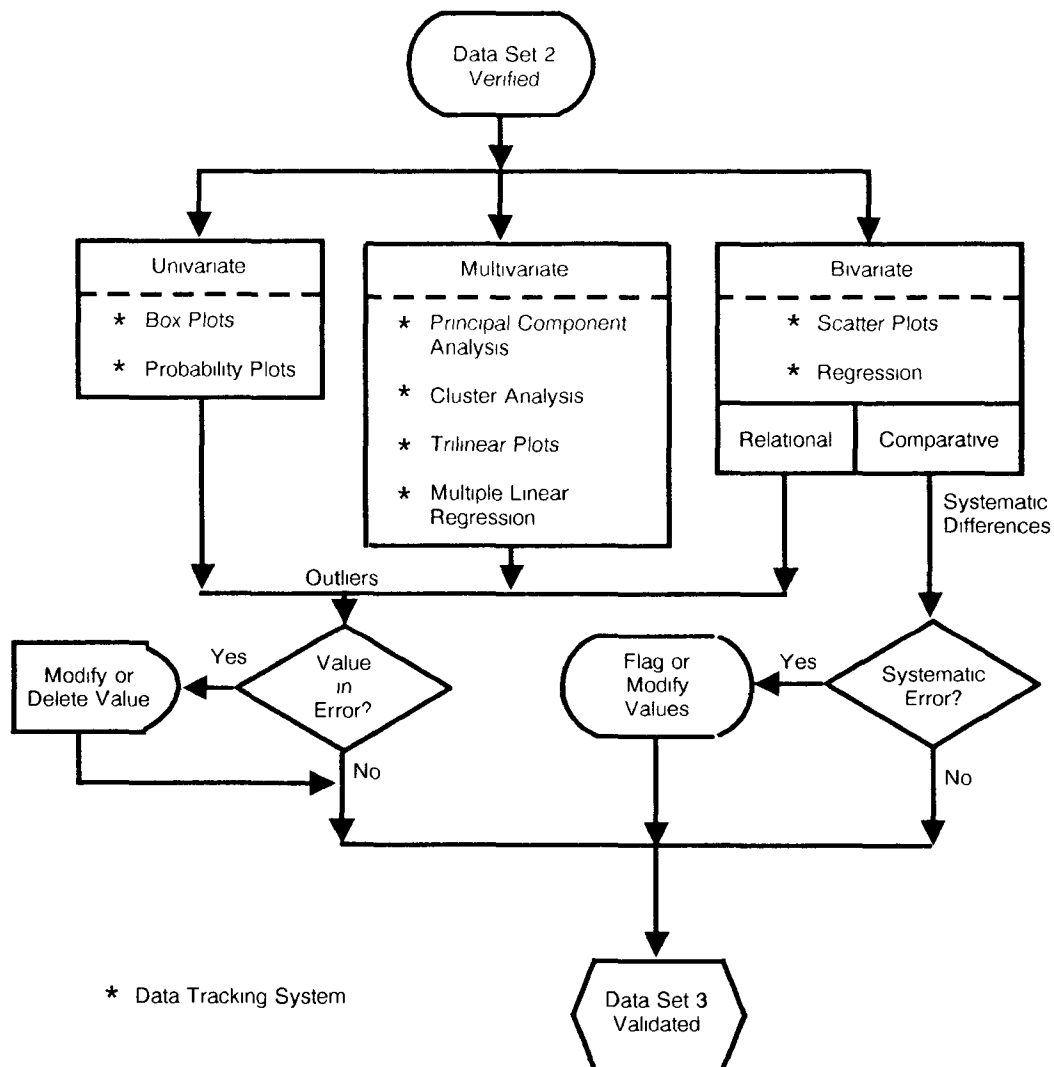
The steps identified in sections 13.2.2 through 13.2.4 are followed to identify suspect data and to correct erroneous data. The information obtained by this process is accumulated by the EMSL-LV QA staff and is placed on magnetic tapes, which subsequently are sent to ORNL. There, the new data are entered into the raw data set to correct and flag the original data. These steps may have to be repeated several times before all the data are verified; however, the aim is to have only two iterations.

14.0 Data Validation

The system of data validation developed for ELS-I also is used for WLS-I. Data validation is discussed

in Section 14 of the ELS-I QA plan (Drou   et al.,1986). A flowchart of the validation process is shown in Figure 14-1.

Figure 14-1. Flowchart of the data validation process, Western Lake Survey - Phase I.



15.0 Development of a Final Data Set

The calculation of population estimates is difficult if values are missing from the data set. A final data set (Data Set 4) is prepared to resolve problems in the validated data set that result from missing values. Data Set 4 also is modified by averaging field duplicate values, substituting for analytical values determined to be in error during validation (Figure 15-1), and modifying (i.e., adjusting to zero) values reported as negative (except for ANC and BNC). The values that have been modified for the final data set are flagged with the appropriate data qualifiers (see Table 15-1).

15.1 Missing Data Substitution

Substitution for missing values is done in one of several possible ways. Values from duplicate samples are used when available. Redundant analyses are performed for pH, DIC, and conductance (see Section 13.2.4). Redundant measurements on split samples (see Section 6.3.2.3.1) are performed for metals and

other elements. If a duplicate measurement is not available, a comparable measurement is chosen and is substituted for the missing value. A linear regression routine is used for this purpose. If redundant measurements are not available or are not acceptable, observed relationships with other variables (e.g., sodium and chloride) are used to calculate a substitution value from the available data. The last option for identifying a substitution value is to use the stratum mean within the subregion. All substitution values are examined a second time for acceptability before they are included in the final data set. Substituted values are flagged as such in the final data set.

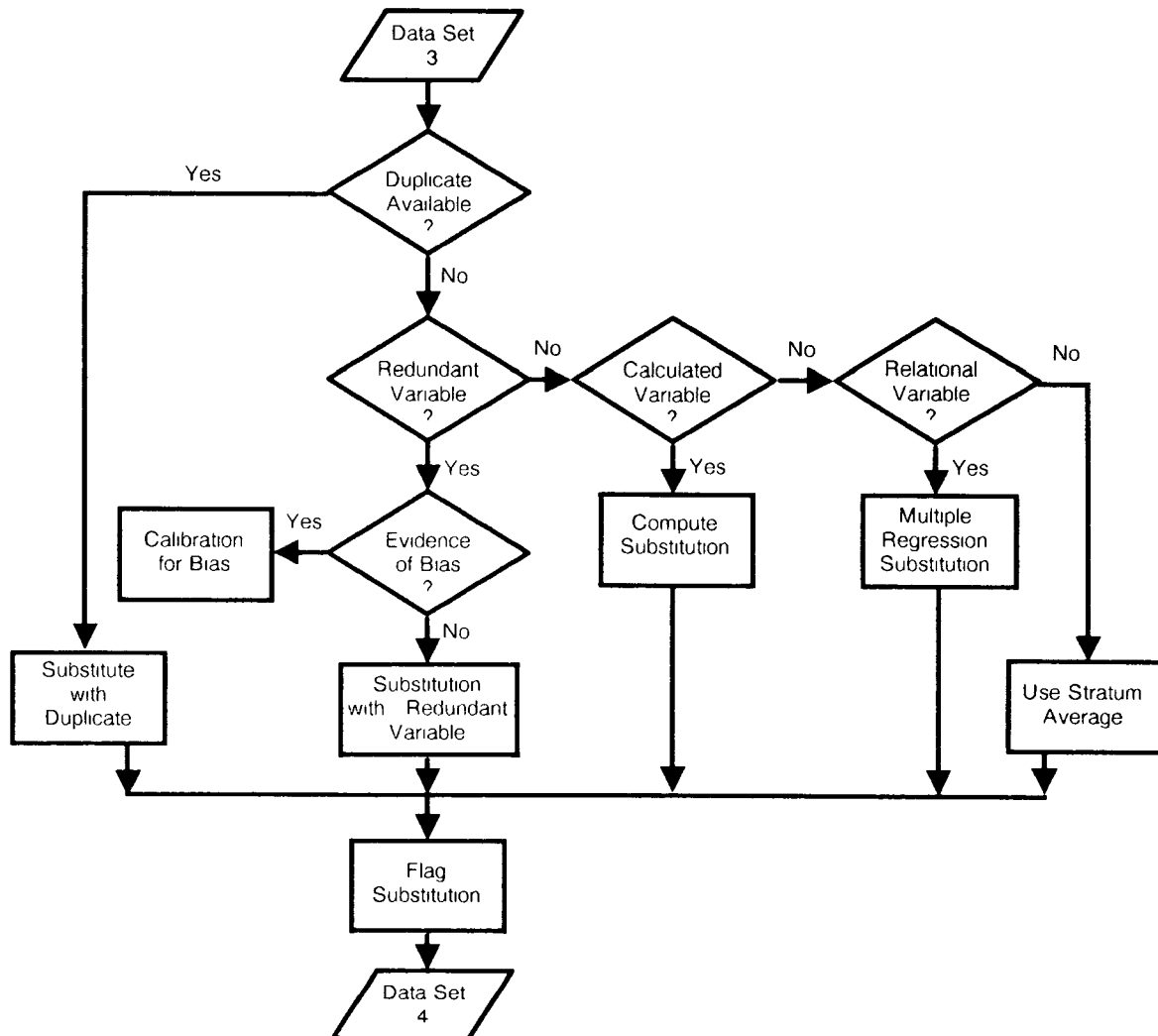
15.2 Averaging of Field Duplicate Pairs

If field duplicate pairs have no validation flags present, the average of the duplicate pair values is used in the final data set. Averaged values are flagged in the final data set.

Table 15-1. Validation Data Qualifiers (Flags) for the Final Data Set, Western Lake Survey - Phase I

U0	Known error based on relationships with other variables or on impossible values; substitutions were made in Data Set 4.
U1	Value is a substitution, original value was missing.
U2	Value is a substitution, original value was considered to be in error.
V0	Data value represents the average from a duplicate split and measurement of the lake sample.
V1	Data value is from the duplicate sample and is not averaged because the regular sample had "WO" flag limitations.
W0	Data value has possible measurement error based on relationships with other variables, has QA violations, or is outside QA windows for acceptable data.
Z0	Original value was less than zero and has been replaced with zero.

Figure 15-1. Development of Data Set 4, Western Lake Survey - Phase I.



15.3 Treatment of Negative Values

Negative values (for parameters other than ANC and BNC) that result from analytical calibration bias (i.e., instrumental drift) are set to zero. The bias in the estimate of variance due to this adjustment likely does not affect data analysis. All negative values modified in the final data set are flagged.

16.0 References

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Appendix
Form Used in On-Site Evaluation of Ground Crews,
Western Lake Survey - Phase I

Western Lake Survey Ground Crew Audit Questionnaire 1.2

Subregion _____

Field Base Location _____

Remote Site Location _____

EPA Base Coordinator _____

USFS Field Manager _____

Dates _____

Auditors _____

Note 1. Circle one or more contact modes on page heading:

R = radio

T = transfer point

L = laboratory or base (sample inspection, no contact)

P = personal contact (on site, transfer point, or laboratory)

Note 2. *In left margin indicates questions to be asked during radio contact time.

GROUND CREW STATISTICS - P

Crew ID	Samplers' Names	Agency	Academic Training	Experience Type and Years

SAMPLERS' NAMES _____ DATE _____

CREW ID _____

STAGING AREA - P

Item	Yes	No	Comments
Has adequate space been provided for predeparture activities?			
Are facilities clean and organized?			
Is equipment clean and organized?			
Is all equipment operational?			
Has the thermistor been through a two-point calibration check? Results?			

Notes:

SAMPLERS' NAMES _____

DATE _____

CREW ID _____

EN ROUTE ACTIVITIES - P - R - T

Item	Yes	No	Comments
* Are the maps adequate?			
* Are there any problems in locating lakes?			
Are the field data forms and notebooks understood? Correctly filled out? Transcriptions verified?			
Are identifications of target lakes verified? How?			
Are pack and riding animals adequate for safe transportation of personnel and gear?			

Notes:

SAMPLERS' NAMES _____ DATE _____

CREW ID _____

PREPARATION - P

Item	Yes	No	Comments
Are checklists followed for loading equipment?			
Is equipment organized and easily accessible on pack animals.			
Is equipment stored properly to prevent injury or damage during transport?			
Are excursion plans made? Adequate? Understood by all personnel?			
Do the field manager and base coordinator know where crew is at any given time?			
Is communication between field base and field crew adequate?			
Are check-in times prearranged? Are there deviations from the times? If so, explain.			
Has trip departure been delayed significantly for any reason? Reasons?			

Notes:

SAMPLERS' NAMES _____

DATE _____

CREW ID _____

ON-SITE SAMPLING - P- R - T

Item	Yes	No	Comments
* Are there problems finding the deepest sampling site while on lake?			
Are the sounding, Secchi, and thermistor lines adequate?			
* Are the procedures clear and easily followed?			
Are required procedures for blanks and duplicates followed?			
Are required safety procedures followed?			
*Are there any problems in obtaining samples?			
Are adequate volumes of sample being taken?			
Are procedures being followed that avoid contamination?			
Are rinse procedures followed correctly?			
Are samples stored correctly?			
Are appropriate comments being recorded in logbook? Form 1?			
			(continued)

SAMPLERS' NAMES _____ DATE _____

CREW ID _____

ON-SITE SAMPLING - P - R - T (Continued)

Item	Yes	No	Comments
Are all labels filled out correctly?			
* Is there effective coordination between the sampling crew and the field laboratory?			
Are samples arriving at the field laboratory within required time?			
Are there any problems loading equipment on horses or llamas? On rafts?			
How long did finding the deep site take?			
Was 10 minutes allowed for pH strip development?			
Were there any problems with air bubbles?			
Were there any problems with cables?			

SAMPLERS' NAMES _____

DATE _____

CREW ID _____

THERMISTOR GENERAL - P - R

Item	Yes	No	Comments
Are copies of the operations manual available?			
Is the instrument cleaned and packed properly?			
Are all personnel capable of routine maintenance? Troubleshooting meter problems?			
Have any maintenance problems occurred?			
Are adequate spare parts available?			
Is meter performing well?			
Are there any continuous problems with the meter?			
Have there been any deviations from standard procedures? Describe.			
Were there any problems in determining stratification?			
What were the meter deviations from field thermometer?			
Were temperature QC checks performed at each lake?			

Notes:

SAMPLERS' NAMES _____ DATE _____

CREW ID _____

ACTIVITIES FOLLOWING SAMPLING - L - P

Item	Yes	No	Comments
Are samples packed properly at lake site?			
Is equipment packed properly after sampling?			
Are samples transferred properly at transfer point?			
Are sufficient supplies provided at transfer point?			
Are supplies being requested in sufficient time to avoid delays.			
Is sample tracking and custody form properly completed?			
Are cooler temperatures being recorded?			
Are gel packs arriving from field still frozen?			
Were cooler temperatures spot-checked when coolers arrived at field base? What were the temperatures? Are they recorded properly?			
Were data forms checked for problems? Were they signed by field manager?			

SAMPLERS' NAMES _____

DATE _____

CREW ID _____

POST SAMPLING ACTIVITIES - L - P

Item	Yes	No	Comments
What was the elapsed time between sample collection and laboratory receipt?			
Were phone check-ins received at field base?			
Were any calibration lakes sampled? Which?			
How were they identified as calibration lakes?			
Were the samplers aware that the lake was a calibration lake?			

Notes:

