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Research and Development

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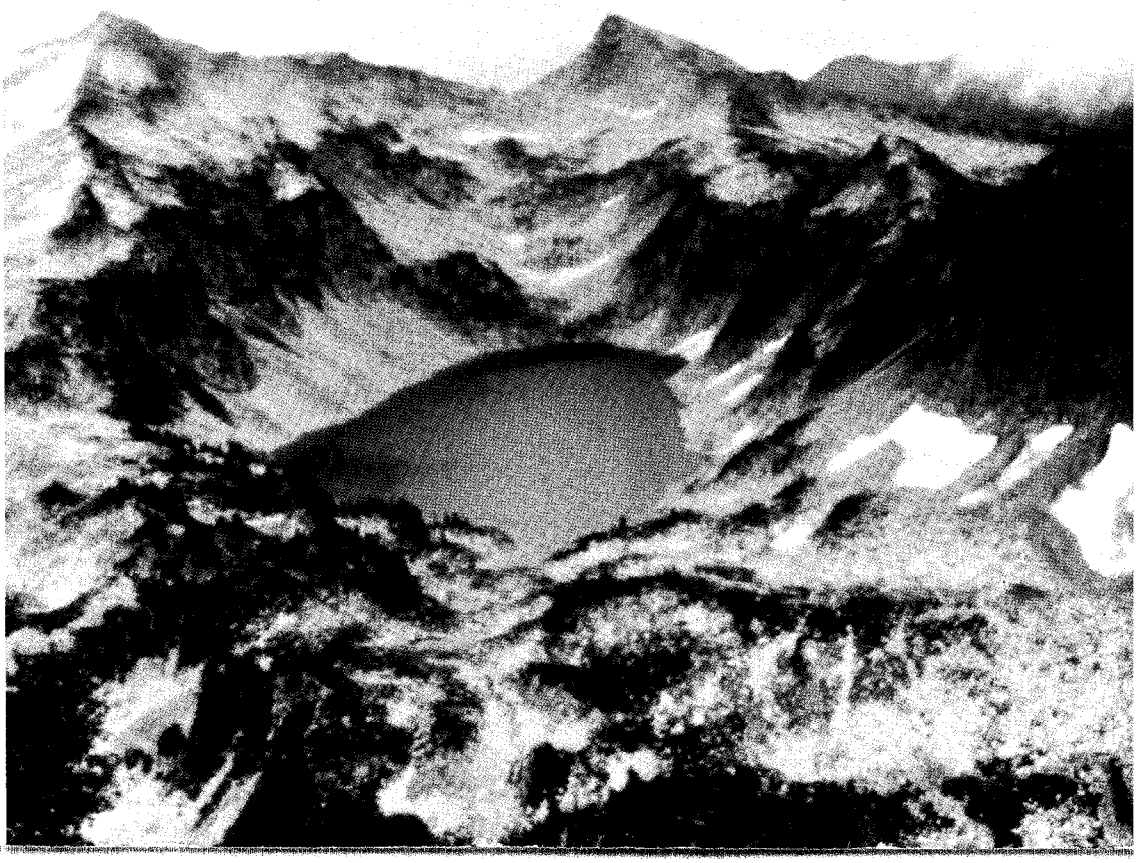
Western Lake Survey Phase I

Quality Assurance Report



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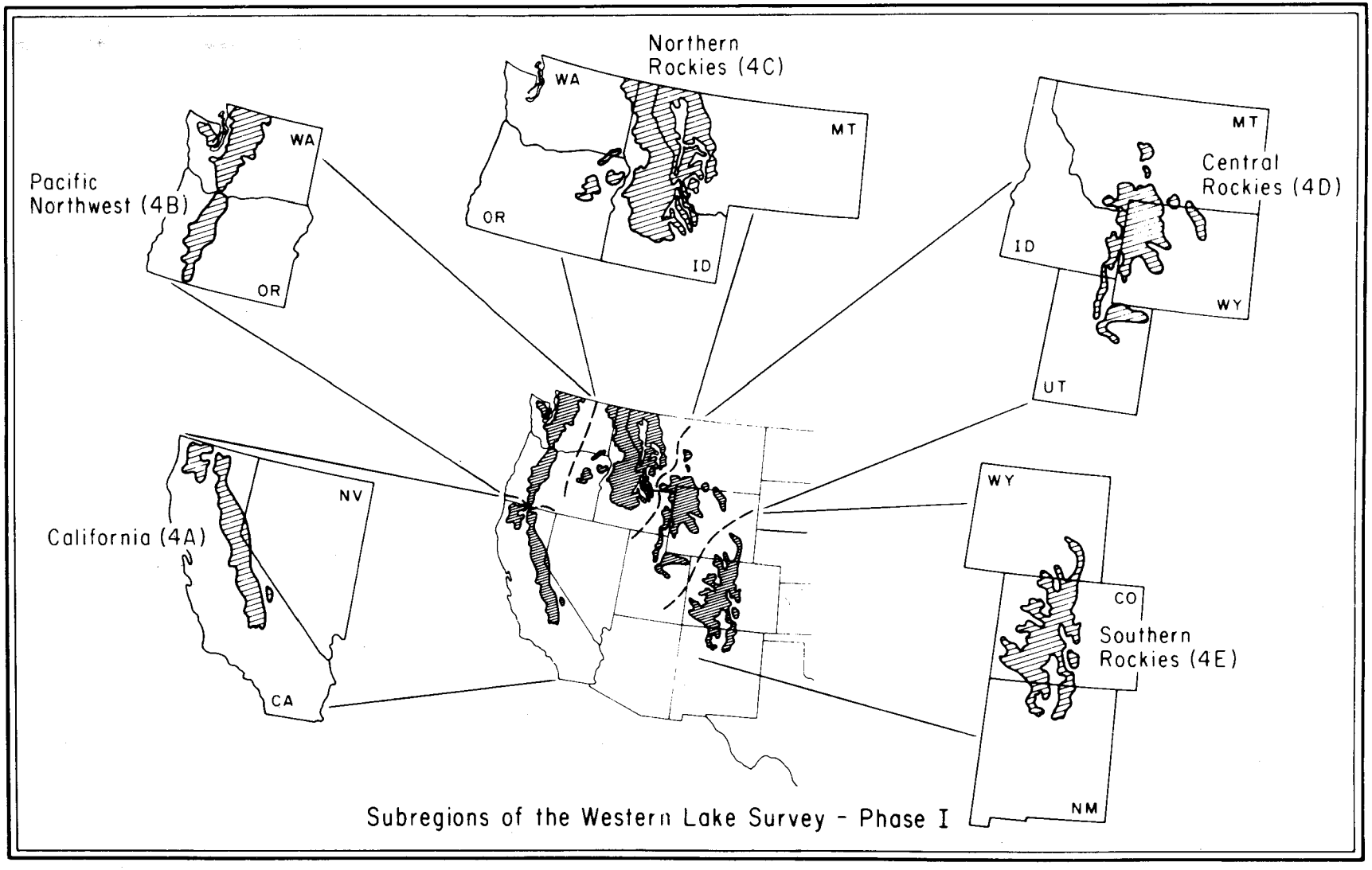

Subregions of the Western Lake Survey - Phase I

EPA 600/4-87/037
November 1987

Western Lake Survey
Phase I

Quality Assurance Report

A Contribution to the
National Acid Precipitation Assessment Program

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

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

Notice

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

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. Similiar 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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Foreword

The primary function of this quality assurance report is to assess the data quality for the Western Lake Survey - Phase I. A known degree of confidence in the data quality is essential to the initial data user, who must rely on the estimates of data quality in the determination of subregional and regional population estimates (a major goal of Phase I of the National Surface Water Survey). Confidence in data quality is also essential to future data users, who can use this report as a reference guide in determining levels of performance for their own research purposes.

This document is also directed to numerous individuals, contractors, and government agencies that were involved in the planning and the day-to-day survey operations. Each of these participants has a unique interest in the specific performance aspects of the survey. The U.S. Department of Agriculture Forest Service, the National Park Service, the analytical and preparation laboratories, the field sampling personnel, and the field laboratory personnel all have interests in specific information on performance and participation. The detailed discussions, however, are not included solely for the benefit of individual participants or groups; they are intended to aid program managers and future survey designers in refining data quality objectives and methods on the basis of past performance and sampling design.

The final goal of the document is to ask questions that do not, at present, have answers. These questions are directed toward present and future data users and survey designers. Thus, the document is intended as a guide for present and future data users and as a history of events that may prove valuable to designers of similar surveys. The specific expertise that these individuals bring to their reading of this document will be the ultimate source of more efficient and meaningful survey designs and quality assurance programs.

Abstract

The quality assurance program for the Western Lake Survey - Phase I was designed to ensure that the data collected were of known and acceptable quality. The quality assurance program was based on similar activities conducted for the Eastern Lake Survey - Phase I and included the following major elements: selection of analytical laboratories, training of field sampling and field laboratory crews, on-site evaluation of field and analytical laboratories, daily communications with survey participants, and verification and evaluation of data collected. Numerous quality assurance and quality control samples (e.g., blanks, duplicates, audits, spikes, and check samples) were used to identify, qualify, and quantify sources of sampling and analytical variability in terms of precision, accuracy, bias, and analytical detectability. The relative importance of these sources of variation was assessed by comparative statistical evaluations.

Until all of the phases of the National Surface Water Survey have been conducted and their data sets are available for comparison, an assessment of Western Lake Survey - Phase I data quality cannot be considered complete. It can be stated, however, that the final data set represents data of high quality that can be used with confidence in the calculation of population estimates. Precision, accuracy, and detectability estimates generally met survey data quality objectives. Samples were complete, analyses were performed within specified holding times, and 10 of 15 strata met sampling completeness criteria. Quality assurance samples adequately characterized the routine lake water samples, with the exception that field audit samples did not represent the midrange of the lake water sample analyte concentrations.

For future surveys, refinement of data quality objectives and of the sampling design will be necessary to improve partitioning of the components of variability and to account for circumneutrality, differences in sample concentration, and differences in ionic strength of lake waters. Data from the West can be compared to data from other elements of the National Surface Water Survey; no calibration of data is necessary for procedural differences in sampling or analytical methodology.

By its ability to identify trends and to isolate problems in the survey data, the quality assurance program also confirmed the overall soundness of the survey design, execution, and data generation process. The data verification process yielded numerous suggestions for refining lake sampling, field laboratory, analytical laboratory, and data management and analysis procedures. These suggestions are given in tabular form in the Conclusions and Recommendations section, along with summaries of the associated findings, corrective actions, and impact on data quality.

This report was submitted in partial fulfillment of contract number 68-03- 3249 by Lockheed Engineering and Management Services Company, Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers a field work period from September 10, 1985, to November 4, 1985; data evaluation and verification were completed as of May 14, 1986.

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Data Verification Analyst

Karen A. Cougan	Lockheed-EMSCO

Quality Assurance Aquatics and Technical Support

Lynn W. Creelman	Lockheed-EMSCO
Bryant C. Hess	Lockheed-EMSCO
Mary D. Best	Lockheed-EMSCO
Carol B. Macleod	Lockheed-EMSCO
Stephen J. Simon	Lockheed-EMSCO
Donald A. Hilke	Lockheed-EMSCO
Daniel C. Hillman	Lockheed-EMSCO
C.E. Mericas	Lockheed-EMSCO

Quality Assurance Aquatics and Technical Support (continued)

David V. Peck	Lockheed-EMSCO
Janice L. Engels	Lockheed-EMSCO
Charles M. Monaco	Lockheed-EMSCO
James E. Pollard	Lockheed-EMSCO
Gerald E. Byers	Lockheed-EMSCO
Eugene P. Meier	U.S. EPA, Environmental Monitoring Systems Laboratory - Las Vegas

Statistical Support

Martin A. Stapanian	Lockheed-EMSCO
Forest C. Garner	Lockheed-EMSCO
Thomas Permutt	Systems Applications, Inc.
Alison K. Pollack	Systems Applications, Inc.
Mithra Moezzi	Systems Applications, Inc

Computer Support

Daniel Allison	Lockheed-EMSCO
Brian N. Cordova	Lockheed-EMSCO
Richard K. Maul	Lockheed-EMSCO
John (In Seung) Lau	Lockheed-EMSCO
Martin A. Stapanian	Lockheed-EMSCO
Carol B. Macleod	Lockheed-EMSCO
Michael J. Pearson	Lockheed-EMSCO
Joseph Scanlan	Lockheed-EMSCO
Robert E. Enwall	Lockheed-EMSCO
Charles M. Monaco	Lockheed-EMSCO
John Fountain	Lockheed-EMSCO
David Hoff	Lockheed-EMSCO
Ganise Satterwhite	Lockheed-EMSCO
Thomas Hody	Lockheed-EMSCO
James Pendleton	Lockheed-EMSCO
Merylin Gentry	Science Applications International Corporation
Raymond McCord	Science Applications International Corporation
Les Hook	Science Applications International Corporation
Paul Kanciruk	Oak Ridge National Laboratory

Methods Development

Daniel C. Hillman	Lockheed-EMSCO
F. Xavier Suarez	Lockheed-EMSCO
Eileen M. Burke	Lockheed-EMSCO

Logistical Support

Kenneth Asbury	Lockheed-EMSCO
Valerie A. Sheppe	Lockheed-EMSCO
David V. Peck	Lockheed-EMSCO
Kevin J. Cabble	Lockheed-EMSCO
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Logistical Support (continued)

Alan Groeger	Lockheed-EMSCO
Mel Knapp	Lockheed-EMSCO
Ky Ostergaard	Lockheed-EMSCO
Robert Cusimano	Northrop Services, Inc.

Analytical Support

Daniel C. Hillman	Lockheed-EMSCO
Linda A. Drewes	Lockheed-EMSCO
John M. Henshaw	Lockheed-EMSCO
Molly Morison	Lockheed-EMSCO
David V. Peck	Lockheed-EMSCO
C. Hunter Nolen	Lockheed-EMSCO
F. Xavier Suarez	Lockheed-EMSCO
Richard C. Buell	Lockheed-EMSCO
Eileen M. Burke	Lockheed-EMSCO
Jerry Wagner	U.S. EPA, Environmental Research Laboratory - Corvallis
Kenneth Ives	Versar, Inc.
Sally Ann Reed	Versar, Inc.
Linda Carlin	Environmental Monitoring and Services, Inc.
Joe Matta	Environmental Monitoring and Services, Inc.
Sue Czdemir	Environmental Monitoring and Services, Inc.
David L. Lewis	Radian Corporation

Management Team

Dixon H. Landers	U.S. EPA, Environmental Research Laboratory - Corvallis
Joseph Eilers	Northrop Services, Inc.
David F. Brakke	Western Washington University
Rick A. Linthurst	U.S. EPA, Aquatic Effects Research Program, Research Triangle Park

Clerical, Editorial, and Word Processing Support

Linda K. Marks	Lockheed-EMSCO
Ramone W. Denby	Lockheed-EMSCO
Margaret E. Oakes	Lockheed-EMSCO
Annalisa H. Hall	Lockheed-EMSCO
Lynn A. Stanley	Lockheed-EMSCO
Brian N. Cordova	Lockheed-EMSCO
Kit M. Howe	Lockheed-EMSCO
John M. Nicholson	Lockheed-EMSCO

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Lynn A. Stanley	Lockheed-EMSCO
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Section 1
Introduction

Purpose

This report reviews the quality assurance (QA) and quality control (QC) activities and the analytical data quality estimates associated with the Western Lake Survey - Phase I (WLS-I). It is intended to provide baseline information on WLS-I data quality. The final report for the survey (Landers et al., 1987; Eilers et al., 1987) provides an overview of WLS-I activities and results. The WLS-I QA plan (Silverstein et al., 1987), the analytical methods manual (Kerfoot and Faber, 1987), and the field operations report (Bonoff and Groeger, 1987) provide detailed information about specific aspects of WLS-I. These documents, in turn, reference their Eastern Lake Survey - Phase I (ELS-I) counterparts: Drousé et al. (1986), Hillman et al. (1986), and Morris et al. (1986).

Organization

This QA report describes QA and QC activities related to collecting, processing, analyzing, and handling samples and data. General conclusions and recommendations concerning data quality, as well as supporting conclusions and recommendations concerning QA program design and operation, are presented in Section 2. The QA program used during WLS-I sampling and sample analysis is described in Section 3. Data review and data verification procedures are described in Section 4. Results and discussion related to the operational aspects of the QA program are given in Section 5. Subsequent sections present the statistical evaluations and quality assurance results for three primary analytical data quality objectives (DQOs): precision (Section 6), accuracy (Section 7), and detectability (Section 8). Sections 6 through 8 also provide guidance for using the QA and QC data in interpreting WLS-I overall results. Section 9 summarizes the special studies conducted in conjunction with WLS-I and presents QA and QC results associated with those studies. The appendices provide supporting data, and a glossary at the end of the document defines abbreviations and terms used throughout.

Specific Applications

The sampling and QA designs of WLS-I were complex. As a result, this document contains detailed information about situations that may have affected data quality. Readers interested solely in the impact of data quality on population estimates are directed to the following sections, tables, and figures:

- Section 2, "Lake Water Characteristics," is an analyte-by-analyte synopsis of the QA and QC data interpretation.
- Appendix J summarizes data quality analyte by analyte. The figures illustrate data detectability and the variability of the data used to calculate the population estimates for all analytes over the range of concentrations of WLS-I lake waters.
- Tables 15 and 21 present precision statistics that indicate how variability affects the routine lake sample results.
- Table 16 interprets the statistical results of Tables 15 and 21.
- Table 20 summarizes the success of the major precision components by sampling method and by analytical laboratory.
- Table 29 presents estimated accuracy statistics.
- Table 30 summarizes Table 29 by presenting analytes that exhibit a high degree of inaccuracy.
- Table 31 presents the statistical relation between detectability and the routine sample. The system decision limit (P_{95}) should be of particular interest.

Readers interested in assessing whether or not the DQOs were met and in determining how WLS-I experience can be applied to future surveys are directed to the following sections, tables, and figures:

- Tables 4 through 7 present significant findings concerning WLS-I sampling, sample preparation, sample analysis, and data analysis. The problems, corrective actions, effects on the

data, and recommendations for future surveys are described for each aspect.

- Tables 22 and 23 present statistical results of the intralaboratory precision estimates, which relate directly to the DQOs for precision.
- Table 25 presents an interpretation of Tables 22 and 23.
- Table 29 presents a statistical analysis of accuracy estimates.
- Table 30 summarizes Table 29 by presenting analytes that exhibit a high degree of inaccuracy.
- Section 8, "Estimating Detectability from Calibration and Reagent Blanks"compares the results of analytical instrumental detection limits to the required detection limit, the DQO for detectability.
- Appendix D, Table D-3 presents the statistical results of the instrument detection and calibration blank data discussed in Section 8.
- Section 9, "Special Studies," presents results of the calibration study and nitrate-sulfate stability study.

Survey Design and History

WLS-I was conducted during fall 1985 as a part of the National Surface Water Survey (NSWS). NSWS, which was initiated by the U.S. Environmental Protection Agency (EPA) in 1983, is a project within the National Acid Precipitation Assessment Program (NAPAP). The goals of NSWS are (1) to describe and evaluate, through a series of regional field surveys and monitoring projects, the present chemical status of lakes and streams in areas of the United States that are potentially susceptible to the effects of acidic deposition, (2) to study the temporal variability associated with the chemical status of these waters, (3) to identify associated biological resources, and (4) to monitor changes over time in a representative subset of the aquatic systems studied (Landers et al., 1987).

Between mid-September and mid-November 1984, the U.S. Department of Agriculture - Forest Service, in conjunction with EPA Region 8, conducted a pilot study to test the procedures that would be used in WLS-I. The Forest Service selected 62 lakes from among those in the Weminuche Wilderness (San Juan Mountains, Colorado), the Uintas Wilderness (Utah), and the Cloud Peak Wilderness (Big Horn Mountains, Wyoming). When the pilot study lakes proved difficult to reach from the ground within the time constraints imposed by the sampling design, concern arose that some of the approximately 900 lakes scheduled for sampling in WLS-I could not be accessible from the ground. As a result, helicopters were introduced as an alternative method of reaching WLS-I lakes.

The pilot study helped anticipate problems that might be encountered during WLS-I and contributed to the refinement of procedures used to reach wilderness lakes from the ground. Pertinent results from the pilot study are summarized in Table 1.

In most respects, WLS-I followed the survey design and protocols used for ELS-I. The major difference between the two surveys was that WLS-I used two access methods. Ground crews sampled the lakes from boats; helicopter crews landed the helicopters on the lakes in order to conduct sampling activities. ELS-I crews used helicopter access only. Because two methods of access were used, it was necessary to develop a method for quantifying differences between them. To provide this comparative information, a calibration study (Section 9) was incorporated into the WLS-I sampling design.

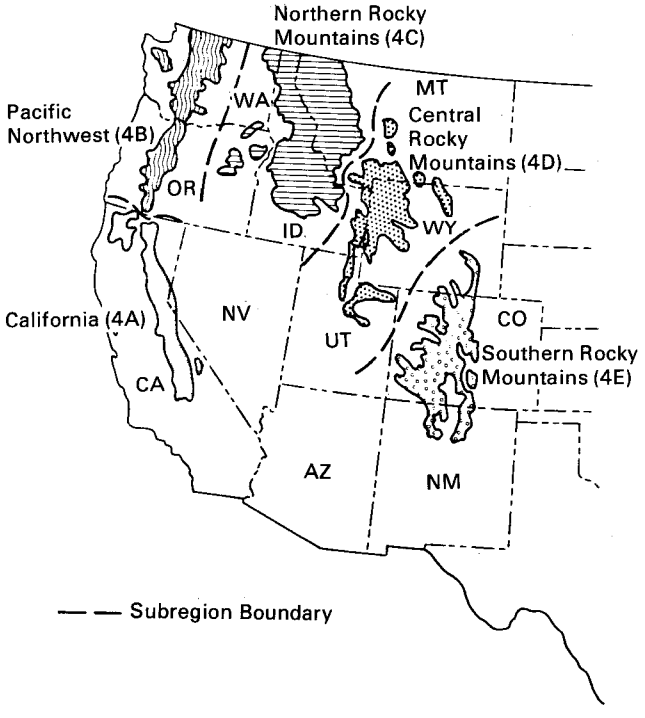
The mountainous areas studied were categorized as subregions as shown in Figure 1, and the subregions were divided into alkalinity classes. WLS-I ground crews and helicopter crews collected samples from 757 of the 920 lakes originally scheduled for sampling. (Bonoff and Groeger [1987] and Section 5 of this QA report discuss the reasons that some lakes were not sampled.) This sample represented nearly 10,400 lakes in the target population. Most of the lakes sampled were chosen randomly for use in population estimates (Landers et al., 1987); these lakes are referred to as the probability sample (719 of the 757 lakes). Other lakes were chosen as special-interest lakes; these lakes were not part of the probability sample and were not used in population estimates. For WLS-I, the term "population estimate" refers to an estimate of the number of lakes in the target population that have a particular characteristic (i.e., alkalinity class of a subregion). The estimate is extrapolated from the number of lakes sampled (the probability sample).

Each lake was represented by a single routine sample, for which 24 chemical and physical characteristics were measured at the lake sites, field laboratories, or analytical laboratories (see Table 2). Descriptions of these characteristics and of the analytical methods are given in Hillman et al. (1986) and in Kerfoot and Faber (1987). The WLS-I sampling design was based on the premise that measurement of 24 variables for a single routine sample from each lake would provide information sufficient to evaluate the present chemical status of the lakes studied. See Landers et al. (1987) for a detailed discussion of population estimates.

Table 1. Summary of Results, Western Lake Survey Pilot Study

Pilot Activity	Situation Encountered	Application to WLS-I
Lakes Access was by ground (boat) only	Bad weather (snow storm) closed trails in Wyoming; 75% of lakes could not be sampled	Emphasized need for (1) helicopter access and (2) coordinating sampling time with weather forecasted
Lakes selected for proximity to trailhead	Phase I lakes were selected randomly; some were far from trailhead	Emphasized need for helicopter access
Lake samples preserved and processed in tents or outdoors	High risk of contamination	Emphasized need for central, accessible field laboratory
Lake samples processed without electricity	Unable to process extractable Al aliquot, perform sample filtrations, or analyze for DIC (closed system), pH (closed system), or turbidity	Emphasized need for central field laboratory
Ground crews used a Hydrolab for in situ measurements of conductance, pH, and temperature	An extra pack animal was needed to carry CO_2 tank for Hydrolab calibration	Emphasized complex logistics necessary to obtain in situ measurements by ground access
Samples shipped from field every three days	Protocol stated that extractable Al, NO_3^-, and pH had to be analyzed within 7 days; improbable that analytical laboratory could perform analysis within holding times	Emphasized need for daily shipments as in ELS-I
Field communications	Considered inadequate; possibility of safety hazards for sampling crews	Emphasized need for coordinated communications network
Data not collected on standardized NSWS form; no QA/QC data documentation	Inability to compare pilot survey data to other data bases confidently	Emphasized need for data base management and QA/QC input

Figure 1. Subregions studied, Western Lake Survey - Phase I.



Survey Participants

The EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV), had primary responsibility for the WLS-I sampling operations and QA program. EMSL-LV received assistance in these areas from its prime contractor, Lockheed Engineering and Management Services Company, Inc. (Lockheed-EMSCO). Lockheed-EMSCO personnel performed the helicopter-access sampling activities, and Forest Service personnel performed most of the ground-access sampling activities. State agencies and EPA regional offices also were involved in the sampling activities. Environmental Monitoring and Services, Inc., in Thousand Oaks, California, and Versar, Inc., in Alexandria, Virginia, provided analytical laboratory services. The two laboratories were selected according to procedures established for the EPA's Contract Laboratory Program (CLP). Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee, was responsible for data base management. The EPA Environmental Research Laboratory in Corvallis, Oregon (ERL-C), had primary responsibility for survey design, data validation, and data interpretation.

Data Quality Objectives

WLS-I analytical data quality objectives (DQOs) established the measurement criteria for the 24 variables studied. The statistical design, sampling and analytical methods, and QA activities for WLS-I were

Table 2. Chemical and Physical Characteristics Measured, and Associated Data Quality Objectives for Detectability, Precision, and Accuracy, Western Lake Survey - Phase I

Measurement Site[a]	Variable (dissolved ions and metals unless noted)	Analytical Method	Unit	Detectability: Expected Range (for lake waters)	Detectability: Required Detection Limit	Intralaboratory (Laboratory Duplicate) Precision: Percent Relative Standard Deviation (%RSD), Upper Limit[b]	Accuracy: Maximum Absolute Bias
A	Al, extractable	Complexation with 8-hydroxyquinoline and extraction into methyl isobutyl ketone followed by atomic absorption spectroscopy (furnace)	mg/L	0.005-1.0	0.005	10 (if Al conc. > 0.01 mg/L) 20 (if Al conc. ≤ 0.01 mg/L)	10% 20%
A	Al, total	Atomic absorption spectroscopy (furnace)	mg/L	0.005- 1.0	0.005	10 (if Al conc. > 0.01mg/L) 20 (if Al conc. ≤ 0.01 mg/L)	10% 20%
A	Acid Neutralizing Capacity (ANC)	Titration and Gran analysis	µeq/L	-100 - 1,000	c	10	10%
A	Base Neutralizing Capacity (BNC)	Titration and Gran analysis	µeq/L	-10 - 150	c	10	10%
A	Ca	Atomic absorption spectroscopy (flame) or inductively coupled plasma atomic emission spectroscopy[d]	mg/L	0.5 - 20	0.01	5	10%
A	Cl^-	Ion chromatography	mg/L	0.2 - 10	0.01	5	10%
A,L	Conductance (at 25°C)	Conductivity cell and meter	µS/cm	10 - 1,000	e	2	5%
A,F	Dissolved Inorganic Carbon (DIC)[f]	Instrumental (acidification, CO_2 generation, IR detection)	mg/L	0.05 -15	0.05	10	10%
A	Dissolved Organic Carbon(DOC)	Instrumental (uv-promoted oxidation, CO_2 generation, IR detection)	mg/L	0.1 -50	0.1	5 (if DOC conc. > 5 mg/L) 10 (if DOC conc. ≤ 5 mg/L)	10% 10%
A	F^-, total dissolved	Ion-selective electrode and meter	mg/L	0.01 -0.20	0.005	5	10%
A	Fe	Atomic absorption spectroscopy (flame) or inductively coupled plasma atomic emission spectroscopy [d]	mg/L	0.01 - 5.0	0.01	10	10%
A	K	Atomic absorption spectroscopy (flame)	mg/L	0.1 -1.0	0.01	5	10%
A	Mg	Atomic absorption spectroscopy (flame) or inductively coupled plasma atomic emission spectroscopy[d]	mg/L	0.1 - 7.0	0.01	5	10%
A	Mn	Atomic absorption spectroscopy (flame) or inductively coupled plasma atomic emission spectroscopy [d]	mg/L	0.01 - 5.0	0.01	10	10%

(continued)

Table 2. (Continued)

Measurement Site[a]	Variable (dissolved ions and metals unless noted)	Analytical Method	Unit	Detectability: Expected Range (for lake waters)	Detectability: Required Detection Limit	Intralaboratory (Laboratory Duplicate) Precision: Percent Relative Standard Deviation (%RSD), Upper Limit[b]	Accuracy: Maximum Absolute Bias
A	Na	Atomic absorption spectroscopy (flame)	mg/L	0.5-7.0	0.01	5	10%
A	NH_4^+	Automated colorimetry (phenate)	mg/L	0.01- 2.0	0.01	5	10%
A	NO_3^-	Ion chromatography	mg/L	0.01- 5.0	0.005	10	10%
A	P, total	Automated colorimetry (phospho-molybdate)	mg/L	0.005 - 0.070	0.002	10 (if P conc. > 0.01 mg/L) 20 (if P conc. ≤ 0.01 mg/L)	10% 20%
F,L	pH[f]	pH electrode and meter	pH units	3 - 8	N/A	±0.1 (pH unit)	±0.05 pH
A	pH[f]	pH electrode and meter	pH units	3 - 8	N/A	±0.05 (pH unit)	±0.05 pH
A	SiO_2	Automated colorimetry (molybdate blue)	mg/L	0.2 - 25	0.05	5	10%
A	SO_4^{2-}	Ion chromatograpy	mg/L	1.0 - 20.0	0.05	5	10%
F	True Color	Comparison to platinum-cobalt color standards	platinum-cobalt units (PCU)	0 - 200	0	+5 (PCU)	N/A
F	Turbidity	Instrument (nephelometer)	nephelometric turbidity units (NTU)	2 - 15	2	10	10%

[a] A = analytical laboratory, F = field laboratory, L = lake site.
[b] This limit was the %RSD at concentrations 10 times the required detection limit, unless otherwise noted.
[c] Absolute value of each blank had to be ≤ 10 µeq/L.
[d] Atomic absorption spectroscopy used by Laboratory II; inductively coupled plasma atomic emission spectroscopy used by Laboratory I.
[e] The mean of six nonconsecutive blank measurements had to be ≤ 0.9 µS/cm.
[f] Although more than one sample preparation procedure was used (e.g., air equilibration, closed system, open system), the data quality objectives were identical.
NOTE: No specific data quality objectives were set for in situ Secchi disk transparency and temperature measurements.

structured to meet the DQOs for reporting population estimates and chemical variability. The DQOs also were applied to the statistical assessment of sampling, field laboratory, and analytical laboratory performance.

The primary DQOs were measures of precision, accuracy, and detectability (see Table 2). Precision was expressed as (1) standard deviation, (2) percent relative standard deviation (%RSD), and (3) the root-mean-square (RMS) of the %RSD, that is, as a "pooled" precision or coefficient of variation. (See Section 6 and Glossary for further explanation of RMS and %RSD.) Accuracy was expressed as maximum absolute bias, in percent. Detectability was expressed in applicable units as an expected range of values and as a detection limit. Each laboratory had to meet the detection limit specification, which is referred to throughout this report as the required detection limit, for each analyte. For the variables studied, measurements taken at the lake sites, in the field laboratories, and in the analytical laboratories were compared directly or indirectly to the values and the ranges of values established for the DQOs. During the survey, these comparisons were used to locate potential sampling, analytical, and reporting errors so that problems could be identified and corrected early.

The values and the ranges of values originally were determined on the basis of known instrument performance as specified by the manufacturers, standard laboratory practices (U.S. EPA, 1979), and practical knowledge applied to statistical modeling of chemical population estimates. The WLS-I values and ranges were identical to those used in ELS-I (Drousé et al., 1986), except that the precision requirement for conductance was changed from 1 percent in ELS-I to 2 percent in WLS-I.

Three other DQOs, completeness, comparability, and representativeness, also were considered in the survey design. Completeness is a measure of the quantity of data actually collected in relation to the quantity that is expected to be collected. On the basis of ELS-I results, completeness for WLS-I was set at 90 percent or better for all variables. That is, of the lakes selected for sampling, 90 percent or more were expected to yield samples that would meet the QA criteria and that could be used to estimate populations. In addition, completeness refers to the relation between the number of QA samples analyzed and the number of routine samples analyzed. Completeness also refers to the percentage of samples that meet internal consistency checks and that are analyzed within required holding times.

Comparability is the confidence level with which one data set can be compared to another. For WLS-I, comparability was ensured by requiring all sampling crews and laboratory analysts to use uniform procedures and by ensuring that a uniform set of units was used for reporting the data. The calibration study quantified the comparability of the helicopter-access and ground-access sampling methods. Comparability between WLS-I and other NSWS surveys and between WLS-I and surveys conducted under non-NSWS programs is discussed further in Landers et al. (1987). In addition, significant design and protocol changes that were implemented for WLS-I as a result of ELS-I experience are given in Table 3.

Representativeness, defined as 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 each stratum ensured good geographic coverage without bias (Landers et al., 1987). Other aspects of representativeness apply to (1) the degree to which a subset of lakes sampled represents the subregional and regional population of lakes and (2) the degree to which a single lake sample characterizes the chemistry of the lake spatially or temporally. Theseaspects of representativeness are discussed in Landers et al. (1987). Finally, representativeness applies to the degree to which QA and QC samples represent routine lake samples. The ranges of analyte concentrations in the QA and QC samples and in the routine samples are evaluated to assess this aspect of representativeness.

Sampling, Analytical, and Data Management Operations

Field sampling activities conducted by ground crews and by helicopter crews included locating and describing lake sites, collecting lake water samples, and collecting and recording physical and chemical lake data at the sampling sites (see Figure 2). Detailed field sampling procedures are given in Bonoff and Groeger (1987). Ground-access and helicopter-access sampling protocols are described in Silverstein et al. (1987).

Sampling support facilities and mobile field laboratories were located at the five WLS-I field bases in Carson City, Nevada; Wenatchee, Washington; Missoula, Montana; Bozeman, Montana; and Aspen, Colorado. The primary goals of the field laboratory operations were to receive samples, to prepare sample batches, to perform selected chemical analyses, and to preserve the integrity of samples until their analysis at the analytical laboratories. WLS-I analytical laboratories received samples from the field laboratories, analyzed the samples, and generated a report on the analytical data (see Figure 2). The WLS-I analytical methods are discussed in Kerfoot and Faber (1987); these

Table 3. Changes in Protocol Between Eastern Lake Survey - Phase I and Western Lake Survey - Phase I

Sampling Method and Field Data Collection

Protocol Change	ELS-I	WLS-I	Effect on Data
Recording lake site locations (latitude and longitude) on lake data form	Only Loran-C guidance system coordinates recorded	Loran-C and map (USGS; Forest Service) coordinates recorded	Easier to confirm that lake sampled was the correct lake
Van Dorn sampling apparatus dimensions	Length 43 cm (volume 6.2 L)	Length 81 cm (volume 6.2 L)	Shallow lakes sampled in ELS-I could be as much as 0.5 m shallower than shallow lakes sampled in WLS-I
In situ lake measurements (conductance, pH, temperature)	Hydrolab used for all measurements	Only helicopter crews used Hydrolab; ground crews used indicator strips for pH, used thermistor for temperature, and did not take conductance measurement	No in situ conductance measurements for 362 lakes; questionable in situ pH measurements for 362 lakes
Access to lakes for sampling	Only by helicopter	By helicopter and by boat (ground crew)	No apparent effects on population estimates

Field Laboratory Protocols

Protocol Change	ELS-I	WLS-I	Effect on Data
Sampling filtering procedures	All aliquots of each sample filtered in one filtration apparatus	Segregated aliquots filtered for NO_3^- analysis from apparatus that was washed with 5% HNO_3 (used for aliquots filtered for metals analyses); procedure used first in NSS-Pilot after development during ELS-I	Reduced the level of NO_3 background contamination detectable in field blank samples
Preparation of aliquots analyzed for total aluminum	Aliquots prepared (poured) at workbench	Aliquots poured under laminar-flow hood	Minimized chance of sample contamination from dust particles in ambient air of field laboratory
Color of labels used on aliquot bottles	All labels one color	Color-colored labels used to distinguish aliquots preserved with nitric acid, with sulfuric acid, and by refrigeration only	Minimized chance of analyst switching or improperly preserving aliquots of one sample or of multiple samples
Reanalysis of field duplicate pair samples when precision not within control limits for turbidity, true color, and closed-system DIC and pH	Only the duplicate sample reanalyzed	Routine and duplicate samples both reanalyzed	Better assessment of which sample may have caused the poor precision.
Safety check for MIBK in ambient laboratory air	Organic vapor monitors	Photoionization detector	None; immediate response time of photoionization detector minimized health risks

(continued)

Table 3. (Continued)

Protocol Change	Analytical Laboratory Protocols		
	ELS-I	WLS-I	Effect on Data
Calculating the starting date of analytical laboratory sample holding time	Began on date sample was collected	Began on date sample was processed and preserved in field laboratory	Affected some ground-access samples only; no apparent effect on data (see results of calibration study, Section 9)

Protocol Change	Data Verification and Data Analysis		
	ELS-I	WLS-I	Effect on Data
Use of laboratory synthetic audit samples	Employed; possible problems in sample preparation	Not employed due to results obtained in ELS-I	Unable to estimate accuracy of analytical laboratory performance only
Synthetic audit concentrations	Low and high concentrations used	Only low concentrations used; WLS-I lakes expected to be dilute	Without a variety of concentrations, bias calculations cannot be performed
Determination of field blank control limits in AQUARIUS program	Based on QA chemists' experience with environmental sample analysis	Based on ELS-I field blank data results (Appendix B)	Historic NSWS data provided *a priori* information unavailable in ELS-I; provided more confidence in assessing blank data for acceptable background concentrations
AQUARIUS program developed to compare extractable and total aluminum concentrations for each sample	Not a part of the AQUARIUS system	Employed in WLS-I	Minimized possibility of overlooking reporting or analytical errors evident from examining the total/extractable aluminum relationship
Anion-cation balance program in AQUARIUS	All ANC values in the ion balance calculation used as they were reported by the analytical laboratory	All ANC values between -10 μeq/L and +10 μeq/L changed to 0 μeq/L for the ion balance calculation only (Section 4)	Eliminated unnecessary flagging of data
Identifying erroneous or unreliable data in the verified data set (e.g., pH = 15.2)	No mechanism	Creation of the "X0" data qualifier flag	Easier for data user to isolate questionable data in statistical analyses
Applying data qualifier flags to raw data set	Employed	Not employed	Minimized confusion concerning source of data problems
System of QA staff requesting confirmation and reanalysis of analytical laboratory data	No systematic tracking system used	Application of a new NSWS standardized form for tracking requests (Appendix A)	Easier to track requests; established documentation system for data changes
Data tape transfer among ORNL, EMSL-LV, and ERL-C	Approx. 10 tapes used to transfer data from raw to verified data set	Two tapes used to create a verified data set from the raw data	Eliminated confusion in data transfer by minimizing number of iterations

(continued)

Table 3. (Continued)

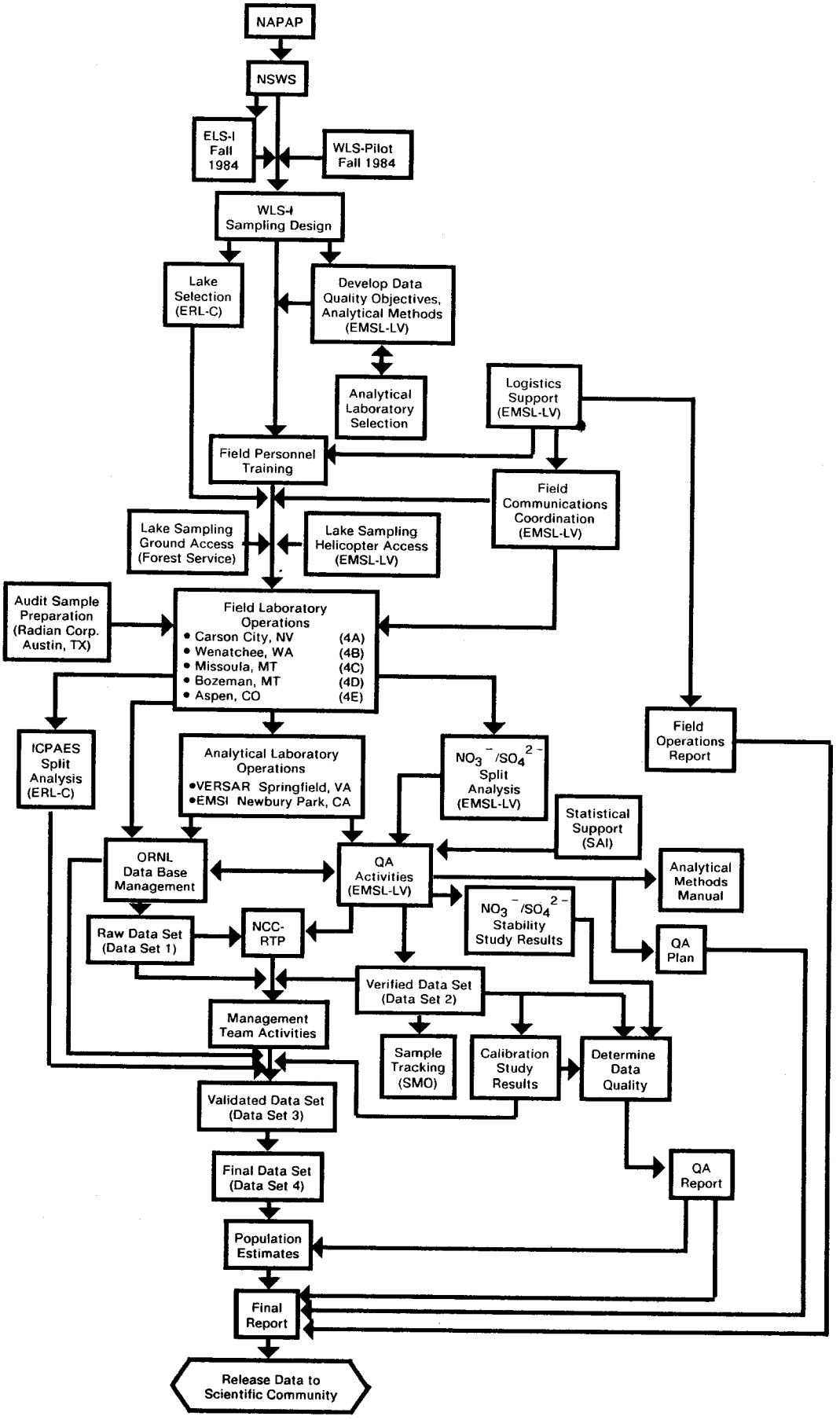
Protocol Change	Data Verification and Data Analysis (continued)		
	ELS-I	WLS-I	Effect on Data
Preparation of natural audit lot as 2-L samples at Radian Corporation	Prepared samples as needed	Prepared total lot volume en masse as 2-L samples	Ensured homogeneity of lot by eliminating chance of day-to-day contamination
Use of sample codes to distinguish samples collected by helicopter and ground crews	Not necessary, only helicopter access used	Employed	Ease of statistical analysis to detect potential differences in data collected according to different sampling methods
Data quality objective for conductance (intralaboratory precision goal)	1%	2%	Probably none; 1% may have been too strict

methods paralleled ELS-I methods (Hillman et al., 1986) to ensure data comparability.

Standardized, multicopy, field data reporting forms were developed for use in recording site descriptions and data collected at the lakes and the field laboratories. One copy of each form was sent by overnight mail service to ORNL for entry into the NSWS data base, and a second copy was sent to the EMSL-LV QA staff (see Figure 2). The field forms are illustrated in Drousé et al. (1986) and in Bonoff and Groeger (1987).

Data management and data review activities were coordinated by EMSL-LV, ERL-C, and ORNL (see Figure 2). A description of the data base management system is given in Kanciruk (1986). Data review and data verification procedures are described in Silverstein et al. (1987) and are summarized in Section 4 of this QA Report. Data validation procedures are described in Landers et al. (1987) and are summarized in Section 4.

Figure 2. Overview of activities, Western Lake Survey - Phase I.



Section 2
Conclusions and Recommendations

Data Quality Objectives

Precision

- For most analytes, system precision met the DQOs for intralaboratory precision. This is the only precision goal established before the survey and, therefore, is the only gauge applicable for comparing system precision results. Precision for 19 of the 28 analytical laboratory and field laboratory variables met or approached the DQO (see Table 16 in Section 6). Poor precision for most of the remaining analytes was attributed to the low analyte concentration levels or the circumneutrality of most WLS-I lake samples. The few remaining poor precision estimates were related to procedural (method or analytical) problems.
- Field laboratory precision was acceptable for analyses performed in all five WLS-I field laboratories. Acceptable field laboratory precision is especially critical for the closed-system dissolved inorganic carbon and pH measurements, which are used in population estimates.
- Analytical laboratory precision met the DQOs for all analytes except manganese.
- Precision differences between helicopter-access and ground-access methods were minimal.
- DQOs for precision must be developed to account for different sample concentrations, different ionic strengths, and circumneutrality of lake water samples.
- DQOs must be developed that differentiate between system (field related) precision and laboratory precision.
- Audit sample precision estimates are most useful if the mean concentrations of audit samples are similar to the analyte concentrations of the lake samples in the subregion. WLS-I audit sample concentrations did not always bracket the concentrations of the lakes in WLS-I subregions.

Accuracy

- On the basis of field synthetic audit sample data, accuracy could only be estimated for 15 of the 28 variables analyzed in WLS-I laboratories. Of those 15 analytes, only calcium and total aluminum exhibited levels of inaccuracy that were higher than the DQO criteria.
- Accuracy estimates can be affected by analyte concentration. WLS-I used one synthetic audit sample at one theoretical concentration to estimate accuracy for each analyte. Varying analyte concentrations that represent the range of concentrations in the routine lake samples could improve the estimation of accuracy. For future surveys, DQOs must account for this relationship. Concentrations of analytes in the synthetic audit samples and the number of synthetic audit samples at different concentrations should be established accordingly.
- It is difficult to ensure the theoretical values for the analyte concentrations in WLS-I synthetic audit samples. Methodological changes in the preparation of synthetic audit samples or use of applicable samples certified by the National Bureau of Standards (NBS) will be necessary if future surveys require accuracy estimates for acid neutralizing capacity, base neutralizing capacity, dissolved inorganic carbon, and pH.
- For WLS-I, synthetic audit samples were processed in the field laboratory only; therefore, there is no means of isolating analytical laboratory accuracy by using the data collected. To provide an estimate of analytical accuracy in future surveys, reliable audit samples (such as those certified by NBS) must be sent directly to the analytical laboratory. Conversely, if an estimate of system accuracy is desired, a synthetic audit sample must be processed through the sampling apparatus at the lake site, as are field blanks and field duplicates.

Detectability

- For most analytes, system background contamination was within expected and acceptable limits. Significant exceptions were calcium, nitrate, and silica (see discussions later in this section and in Section 8).
- Background contamination contributed by the field laboratories was negligible for most

analytes; nitrate, silica, and sulfate were exceptions. In future surveys, trailer blanks should be used regularly to allow estimation of the effect of the sample processing component on the sampling and analytical system.

- On the basis of calibration blank and reagent blank analyses, both analytical laboratories met the required detection limit criteria (see Table 2) for every applicable analyte. Background contamination and instrumental signal variability contributed by the analytical laboratories, therefore, was negligible.
- Helicopter crews and ground crews had similar success in minimizing contamination in lake water samples.
- DQOs were not set for field blank and trailer blank concentrations prior to the survey; they were set for analytical instrument detection of calibration blanks and reagent blanks only. Consequently, DQOs did not apply to field blank or trailer blank analyses in WLS-I. Objectives for field blank and trailer blank analyses should be developed for future surveys.

Representativeness

- Duplicate pair samples adequately represented the sampling methods and the ranges of concentrations found in lake samples.
- One portion of the lake samples was not adequately represented by field audit samples because there were no audit samples with concentrations of analytes in the midrange of the routine lake water samples analyzed during WLS-I. This lack of representativeness affected the ability to quantify possible biases attributable to the analytical laboratories.
- The field synthetic audit was used to estimate accuracy, but it represented a single theoretical concentration.
- Field blank samples adequately characterized background contamination.
- Matrix spike percent recovery analyses indicated that the reported concentrations were representative of the analytes in the samples.

Completeness

- Each of the five WLS-I subregions represented three alkalinity classes (strata) for a total of 15 strata. Fifty lakes were to be sampled within each stratum. Of the resulting 750 lakes that were expected to be sampled, (referred to in Landers et al. [1987] as probability sample lakes), 720 were sampled. (When population estimates were performed, one of the 720 lakes was deleted from the statistics because it was too large.) The completion rate of 90 percent (45 lakes) per strata was met for 10 of the 15 strata. Two strata in the 4D (Central Rocky Mountain) subregion were undersampled to the point that confidence in the population estimates could be low. Most of the unsampled lakes in these two strata were high-altitude lakes that were frozen when visited by the sampling crews.
- Most WLS-I samples were complete in internal consistency; 99.1 percent were within QA criteria for anion-cation balance, and 97.6 percent met the conductance balance criteria.
- Of the 39,400 analyses performed in the analytical laboratories, 98.6 percent were completed within prescribed holding times.
- Each type of QA and QC sample was represented by a large enough population to allow statistical analyses of data quality to be performed. Field blanks, field duplicates, field audits, and the extra samples collected to perform the calibration study constituted 54 percent of the WLS-I field samples analyzed.
- All on-site laboratory reviews were completed. Both analytical laboratories, all field laboratories, and all helicopter crews were evaluated. Five of the sixty ground crews also were evaluated. No criteria were set for the percentage of field crews that should have been evaluated. This aspect of completeness should be assessed if future surveys warrant the use of a large number of sampling crews.

Comparability

- The WLS-I data base can be compared to other National Surface Water Survey data bases. For most protocols, the field sampling and analytical methodologies were identical to those used in ELS-I. Where protocols differed (i.e., helicopter access versus ground access), no calibration of data was necessary (see Section 9). Differences between data collected by helicopter-access and ground-access sampling methods were determined to be of small enough magnitude that they do not affect data interpretation or population estimates.
- Little difference between measurements was indicated for samples preserved at the lake site and at the field laboratory for nitrate and sulfate (Section 9).
- Some biases between the two analytical laboratories were detected for some analytes, but the biases were relative, as well as small, in most cases. The ability to quantify bias at different analyte concentrations and to compensate for those biases should be investigated for future surveys.

Lake Water Characteristics

Extractable Aluminum

- All detectability data for extractable aluminum met the DQOs; contamination was not a significant factor.
- The low concentrations of extractable aluminum found in the lake water samples made it difficult to compare the precision results to the DQOs. Only 2 of 210 field duplicate pairs had mean concentrations above 0.04 mg/L, and only 1 of 6 audit sample lots had a mean concentration above 0.01 mg/L. The data user should take note of the low extractable aluminum concentrations when assessing data quality.
- Accuracy could not be estimated because of a methodological problem caused by the instability of the extractable Al species in the field synthetic audit sample solution. Methodologies for preparing field audit samples should be modified, or an alternative method should be investigated for future survey efforts.

Total Aluminum

- Most of the field routine, duplicate, and audit samples used in calculating precision estimates were near or below the detection limit for total aluminum.
- Although accuracy can be estimated, the low theoretical concentration of the synthetic audit (0.02 mg/L) was also near the detection limit.
- Because precision and accuracy estimates are concentration dependent (especially for low concentrations), the DQOs did not account for most total Al sample concentrations that were near the detection limits. Data for concentrations that were sufficiently above the detection limits (usually, about 10 times the required detection limit) are more useful for the calculation of population estimates.
- There was good agreement in the QA check comparing total aluminum and extractable aluminum concentrations: 99.8 percent of the 1,642 samples analyzed for both variables had total aluminum concentrations that were higher than the respective extractable aluminum concentrations.

Acid Neutralizing Capacity

- All quality assurance data estimates indicated that results for acid neutralizing capacity are of acceptable quality and are suitable for use in calculating subregional population estimates.
- The analysis of field blank data indicated that the required detection limit was met for acid neutralizing capacity.
- For measurements of acid neutralizing capacity, precision met the DQOs over the range of routine sample concentrations. A method should be developed for determining a quantitation limit for use in assessing laboratory duplicate (intralaboratory) precision.
- The WLS-I quality assurance program did not include methods applicable to the estimation of accuracy for acid neutralizing capacity. A means of estimating accuracy should be developed for use in future surveys.
- All computer software that the analytical laboratories use to calculate ANC should be checked to ensure that the programs are calculating the titration data results correctly. This procedure would minimize the possibility of miscalculating ANC results, as did one analytical laboratory during the initial stages of WLS-I. Performing standardization checks on the computer programs before survey analytical activities commence will ensure consistent data reporting and comparability among data bases.

Base Neutralizing Capacity

- Detectability estimates were higher than the required detection limit for about 50 percent of the field blank samples measured.
- Precision improved as concentration increased; many of the field duplicate pair and field audit sample mean concentrations were near or below the detection limits.
- Accuracy could not be estimated by using the QA samples employed in WLS-I. A means of calculating accuracy estimates should be developed for future surveys.
- The DQOs for base neutralizing capacity may be too stringent. Alternatively, modifications to the measurement system may be needed. Base neutralizing capacity was not assessed for population estimates. The uncertainty of the estimation of base neutralizing capacity results for WLS-I should be noted by the data user concerned with this analytical measurement.
- In the future, all computer software that the analytical laboratories use to calculate BNC should be checked to ensure that the programs are calculating the titration data results consistently and correctly.

Calcium

- QA data for calcium indicated that data for the routine samples are of acceptable quality and can be used with confidence.
- Background contamination (as much as 0.07 mg/L) may be related to the fact that high concentrations of Ca (mean of 3.7 mg/L) were found in routine lake samples, which may have resulted in the analyte carryover indicated in the field blank sample. This carryover may relate to residual analyte concentrations (i.e., inefficient rinsing of the sampling apparatus or the filtration apparatus) or to the way in which the instrument

analyzes the sample and interprets the findings. This slight contamination should not affect population estimates.

- Precision estimates met the DQOs.
- A relative analytical bias of 4 percent to 8 percent was indicated for the two analytical laboratories on the basis of calibration study data. Field audit sample data indicate a bias of 8 percent. Measurements from Laboratory I were higher than those from Laboratory II. When assessing population estimates by subregion, knowing which analytical laboratory analyzed the samples may be important to the data user investigating the anion deficit described in Landers et al. (1987). Because the biases are relative, however, no conclusion can be drawn concerning the accuracy of one laboratory over the other in the measurement of calcium (except in the case of field synthetic audit samples; see below).
- The accuracy estimates calculated from the field synthetic audit sample data indicate that one analytical laboratory exhibited better accuracy than the other at the theoretical concentration of 0.19 mg/L. Laboratory II's accuracy estimate (+1.6%) was within the DQO, but Laboratory I had an accuracy estimate well outside the DQO and values that were much higher (+28.7%) than the theoretical concentration. This absolute bias (as accuracy) is consistent with the relative bias results indicated by field natural audit sample data and calibration study data. This bias may be correlated with an anion deficit described in Landers et al. (1987). However, because the accuracy estimate for Ca was based on only one theoretical concentration, confidence in calculating an absolute bias as accuracy is restricted to that concentration and cannot be extrapolated with confidence across the entire range of routine sample concentrations.

Chloride

- The analytical results for the chloride measurement indicate that the data are of acceptable quality.
- Slight background concentrations of chloride (as much as 0.05 mg/L, but generally lower) were seen in field blank and trailer blank measurements, but population estimates should not be affected.
- Precision estimates indicate that, for samples above the detection and quantitation limits, the DQOs were met.
- At sample concentrations of 0.34 mg/L (the theoretical concentration of chloride in the field synthetic audit), accuracy estimates met the DQO.

Conductance

- Conductance data are of acceptable quality and can be used confidently in calculating population estimates.
- Background concentrations were found to be as much as 1.0 µS/cm (at 25°C) above the required detection limit, but contamination was at very low levels and should not affect data interpretation.
- The distribution of field duplicate pair and field audit mean conductance values indicated that precision improves with the increasing ionic strength of the sample. Because many lakes of low ionic strength were sampled in the West, precision estimates for such samples can be expected not to meet the DQOs. Imprecision at these low levels should not affect data interpretation.
- The WLS-I QA program did not provide a means of estimating accuracy for conductance. A method of performing this estimate should be incorporated in future survey designs.

Dissolved Inorganic Carbon (air equilibrated)

- The QA data for this analyte indicated that the lake data are of high quality and can be used with confidence.
- Background concentrations between 0.15 and 0.35 mg/L (compared to a required detection limit of 0.05 mg/L) were found in most field blanks and trailer blanks. Although these measurements were above the required detection limit, they may still be considered acceptable for deionized blank water samples.
- Above concentrations of 1.5 mg/L, field audit samples exhibited precision that met the DQO. Significant imprecision at lower concentrations may have been caused by slight differences between samples and between laboratories in the process used to sparge the sample. In addition, higher precision estimates were expected for samples at lower concentrations.
- There was no mechanism for estimating accuracy for this analyte in the WLS-I QA program. A means of performing the estimate should be incorporated in future survey designs.

Dissolved Inorganic Carbon (open system)

- The QA data for this analyte indicated that the lake data are of high quality and can be used with confidence.
- Field blank background concentrations were similar to those for air-equilibrated dissolved inorganic carbon. These background concentrations are unavoidable when the methodology employed in the West is used, but they should not affect data quality.

- For sample concentrations above the quantitation limit, precision generally met the DQO.
- Although a theoretical value was calculated for estimating accuracy, the field synthetic audit sample exhibited sample matrix problems that made the accuracy estimate unreliable. A means of confidently estimating accuracy for open-system dissolved inorganic carbon measurements should be incorporated in future survey designs.

Dissolved Inorganic Carbon (closed system)

- The QA data for closed-system dissolved inorganic carbon indicated that the lake data are of acceptable quality and can be used in calculating population estimates.
- Background contamination could not be assessed because field blanks and trailer blanks were not analyzed for this measurement. Field blanks or other means of determining field-related background contamination should be considered for inclusion in future sampling designs.
- Precision was good for this measurement in each of the field laboratories.
- No applicable accuracy checks were available for this measurement; such checks should be developed for use in future surveys.

Dissolved Organic Carbon

- The QA data indicated that the lake data for this analyte are of acceptable quality.
- Background concentrations generally were between 0.05 and 0.35 mg/L; the required detection limit was 0.1 mg/L.
- Field duplicate pair and field audit analyses showed a strong relationship between pooled precision and concentration. Precision for mean concentrations above the quantitation limit met the DQO (except for two values). Precision for many QA samples was above the DQO. Routine lake sample concentrations, however, were generally low. Thus, the precision may still indicate high-quality data at these concentrations.
- The accuracy estimate was within acceptable limits.

Fluoride (total dissolved)

- The QA data indicate that the routine data are of acceptable quality and will be useful in calculating population estimates.
- The blank data met the DQO for detectability.
- Precision above sample concentrations of 0.08 mg/L met the DQO. Field duplicate pair mean concentrations, field audit sample concentrations, and most concentrations in routine lake samples were below that level. Some imprecision is indicated for analyses performed by Laboratory I, where samples from subregions 4D (Central Rocky Mountains) and 4E (Southern Rocky Mountains) were analyzed.

Iron

- Background concentrations were 0.01 mg/L above the required detection limit.
- Mean concentrations of most field duplicate pairs and of five of the six field audit sample lots were below the quantitation limit and near or below the detection limits. This observation correlates well with the low concentrations of iron found in lakes in the West: most concentrations for routine samples, field duplicate pairs, and field audit samples were less than 0.06 mg/L. Although contamination was negligible, precision at low concentrations did not meet the DQO. The data user should consider that the poor precision estimates may have been a function of concentration and not a reflection on sampling or analytical methods.
- The accuracy estimate was poor. It was directly related to methodological problems associated with the field audit sample instability and was not related to the analytical measurements. A different method of estimating accuracy should be incorporated in future survey designs.

Potassium

- The QA data indicated that the lake data for this analyte are of high quality and can be used confidently in calculating population estimates.
- Contamination was negligible (0.01 mg/L); background concentrations were near the required detection limit.
- Precision and accuracy estimates met the DQOs.

Magnesium

- The QA data indicated that the lake data for magnesium are of high quality and can be used confidently in calculating population estimates.
- The DQOs were met for detectability, precision, and accuracy.

Manganese

- Contamination was negligible; most values for field blanks were near the required detection limit. Laboratory II showed some negative bias for about 25 percent of the field blanks analyzed there.
- Lake sample data for concentrations above 0.030 mg/L can be used confidently in calculating population estimates. Field duplicate pairs and field audit samples that had

concentrations above 0.030 mg/L met the DQOs for precision and accuracy. Because the manganese concentrations in most lakes in the West were below or slightly above the detection limits, imprecision at those concentrations should have little impact on the calculation of population estimates.

Sodium

- The QA data indicated that the lake data are of high quality and are suitable for use in calculating population estimates.
- Negligible contamination (0.01 mg/L), was seen in relation to the required detection limit.
- Precision and accuracy estimates generally met the DQOs.

Ammonium

- Very low concentrations of ammonium were measured in all lake and QA samples; most were below the required detection limit.
- There was negative bias for 51 percent of the field blanks analyzed in Laboratory I.
- Precision estimates for the field synthetic audit samples were near the DQO at measurable concentrations.
- Accuracy estimated from one of the two field synthetic audit sample lots was good; for the other field synthetic audit sample, analyte degradation may be the cause of accuracy estimates that did not meet the DQOs.
- At the concentrations measured, imprecision and inaccuracy should not affect population estimates.

Nitrate

- Measurable concentrations of nitrate (as much as 0.071 mg/L) were detected in field blanks. Analytical laboratory calibration showed minimal contamination. Trailer blank measurements, on the other hand, detected as much as 0.074 mg/L nitrate, which indicates that the contamination may have been introduced in the field laboratories and probably was not related to field sampling methodology. Because concentrations in the field and trailer blanks were substantially higher than the required detection limit and because concentrations in many of the lake samples were low, background contamination may have been a significant contributor to the analytical results for some lake samples. The data user should note the possible source of contamination. This factor, however, may not be of concern in calculating population estimates because the nitrate concentrations were low in the lake samples. If contamination at these low concentrations is of concern, sample-processing and sample-handling protocol modifications should be considered in the design of future surveys.
- Precision estimates for samples above the quantitation limit (0.342 mg/L) met the DQOs, but imprecision was indicated in some field duplicate pair mean concentrations below the quantitation limit.
- Accuracy estimates met the DQO.
- The results of the nitrate-sulfate stability study indicated that there was little difference between nitrate concentrations in lake samples preserved with mercuric chloride at the lake site and concentrations in samples processed according to NSWS protocol in the field laboratories.
- The length of time that a sample was held before preservation had minimal effect on data quality.

Phosphorus (total)

- Some contamination was detected at concentrations of as much as 0.017 mg/L for analyses performed in Laboratory I.
- Most concentrations of total phosphorus for routine lake samples and for field duplicate pair and field audit samples were less than 0.025 mg/L. Precision estimates have little meaning at these low concentrations. QA samples that had higher concentrations met the DQO for precision.
- Estimated accuracy was within acceptable limits.

pH (acidity; open system)

- The QA data indicate that the open-system pH measurements are of high quality. Closed-system pH measurements made in the field laboratory, however, are used in calculating population estimates. The open-system pH measurements performed in the analytical laboratory were used as a redundant check on the closed-system measurements.
- Field blank analyses indicated that background contamination had minimal effect on pH values.
- Precision was greatly affected by the ionic strength and circumneutrality of the sample. Precision estimates improved as pH increased or decreased from pH 7.0. A means of calculating quantitation limits that can be related to ionic strength and circumneutrality should be developed for use in future surveys.
- The survey design did not allow accuracy to be determined for pH. A means of determining accuracy for pH should be developed for use in future surveys.

pH (alkalinity; open system)

- Conclusions and recommendations for open-system pH (alkalinity) are identical to those for open-system pH (acidity).

pH (air equilibrated)

- Conclusions and recommendations for open-system pH (acidity) are related directly to this pH measurement.

pH (closed system)

- QA data indicated that the field laboratory pH measurements are of high quality and can be used confidently in calculating population estimates.
- Field blanks were not analyzed for this measurement, so background contamination could not be assessed. A means of determining background contamination levels should be incorporated in future sampling designs.
- The trailer duplicate precision for pH measured in the field laboratory (0.03 pH units) met the DQOs.
- When field duplicate pair measurements for all five field laboratories were pooled, however, the precision was 0.12 pH unit. Field audit sample data indicated precision near the DQO for all field laboratories. A quantitation limit related to ionic strength and circumneutrality should be considered for use in future sampling efforts.
- The WLS-I QA program did not provide a mechanism for estimating accuracy for closed-system pH. A means of estimating accuracy of pH measurements should be developed for use in future surveys.

Silica

- Although field blank measurements indicated background contamination (as much as 0.18 mg/L) that was higher than the required detection limit, the average SiO_2 concentration for a routine lake sample was about 3.7 mg/L. Therefore, background contamination should have a negligible effect on population estimates.
- For mean concentrations above the quantitation limit, precision estimates were slightly above the DQO. Some imprecision indicated from field duplicate pair measurements may be related to the digestion process used in the analytical laboratory. Population estimates, however, should not be affected; the precision may still be reasonable for the specific purpose defined by the data user.
- Accuracy estimates met the DQO.

Sulfate

- The QA data indicated that the routine lake sample data are of high quality and can be used confidently in calculating population estimates.
- Background contamination was 0.02 mg/L higher than the required detection limit.
- Precision and accuracy estimates met the DQOs.
- A relative interlaboratory bias of 2 percent was calculated on the basis of field audit sample data, and a relative interlaboratory bias of 5.5 percent was calculated on the basis of calibration study sample data. Because these biases are relative determinations in the evaluation of population estimates, it may be necessary to assess the data by the subregions for which each laboratory analyzed samples.

True Color

- The QA data indicate that the true color data for the routine lake samples are of acceptable quality.
- Negligible contamination was indicated for this field-laboratory measurement.
- Precision was acceptable, considering the low levels of color found in the routine lake samples.
- There were no applicable accuracy measurements for true color.

Turbidity

- Turbidity QA data indicated that the lake sample turbidity data are of acceptable quality. Many routine lake samples, however, were very low in turbidity.
- Background contamination was below the required detection limit.
- Precision was acceptable, considering the low turbidity observed in most samples. Field audit samples should not be used to estimate precision for turbidity; they were filtered in the audit sample preparation laboratory and, therefore, received different treatment than did the routine lake samples.
- Accuracy estimates were not calculated for turbidity. A means of estimating accuracy should be developed for use in future surveys.

Overall Operations

- The QA data indicate that the sampling, analytical, data management, and data analysis activities were successful. These operational aspects of the survey resulted in recommendations for future survey efforts (see Tables 4 through 7).
- The formal audit of the WLS-I data base (field data forms through the final data set) reported a data documentation and consistency rate of more than 99.5 percent.
- All 1,642 samples (149 batches) were received and analyzed by the analytical laboratories.
- Analytical differences between samples collected by helicopter crews and by ground crews were negligible.
- Ninety percent of the samples collected by ground crews in wilderness areas were received

and processed in the field laboratory within one day of sampling.

- The high quality of data generated in WLS-I shows that personnel training and analytical laboratory selection were effective.
- ELS-I and the WLS-I pilot survey provided information useful in the planning of WLS-I field, analytical, and data management operations.

Table 4. Significant Findings, Conclusions, and Recommendations Concerning Lake Sampling and Field Data Collection, Western Lake Survey - Phase I

Finding	Corrective Action	Effect on WLS-I Data	Conclusion or Recommendation
Lake sampled twice (once when stratified, then when isothermic)	Both samples analyzed and evaluated during data verification and data validation	Sample from isothermic lake provides data more related to goals of WLS-I	Final data set (No. 4) includes data from isothermic sampling in population estimates
pH indicator strip measurements proved to be unreliable	Data not modified during data verification and data validation	pH indicator strip measurements not used in population estimates	Future data users must be alerted that this portion of data base is unreliable; relationship of pH measurement method requires further investigation; do not use pH indicator strip method in future surveys
Hydrolab pH measurement was difficult to stabilize in situ (in some lakes with dilute systems)	Two minutes additional time allotted to stabilize in situ; any unstable lake measurements tagged	Minimal; closed-system pH measurements used in population estimates	Method modification noted for use in future surveys
Loran-C guidance system malfunctioned at many lake sites in the 4B subregion (Wenatchee, WA)	None; lake data tagged	Negligible; maps, lake photo information are additional checks on lake identification and verification	Continue use of Loran-C system
Helicopter crew safety training not tailored to WLS-I sampling protocols	None	None	Emphasize "on-board" field training to complement classroom presentations

Note: See glossary for explanation of abbreviations.

Table 5. Significant Findings, Conclusions, and Recommendations Concerning Field Laboratory Activities, Western Lake Survey - Phase I

Finding	Corrective Action	Effect on WLS-I Data	Conclusion or Recommendation
One presampling "practice run" performed in field laboratories at Wenatchee, WA, and Bozeman, MT (two runs were recommended)	None	None	One practice run may be sufficient for experienced crews
Laminar-flow hood not heated; reagents, filtration apparatuses, and the hands of the analysts subject to external cold air temperatures	Portable heaters used in field laboratories when cold temperatures warranted their use	None	Field laboratories require insulatory modifications if used in cold environments (outside air temperature $< -5°C$)
Field duplicate pair samples (collected by ground crews) that arrived late were not inserted randomly in batches	None; it was more desirable to process the samples on date of receipt than to hold them for next sample-processing day	None apparent	Continue to strive for random allocation of QA samples to each batch
One batch (14 samples) lost in transit to analytical laboratory for 3 days	Samples located and analyzed as quickly as possible	Negligible; samples arrived at 10°C; most sample measurements were performed within holding times	None; overall (>99%) sample shipment protocols met in WLS-I
Occasionally samples arrived at field laboratory with ice in syringes and Cubitainers	Field sampling crews notified to moderate number of frozen refrigerant gel-packs used in sample transport; data qualified (tagged) for use during data verification and validation	Unknown; approximately 2% of WLS-I lakes involved	Investigate correlation between lake water sample temperature, transport time, and number of gel-packs used per shipping container
Container leakage in extr. Al aliquot bottle because of inadequate sealing rings	Removed rings; oriented aliquots in shipping container to minimize leakage; tagged data where appropriate	Tagged data inspected; no effect on data detected	Investigate use of different aliquot containers
Field laboratory pH (closed system) measurement took a long time to stabilize for some samples of low ionic strength; one day's analyses began to overlap with the next	Etch pH electrode with 50% NaOH (Knapp et al., 1987)	None; relieved overloaded pH analysis schedule	Continue the etching practice in future surveys when applicable
Proposed pH and DIC QCCS solution (prepared by equilibrating 300-ppm CO_2 in air) was unstable	None; the procedure was cancelled for logistical and technical reasons (e.g., atmospheric pressure, laboratory temperature); time needed would have hindered other required analyses	None, although the trial was time-consuming	If future surveys sample many circumneutral waters of low ionic strength, this QCCS method needs further investigation and development (see Appendix M)

(continued)

Table 5 (Continued)

Finding	Corrective Action	Effect on WLS-I Data	Conclusion or Recommendation
Field duplicate pair samples yielding turbidity values < 2.0 NTU did not meet 10% precision DQO; protocol required reanalysis of both samples	If sample < 1.0 NTU, reanalysis not required	None	Continue practice; modify DQO to consider precision at low levels
For first seven batches processed at Missoula, MT, field base (subregion 4C) technician used only one pipet tip per batch for MIBK transfer into aliquot bottle	Correct procedure used for all subsequent batches; confirmation made that other subregions performed protocol correctly.	None; the seven affected batches were checked, and no contamination carryover was found	Reinforces need for close inspection at on-site evaluations
Single routine sample arrived at field laboratory without QA samples	Trailer blank and audit sample added to single-sample batch	None; determined better to process single sample on day sampled than to wait for more samples the next day	None
One field duplicate sample and one field blank arrived at field laboratory with obvious contamination (high in sediment)	Laboratory supervisor discarded the duplicate and blank samples, processed routine sample	Probably none; all data generated from the contaminated samples would have been deleted from statistical analyses	Do not discard samples until QA manager has approved, even if obvious contamination
Field laboratory pH measurement not in agreement (within 0.5 pH unit) with pH indicator strip measurement. Field laboratory protocol was to reanalyze all pH readings not in agreement	Part way through field effort, protocol changed to reanalyze only one sample at the low end, the middle, and the upper end of the range of samples in the batch	None; pH indicator strip values considered unreliable	QA programs should remain flexible to deal with deviations

Note: See glossary for explanation of abbreviations.

Table 6. Significant Findings, Conclusions, and Recommendations Concerning Analytical Laboratory Activities, Western Lake Survey - Phase I

Finding	Corrective Action	Effect on WLS-I Data	Conclusion or Recommendation
Contingency plan needed to accommodate possible emergency shutdown of an analytical laboratory during sample analysis ("acts of God")	None needed	None	Have back-up laboratory available when planning any major analytical effort
Dilute nature of many WLS-I lake samples made it difficult for analytical laboratory to meet intralaboratory precision criteria (DQO) for laboratory duplicates; SOW stated that if criteria not met, additional duplicate sample analysis was required	Modified requirement: if precision criteria not met and no samples in batch had analyte concentration at least 10 times required detection limit, further duplicate analyses not required	Negligible; duplicate precision statistical analysis (precision estimates) uses the quantitation limit to eliminate low-level duplicate pairs near the detection limit from statistical evaluation	New DQOs for precision are necessary to account for the fact that precision depends on analyte concentration (see Figure 8)
DIC and pH QCCS unstable	See discussion in Table 5	See discussion in Table 5	See discussion in Table 5
A non-standard NSWS aliquot (No. 1) bottle was used for one sample (blank); aliquot showed gross contamination	QA staff investigated, but source of bottle could not be identified. Data flagged to be deleted from any statistical analyses; analytical laboratory manager noted deviant bottle in data package cover letter to QA staff	None; data discarded; this is the only case (1 in 15,000 aliquot bottles) in which a non-standard bottle was used	Delete data generated when nonstandard protocols yield questionable data
For total Al, matrix spike (% recovery) criteria not met for 3 consecutive samples in one batch	Standard additions performed, data tagged, and QA staff notified as required by SOW	None; reliable results obtained;matrix interference negligible in WLS-I analytical results (see Section 8)	None; proper protocols followed by analytical laboratory, and documentation provided to QA staff
Negative bias for NH_4^+ determination indicated from field blank analyses in Laboratory I (51% of all field blanks considered excessively negative)	Problem investigated; raw data inspected but cause not isolated by QA staff or analytical laboratory manager; affected samples were flagged	Probably negligible; NH_4^+ concentrations were extremely low for most WLS-I lakes sampled	None
Negative bias for Mn determination indicated from field blank analyses in Laboratory II (25% of all field blanks considered excessively negative)	Problem investigated; raw data inspected but cause not isolated by QA staff or analytical laboratory manager; affected samples were flagged.	Probably negligible; Mn concentrations were extremely low for most WLS-I lakes sampled	None
Sporadic negative bias for SiO_2 determination indicated from field blank analyses in Laboratory I (9% of all field blanks considered excessively negative)	None; affected samples were flagged	Probably negligible	None

(continued)

Table 6. (Continued)

Finding	Corrective Action	Effect on WLS-I Data	Conclusion or Recommendation
Software problem in the calculation of ANC and BNC was discovered by manager of Laboratory II during survey operations	Software problem corrected; ANC and BNC values in 46 batches (approximately 1,000 analyses) were recalculated and resubmitted to ORNL before data were entered into raw data set	None; correct values in data base	Test software for calculating ANC and BNC before sample analyses
Improper formula used by Laboratory II to calculate laboratory duplicate precision (%RSD) results (1,751 duplicate pairs)	Data corrected in verified data set	None; the intralaboratory precision goals were met after %RSD values were recalculated	Specify the %RSD formula clearly in SOW to avoid misinterpretation
In calculating % recovery for matrix spikes, Laboratory II converted all negative sample results to 0. (240 spikes affected)	% recoveries recalculated during data verification	Minimal; negligible matrix interference detected in WLS-I sample data; (see Section 8)	If matrix spike analyses are used in future surveys, clearly state calculation procedure in statement of work
The mean concentrations of duplicate pair analyses (Laboratory I) were being reported as the routine sample value (discovered during on-site evaluation)	Practice discontinued; affected data corrected to meet protocol reporting requirements	None; data corrected	Modify AQUARIUS program to detect misreporting; modify SOW to avoid misinterpretation; continue on-site evaluations
Calibration blanks not analyzed as specified for Ca, Mg, K, Na, Fe, Mn instrument calibration; instrument "auto-zeroed" with these QC samples; all calibration blanks reported as 0.00 mg/L (for 91 batches from Laboratory II)	None; problem discovered during statistical analysis after data verification	Negligible or none for population estimates; detection limit QCCS results indicate low end of calibration curve (linear dynamic range) adequate; affected calculation of laboratory precision statistics (i.e., quantitation limit)	Modify SOW to minimize misinterpretation; modify verification process to detect problem immediately; emphasize check during on-site evaluations
All open-system initial pH (pH, acidity; pH, alkalinity) values reported by Laboratory I were from Gran analysis calculation rather than that measured from pH meter	None; problem not detected before final data set generated	No impact on population estimates because field laboratory (closed) pH measurements used. Reported (open-system) values are consistently about 0.05 pH unit lower than measured values	Specify reporting procedure in SOW to minimize misinterpretation; modify verification procedure and AQUARIUS programs to detect misreporting

Note: See glossary for explanation of abbreviations.

Table 7. Significant Findings, Conclusions, and Recommendations Concerning Data Management and Data Verification Activities, Western Lake Survey - Phase I

Finding	Corrective Action	Effect on WLS-I Data	Conclusion or Recommendation
Biological growth discovered in the bulk sample of audit lot FN4 before audit sample aliquot preparation(Appendix C) began	Entire lot volume refiltered prior to use; integrity of lot maintained; use of $HgCl_2$ to stop biological growth was rejected in favor of filtration	None; mean analyte concentrations measured after refiltering did not differ significantly from concentrations measured before biological growth was detected	Continue practice of apportioning bulk audit lot into 2-L samples in order to maximize audit lot consistency
The ability to confidently estimate accuracy with synthetic audit samples is in question because "true value" not known	None	Accuracy calculation and results must be qualified	Utilize NBS certified standards to estimate accuracy more confidently
Decision not to use calibration study duplicate and triplicate samples as a QA tool	Calibration study samples can only be compared to samples from same lake to check for outlier data	Keeping calibration study data separate from QA data allowed QA staff to assess calibration study results more efficiently	Sampling methods comparable, data calibration not necessary (see Section 9 and Landers et al., 1987); no need for future calibration study
Decision not to designate separate flags (data qualifiers) for samples collected by helicopter crews and by ground crews	None	None	Calibration study data confirm no need to treat two sampling methods differently
Turbidity precision estimated from field audit sample data misleading (Appendix E)	If audit samples are used to determine precision, they must not be filtered first	Precision estimates should be discarded	Use only field duplicate precision for turbidity or use an unfiltered audit sample lot for this measurement
AQUARIUS field duplicate precision program did not flag pairs when only one sample > 10 times required detection limit (50 pairs had poor precision)	All affected pairs inspected manually; confirmation of sample concentrations performed by analytical laboratory	After confirmation, precision still poor for 33 pairs; data not flagged, but information provided to validation staff for use in calculating population estimates	AQUARIUS program modified for future surveys; new data verification flag created
Of 149 batches in WLS-I, 4 did not contain either a field blank or a trailer blank sample	None; the batches were inspected for all other QA and QC results	Probably none; 236 field blanks and 22 trailer blanks analyzed in WLS-I provided enough blank data for required statistical analysis	Assess NSWS data base to determine the number of blank sample analyses needed to estimate system components and system contamination
One field blank (of 236) sample concentration for NO_3^- was 11.284 mg/L	Analytical laboratory reanalyzed sample and obtained similar results; data flagged	Sample deleted from statistical analysis; assumption made that it was preserved with HNO_3 in field laboratory	None

(continued)

Table 7. (Continued)

Finding	Corrective Action	Effect on WLS-I Data	Conclusion or Recommendation
80 SiO_2 analyses >14 mg/L were diluted improperly or concentration was miscalculated after dilution; trend detected by an audit sample	60 values recalculated; 20 samples reanalyzed	None; affected sample concentrations corrected	Reinforces need to use audit samples that have different concentrations at levels of interest for routine lake sample data
For 74 samples (in 4 batches), columns were switched in reporting initial and air-equilibrated DIC results (148 analyses); discovered by comparing DIC relationship to pH	15 key samples were reanalyzed; provided enough proof that the results originally were reported incorrectly	None; affected values corrected	Minimal reanalysis can achieve maximum efficiency when relationships between pH and DIC are evaluated
AQUARIUS program generated data qualifier flags for every pH indicator strip value that showed poor agreement with other pH measurements (e. g., closed-system and open-system pH)	Flags deleted from data base	Flags considered extraneous information because pH indicator strip values known to be unreliable; these pH values not used in population estimates	Advise future data users about the poor performance of this pH method; consider alternative methods for future surveys
In situ (Hydrolab) conductance measurement for all lakes in the first 22 batches (1501-1522) in subregion 4A (California; Carson City, NV, field base) did not agree with the calculated conductance	None; probable Hydrolab instrument problem; validation staff notified; data properly flagged	No impact on data analysis because analytical laboratory conductance measurement used in population estimates	None

Note: See glossary for explanation of abbreviations.

Section 3
Operational Quality Assurance Program

The QA and QC aspects of WLS-I included several major activities designed to ensure that established survey protocols were followed for collecting, preparing, preserving, shipping, and analyzing samples and for reporting, verifying, and validating sample data. The QA and QC activities included selecting contract analytical laboratories; training the field sampling and field laboratory personnel; collecting and analyzing a variety of QA and QC data in order to evaluate data quality statistically, in terms of the DQOs; maintaining communications with management, sampling, and analytical personnel; and conducting on-site field and laboratory evaluations. The WLS-I QA and QC activities summarized in this section are described in detail in the QA plan (Silverstein et al., 1987). Most of the QA and QC procedures used during WLS-I were previously applied during ELS-I as described in Drousé et al. (1986), although some procedures were modified.

Selection of Analytical Laboratories

The objective of analytical laboratory selection was to award contracts to the fewest number of laboratories possible, yet to ensure that the laboratories had the capability and the qualifications to analyze WLS-I samples. A statement of work (SOW) that defined the analytical and the QA and QC requirements in a contractual format was prepared, and bids were solicited from analytical laboratories. On the basis of the performance-evaluation sample analyses and the on-site evaluations, two qualified laboratories, Environmental Monitoring and Services, Inc. (EMSI), in Newbury Park, California, and Versar, Inc., in Springfield, Virginia, were selected from among the respondents. The laboratory-selection process paralleled the process EPA uses to select CLP laboratories.

Training of Sampling and Field Laboratory Personnel

Before field sampling activities began, Lockheed-EMSCO field sampling and field laboratory personnel received an extended training course in Las Vegas, Nevada. These personnel, most of whom had received extensive sampling experience during ESL-I, were sent to the field bases where they provided EPA and Forest Service personnel with the training necessary to ensure that field activities were performed consistently and according to approved procedures. Time constraints for training limited the curriculum to protocol and procedural information. All personnel received hands-on experience with the activities that they would be expected to perform in the field; all were given practical and written tests on their understanding of pertinent methods (Bonoff and Groeger, 1987). Simulated sampling and field laboratory activities were conducted at the five field bases before routine sampling began. The high quality of the data collected indicates that training was adequate.

Quality Assurance and Quality Control Procedures

The WLS-I sampling design was intended to provide a data set that contained information sufficient for assessing potential sampling, analytical, and methodological bias; contamination; and detection and precision differences related to sampling method. Specified QA and QC procedures and samples were used to maintain data quality and to ensure that data quality could be characterized accurately. Rigid requirements for instrument calibration ensured that measurements were accurate and that instrument malfunctions and drift were readily detected. QA and QC sample data were compared to the expected values and ranges established for the survey (Table 2). The results of these comparisons were used during the survey to correct sampling and analytical errors and after the survey to evaluate overall data quality.

Types of Quality Assurance and Quality Control Samples

The success of the QA program and the evaluation of overall data quality required the appropriate use of QA and QC samples to ensure that sampling and analytical activities were performed according to the QA plan (Silverstein et al., 1987) and the Statement of Work. For this report, QA samples are defined as control samples received by the analyst, who does not know what the analytical results should be. QC samples are defined as control samples for which the analyst knows the theoretical or true analyte

concentrations or values. QA samples were used by the QA staff to evaluate overall method performance for field sampling, field laboratory, and analytical laboratory procedures and to estimate overall data quality. QC samples allowed field sampling personnel, field laboratory personnel, and analytical laboratory personnel to identify and correct local problems (e.g., get immediate feedback on instrument malfunction or reagent contamination) before routine samples were analyzed. Additional QA samples were employed in the calibration study (Section 9) to ensure the quality of the ground-access sampling method. A sample flow diagram (Figure 3) shows the types of QA and QC samples used and delineates their progression through the sampling, processing, and analytical steps of WLS-I. QA and QC sample types are described below.

Quality Assurance Samples--
QA samples collected at the lake site or introduced at the field laboratory were analyzed at the field laboratory and the analytical laboratory. The QA samples comprised field and trailer blanks, field duplicates, and field audits.

Field Blank--Field blanks were prepared at the field laboratory from deionized water that met American Society for Testing and Materials (ASTM) specifications for Type I reagent-grade water (ASTM, 1984). The sampling crew transported the blank water in Cubitainers to the lake sampling site and processed the water through a Van Dorn sampler as if the blank were a routine lake sample. The action of pouring the blank water through the Van Dorn sampler could change the CO_2 concentration in the sample, thereby affecting the pH and dissolved inorganic carbon (DIC) values of the field laboratory measurements. Consequently, for field blanks, the field crews did not collect syringe samples for pH and DIC analysis in the field laboratory. Each helicopter crew collected one field blank on each operating day; each ground crew collected two field blanks during the entire survey.

At the field laboratory, field blank samples were analyzed only for true color and turbidity. Field blanks were inserted into the sample batches and were processed along with the routine lake samples that were sent to the analytical laboratories. The blank samples were used initially to identify possible contamination problems resulting from sampling, sample handling and transportation, and analytical processes. Subsequently, they were used to estimate the background contamination levels, referred to as system decision and detection limits (see Section 8 and glossary). They were also used to estimate the quantitation limit, which is helpful in evaluating precision data (see Section 6 and glossary). For data interpretation, any routine lake data point above the expected value for the field blank was considered to be a positive response for a given variable; any point at or below the expected value is not reliably discernible from a field blank.

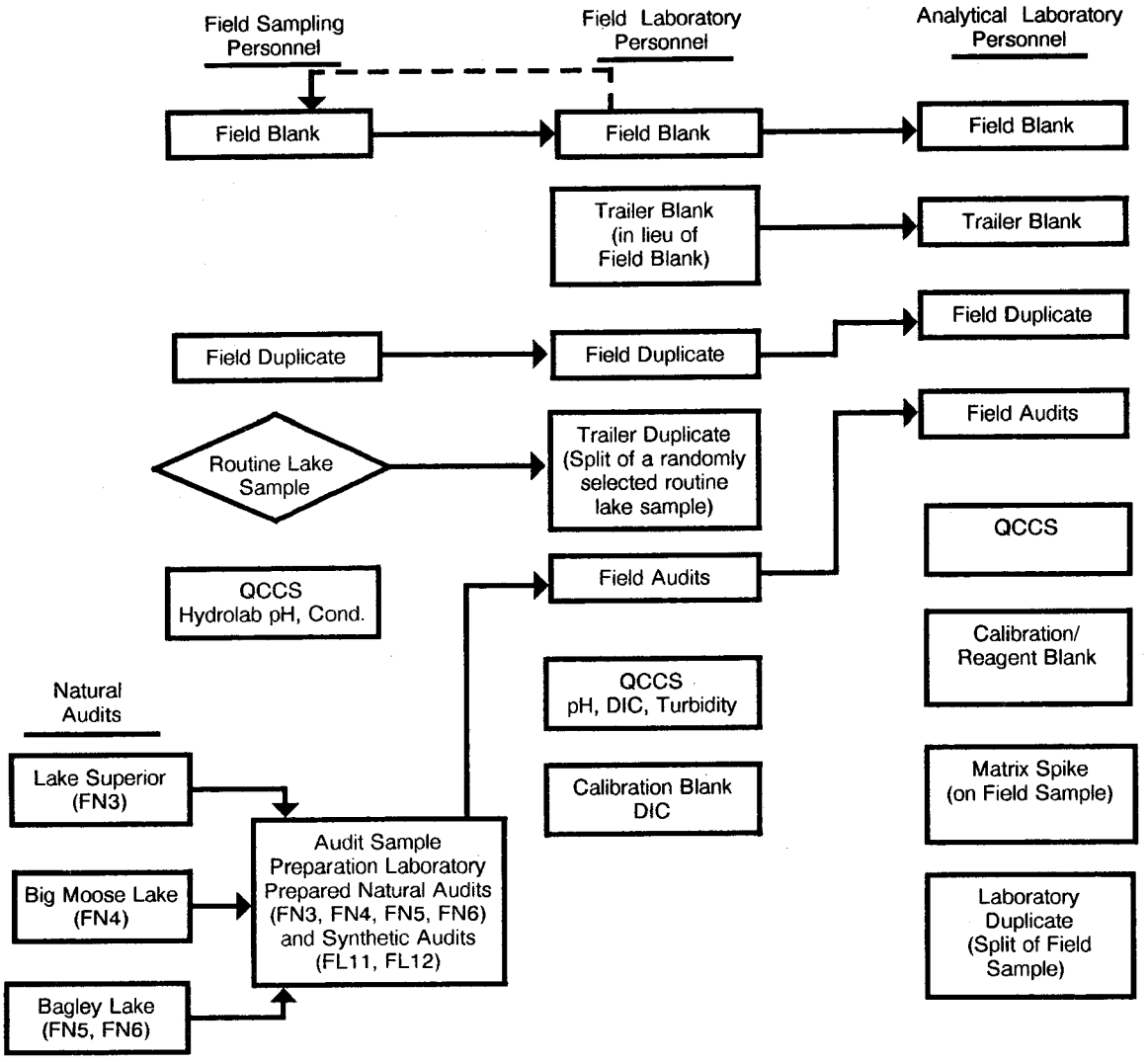
Trailer Blank Sample--Occasionally, the complex WLS-I sampling design yielded a situation in which a field blank was not scheduled to be processed at any lake site for a particular sampling day. In such instances, a deionized water sample was processed in the field laboratory trailer as if it were a field blank. This "trailer blank" was not processed through the Van Dorn sampler; however, the trailer blank was substituted for the missing field blank in the sample batch that was sent to the analytical laboratory.

Field Duplicate Sample--A field duplicate was a second sample collected at the lake site immediately after the routine sample was collected. The sampling crew used the same procedure to collect the routine sample and its duplicate. For each field base, one helicopter crew collected one field duplicate on each sampling day. The ground crews did not collect field duplicates as frequently; each ground crew collected two field duplicates during the entire survey. Field duplicates were processed by the field laboratory and were inserted into the sample batches sent to the analytical laboratories. The routine sample and its field duplicate (referred to in this report as a field duplicate pair) provided the basis for estimating the cumulative variability of field sampling, field laboratory processing, and analytical laboratory analyses. This cumulative variability is referred to in this report as system precision.

Field Audit Sample--Field audit samples were used (1) to determine bias between the two analytical laboratories so that measurements made by the two laboratories could be compared and (2) to indicate the precision and accuracy of those measurements through repeated analysis of the same sample type. Two types of audit samples (field natural and field synthetic) were used to establish overall field laboratory and analytical laboratory performance. Field natural audit samples consisted of natural lake water that was passed through a 0.45-µm filter and was stored at 4°C until use. Field synthetic audit samples were prepared samples that included analytes of interest at specified theoretical concentrations. The concentrations of analytes in the synthetic audit samples were intended to simulate the concentrations in natural lake water (see Appendix C).

Natural and synthetic field audit samples, received by the field laboratory in 2-L aliquots from Radian Corporation Laboratory in Austin, Texas, were subject to the same filtering and aliquot preparation procedures as routine lake samples. These samples were incorporated into the batches and were shipped to the analytical laboratories without any identification that would distinguish them from routine samples. There were four field natural audit samples (designated FN3, FN4, FN5, and FN6) and one low-

Figure 3. Quality assurance and quality control sample flow, Western Lake Survey - Phase I.



concentration field synthetic audit sample (two lots, designated FL11 and FL12). Three of the natural audit samples (FN4 from Big Moose Lake in the Adirondack Mountains of New York and FN5 and FN6 from Bagley Lake in the North Cascade Mountains of Washington) represented surface waters low in ANC and in ionic strength, which were expected to be encountered during the survey. The fourth natural audit sample (FN3 from Lake Superior) had high acid neutralizing capacity (ANC) and high ionic strength.

Through daily QA communications with the analytical laboratories, the QA staff requested preliminary data on field audit samples. The data were checked for trends, and data for each audit sample were compared to data for other samples of the same lot (within WLS-I and from ELS-I and NSS Phase I Pilot Survey historical data). For synthetic audits, the preliminary data were compared to the theoretical values provided by the preparation laboratory. When aliquots of FN6 were prepared in the middle of the field sampling operations, the Radian Corporation's analytical laboratory analyzed three samples that the QA staff used as references for comparison with the preliminary data generated from the two analytical laboratories. When all of the analytical laboratory data (149 batches) had been entered into the raw data set, final audit control limits were generated. The formula for generating the control limits is given in Drousé et al. (1986). Appendix H presents the limits and the numbers of audit samples that did not fall within them. Values that were outside the limits were considered

suspect, and the QA staff requested confirmation. Outlier values also were detected, which indicated reporting error, analytical error, or contamination. Appropriate corrective action then was taken to resolve issues related to suspect data. If any audit data remained outside the control limits after all corrective action had been taken, data qualifier flags were placed on all the samples in the affected batch. The audit data, along with the data for other QA and QC samples, were used then in determining the data quality of each analytical batch, and the cumulative results were used to determine overall data quality.

Caution should be taken in assessing data quality in terms of the numbers of samples that were either within or outside the control limits. In addition, sample concentration levels must be assessed before the control limits are categorized. These distributions can be quantified in terms of the precision estimates, expressed as %RSD, derived from pooled data for an audit sample type (see Section 6). These %RSD results are referred to as precision estimated from field audit samples among batches.

Field Sampling and Field Laboratory Quality Control Samples--

The helicopter crews used quality control check samples (QCCSs) to calibrate Hydrolab pH, temperature, and conductance measurements in the morning, prior to sampling activity. In the evening, after sampling activity was completed for the day, the QCCSs were used to check instrumental drift over time.

The field laboratory staff used three types of QC samples to ensure that instruments and data collection were within specified control limits. Before samples in the batch were analyzed, a *calibration blank* was analyzed to check for baseline drift of the carbon analyzer and to check for contamination. *QCCSs* were analyzed for pH, DIC, and turbidity to check initial instrument calibration and, during sample analysis, to check instrumental drift. The *trailer duplicate* (a subsample or "split" of a lake sample) was used to check the precision of measurements made in the field laboratory. The field laboratory supervisor randomly selected one lake sample per trailer operating day; this sample was analyzed in duplicate for pH, DIC, true color, and turbidity.

Analytical Laboratory Quality Control Samples--

The analytical laboratories used six types of QC samples to ensure that instrument calibration and data collection were within control limits: (1) calibration blanks, (2) reagent blanks, (3) detection limit QCCSs, (4) low-concentration and high-concentration QCCSs, (5) matrix spikes, and (6) laboratory duplicates.

Calibration Blank--The analytical laboratory analyzed one calibration blank for each analyte in each batch of samples. The calibration blank, a 0-mg/L standard, was analyzed after the initial instrument calibration to check for drift in the measured signal and to check for potential contamination during the analytical process.

Reagent Blank--A reagent blank was analyzed for dissolved SiO_2 and total Al because additional reagents were added to the samples as part of the digestion step required for analysis of these variables. The reagent blank sample was composed of all the reagents (in the same volumes) used in preparing a lake sample for analysis. The reagent blank was carried through the routine preparation steps (e.g., digestion) prior to analysis.

Detection Limit Quality Control Check Sample--A detection limit QCCS was analyzed for specified variables to determine and verify the low end of the linear dynamic range and the values for the samples near the detection limits. The detection limit QCCS was analyzed once per batch, prior to analysis of the lake samples.

Low-Concentration and High-Concentration Quality Control Check Samples--The analytical laboratory QCCS was a commercially prepared or laboratory-prepared sample that was made from a stock solution separate from the one that was used for the calibration standards. The QCCS was analyzed to verify calibration at the beginning of sample analysis, after each specified number of sample analyses, and after analysis of the final sample in the batch.

Matrix Spike--A matrix spike, which was analyzed with each sample batch, was a check to determine the effect that the sample matrix had on the analytical response. The analyst spiked a known concentration of analyte into a sample of known measured concentration, then analyzed the spiked sample. Then the percentage of spiked analyte recovered (percent recovery) was calculated in order to determine whether or not there was a significant matrix effect on the analytical results of the original, unspiked sample.

Laboratory Duplicate--An analytical laboratory duplicate was analyzed with each batch of samples. A duplicate analysis was performed on one sample for each specified variable in each batch to estimate intralaboratory precision.

Field Sampling Quality Assurance and Quality Control Procedures

Field sampling QA and QC procedures consisted of calibrating all instruments before and after specified sampling activities and of monitoring changes in instrument performance (Bonoff and Groeger, 1987). All measurements and QC data were recorded on the lake data form. Helicopter crews used the Hydrolab to determine in situ temperature, conductance, and pH. Calibration and a QC check of the Hydrolab for these

three determinations were performed at the field base or remote site at the beginning of each sampling day. Ground crews used a field temperature meter equipped with a thermistor to determine in situ temperature at the beginning of the sampling day. At the lake site, before any scheduled samples were taken, the ground crew checked the temperature recorded by the thermistor probe against the temperature recorded by a thermometer certified by NBS. The ground crews did not measure in situ conductance. They used indicator strips to measure pH; therefore, they were not required to perform QC checks for this variable.

Before WLS-I sampling began, several field sampling protocol changes were made to accommodate logistical difference between ELS-I and WLS-I or to improve data quality in response to recommendations derived from ELS-I experience. The changes instituted pertained to the method of recording lake site location, the model of the Van Dorn sampler used, and the method that the ground crews used to measure pH. The most significant changes are described here; a complete list appears in Table 3 (Section 1).

Size of the Van Dorn Sampler--
Necessary additions to the ELS-I field equipment, including Van Dorn samplers, were ordered before the WLS-I field season began. The dimensions of the Van Dorn samplers delivered differed from the dimensions of the Van Dorn samplers used for ELS-I. Although each sampler had equal volume (6.2 L), the new samplers were almost twice as long (about 81 cm) as the ones used during ELS-I (about 43 cm). Reordering and equipping all helicopter and ground crews with the shorter Van Dorn samplers would have been time and cost prohibitive, so all crews were equipped with the longer model. This action eliminated one possible source of sampling bias within WLS-I.

Use of the longer Van Dorn sampler for WLS-I called for minor procedural changes because shallower lakes (i.e., lakes where a debris-free water sample could not be obtained 1.5 m below the surface) had to be sampled at 0.75-m depth rather than at 0.5 m as in ELS-I. The change was required so that the stopper mechanism on the longer sampler would have enough clearance below the water surface to prevent the introduction of air into the sample. Consequently, lakes classified as shallow in ELS-I may have been as much as 0.5 m shallower than their WLS-I counterparts. Conversely, it is possible that some lakes in the West that were classified as too shallow would have been sampled if the shorter Van Dorn sampler had been used.

Measurement of pH with pH Indicator Strips--
The sampling protocol called for WLS-I ground crews to take in situ pH measurements with pH indicator strips (Bonoff and Groeger, 1987). This method was determined to be the most practical means for the ground crews to use, although it was not a standard NSWS protocol. It was selected because the cost of equipping 60 ground crews with Hydrolabs or portable meters was prohibitive, especially when the possibility of damaging the Hydrolabs in ground transit and the need for back-up units was considered.

Field Laboratory Quality Assurance and Quality Control Procedures

Field laboratory personnel processed and preserved aliquots of samples collected in the field; analyzed water samples for pH, DIC, turbidity, and true color; and prepared and shipped sample batches to the analytical laboratories. Because DIC and pH measurements can be affected by the loss or gain of CO_2 over time, the closed-system field laboratory measurements provided QA and QC data that were helpful for later comparison with air-equilibrated measurements taken in the analytical laboratories. Because turbidity and true color are physical measurements, they could be performed relatively quickly in the field laboratory.

Specified aliquots were stabilized to inhibit biological and chemical activity and to prevent changes that could result from volatility, precipitation, or adsorption. Field laboratory personnel filtered designated aliquots of each sample to remove suspended material and other contaminants that might affect analytical results. Suspended material was removed to reduce biological activity and to eliminate surfaces that could adsorb or release dissolved chemical species. Filtered and unfiltered samples were processed into aliquots. Acid was added to some aliquots to minimize loss of dissolved analytes through precipitation, chemical reaction, or biological action. Aliquots were stored and shipped at 4°C to minimize biological activity and, in the case of extractable Al aliquots, to minimize volatilization of solvent. Silverstein et al. (1987) provide detail of aliquot preparation.

Sample Batching and Shipping--
Field laboratory personnel organized the samples into batches for shipment to the analytical laboratories. A sample batch consisted of a group of routine lake samples and related QA samples collected in the field, processed in the field laboratory on the same date (within 12 hours of sampling, when possible), and shipped as a unit to one analytical laboratory on the following day. Because the WLS-I sampling operation was more complex than its ELS-I counterpart, the number of sample types (and corresponding sample codes) increased from 5 in ELS-I to 24 in WLS-I (see Table 8). Ideally, each WLS-I sample batch contained at least one field (or trailer) blank, one field duplicate, and one field audit sample. Each routine, blank, duplicate, and audit

sample was randomly numbered in the batch. Each sample could be identified by a unique batch ID and sample ID, and thereby could be distinguished from any other sample in the survey. The field laboratory and the analytical laboratory also analyzed QC samples with each batch, but these samples were not associated with any individual lake sample in the batch.

There were occasional deviations from this standard batch structure as the result of the sampling design and of field conditions that altered the sampling pattern on a given day. Two situations led to the preparation of batches that contained only one lake sample each: (1) when, on a given day, helicopter crews were not sampling and only one ground crew delivered one routine lake sample (with no field blanks or duplicates), and (2) when a single calibration lake sample was shipped to the alternate laboratory (see Section 9). When one of these situations occurred, one field audit sample and one trailer blank sample were processed with the routine sample, and the three samples were shipped to the analytical laboratory. In this way, some QA samples were included in each batch, and the data quality of the routine sample could be assessed.

All data and shipping forms were reviewed by the field laboratory coordinator. Copies were sent to the QA staff at EMSL-LV, where the forms were reviewed for data completeness and consistency. Copies of the lake data and batch/QC field data forms were sent to the data base manager at ORNL, where the forms were used for data entry.

Analytical Laboratory Quality Assurance and Quality Control Procedures

Analytical laboratory personnel were responsible for receiving the samples shipped by overnight courier service from the field laboratory, inspecting the samples for damage, logging in the sample batches, analyzing the samples, and preparing and distributing data packages on the analyses performed (Hillman et al., 1986; Kerfoot and Faber, 1987).

After samples were logged in, they were analyzed according to the analytical and QA and QC procedures specified in Kerfoot and Faber (1987) and in the SOW. Each variable (Table 2) had to be measured within a specified holding time (Table 9).

As a part of the contract requirements, the analytical laboratories agreed to follow standard laboratory practices for laboratory cleanliness and for the use and storage of reagents, solvents, and gases. For standard guidelines regarding general laboratory practices, the analytical laboratories were directed to procedures in the *Handbook for Analytical Quality Control in Water and Wastewater Laboratories* (U.S. EPA, 1979). The analytical laboratories operated according to a uniform set of internal QC procedures that served as checks on data consistency (see Silverstein et al., 1987; Kerfoot and Faber, 1987). The laboratories also documented method performance.

Data Packages--

For each batch of samples, analytical laboratory personnel completed a data package that included a set of NSWS forms containing the following information (see Drousé et al., 1986; Silverstein et. al., 1987):

- sample concentration for each variable
- for ANC and BNC, titrant concentrations and titration data points for each sample
- percent conductance difference calculation for each sample (optional; this calculation is an initial check made in the analytical laboratory to ensure data consistency, but it is also performed during data verification under the direction of the EMSL-LV QA manager)
- percent ion balance difference calculation for each sample (optional; this calculation is an initial check made in the analytical laboratory to ensure data consistency, but it is also performed during data verification under the direction of the EMSL-LV QA manager)
- ion chromatograph specifications for Cl^-, NO_3^-, and SO_4^{2-}
- instrument detection limits for applicable variables
- sample holding times and date of sample analysis for each analysis of each sample
- calibration blank, reagent blank, and QCCS concentrations for each applicable variable
- matrix spike percent recovery calculations for each applicable variable (once per variable; two additional calculations if recovery of the first spike not within criteria)
- internal (laboratory) duplicate precision as %RSD, or, for pH, absolute difference (one for each variable analyzed in the batch; one additional duplicate measurement on a different sample if the first measurement did not meet criteria)
- standard additions analysis results, when applicable (on the basis of unacceptable matrix spike percent recovery results)

Table 8. Types and Numbers of Samples Analyzed, Western Lake Survey - Phase I

Sample Code	Sample Type	Number of Samples Analyzed in the Analytical Laboratories
	Routine Samples	
RH	routine sample (helicopter)	395
RG	routine sample (ground)	317
RH2	routine sample (helicopter), lake sampled a second time	5
RG2	routine sample (ground), lake sampled a second time	4
	Duplicate Samples	
DH	duplicate sample (helicopter)	88
DG	duplicate sample (ground)	128
DH2	duplicate of an RH2 sample	1
DG2	duplicate of an RG2 sample	1
TD	trailer duplicate	0[a]
	Blank Samples	
BH	field blank sample (helicopter)	118
BG	field blank sample (ground)	116
BH2	field blank associated with an RH2 sample	1
BG2	field blank associated with an RG2 sample	1
TB	trailer blank	22
	Audit Samples	
FN3	field natural, lot 3, Lake Superior	38
FN4	field natural, lot 4, Big Moose Lake, New York	20
FN5	field natural, lot 5, Bagley Lake, Washington (lst sampling)	68
FN6	field natural, lot 6, Bagley Lake, Washington (2nd sampling)	37
FL11	field synthetic, lot 11	21
FL12	field synthetic, lot 12	26
	Calibration Lake Samples	
RHC	routine calibration sample (helicopter)	32
RGC	routine calibration sample (ground)	45
DHC	duplicate calibration sample (helicopter)	29
DGC	duplicate calibration sample (ground)	38
THC	triplicate calibration sample (helicopter)	29
RHCW	RHC sample withheld for holding-time study	13
DHCW	DHC sample withheld for holding-time study	16
THCW	THC sample withheld for holding-time study	16
BHC	field blank collected at calibration lake (helicopter)	10
BGC	field blank collected at calibration lake (ground)	6
	Miscellaneous	
SG	special sample (ground) - not sampled according to NSWS protocols	1[b]
	TOTAL	1,642

[a] Not analyzed in analytical laboratory.
[b] This sample was deleted from the data base.

The data package included a cover letter from the analytical laboratory manager to the QA manager. The letter specified the batch ID number and the number of samples analyzed, identified all problems associated with the analyses, described all deviations from protocol, and contained other information that the laboratory manager considered pertinent to a particular sample or to the entire batch. Copies of the completed data package were sent to the QA staff for initial review and to ORNL for entry into the raw data set (see Section 4).

On the basis of the analytical results reported for all QA and QC samples, the QA staff, with the approval of the QA manager, could direct the analytical laboratory to confirm reported values or to reanalyze selected samples or sample batches. A tracking form for data confirmation and sample reanalysis requests (NSWS Form 26, Appendix A) was developed and implemented for WLS-I. This provided a standard documentation format for data transfer between the QA staff and the analytical laboratories.

Table 9. Maximum Holding Times for Samples, Western Lake Survey - Phase I

Holding Time[a]	Variable
7 days	NO_3^-, air-equilibrated pH, extractable Al
14 days	ANC, BNC, conductance, DIC, DOC
28 days	Total P, NH_4^+, Cl^-, SO_4^{2-}, total dissolved F^-, SiO_2
28 days[b]	Ca, Fe, K, Mg, Mn, Na, total Al

[a] Holding time commenced on the day that the field laboratory processed the sample.
[b] Although holding time has been established at 6 months, samples had to be analyzed within 28 days to conform with WLS-I data reporting restrictions.

Communications

The QA staff communicated regularly with the logistics staff, field and analytical laboratory personnel, data base manager, and EPA management team throughout the survey to confirm progress, resolve protocol problems, and modify procedures. During the sampling and analytical phases, the Lockheed- EMSCO QA staff made daily calls to the field bases and to the analytical laboratories (1) to ensure that QA and QC guidelines were being followed, (2) to ensure that samples were being processed and analyzed properly, (3) to obtain current sample data and QA and QC data, and (4) to discuss sampling, processing, and analysis issues so that problems could be resolved quickly and efficiently, before they affected data quality or interfered with the completion of the survey. Throughout the data verification process, QA and analytical laboratory personnel communicated as necessary to confirm reported values, and to make sample reanalysis requests, and to receive results for reanalyzed samples. All communications were logged on appropriate field communications forms and in bound notebooks.

On-Site Evaluations

On-site evaluations of field sampling activities, field laboratories, remote sites, and analytical laboratories were conducted during WLS-I to ensure that sampling and analytical activities were being performed according to survey protocol. The results of these evaluations were documented in site-evaluation reports prepared by the QA staff, and the reports were submitted to the QA manager at EMSL-LV. Significant results of the on-site evaluations are discussed in Section 5, and overall results are summarized in Tables 4 through 6 (Section 2).

Section 4
Data Base Quality Assurance

Data Management System

The data base management system (DBMS) incorporates the results from data collection, evaluation, verification, and validation. By means of the DBMS, data generated during WLS-I and other NSWS surveys can be assembled, stored, and edited. The DBMS also provides basic reports of the survey results, performs certain statistical analyses, and provides data security. A detailed description of the system is given in Kanciruk (1986). The relationship of data base management to other survey activities is shown in Figure 4.

The WLS-I data base comprises four major data sets as summarized below. See Kanciruk et al. (1987) and Silverstein et al. (1987) for further discussion.

Raw Data Set (Data Set 1)

The raw data set includes all analytical results and data qualifiers (Silverstein et al., 1987). Data entry operators at ORNL employed the Statistical Analysis System (SAS; SAS Institute, 1982) to enter the field data from the lake data and batch forms and the analytical laboratory data from the analytical data forms (see Appendix A in Drousé et al., 1986) into the raw data set. All data were entered into two separate data sets by two different operators. A custom program was developed to compare the two data sets and to identify inconsistencies. Copies of the field forms and analytical data packages were sent to the EMSL-LV QA staff for concurrent data analysis and as confirmation that all forms were received by ORNL.

Field data errors identified through daily communication between QA and field personnel were corrected immediately. If the data in question had not been entered by ORNL, the changes were included in the raw data set; otherwise, the data changes were included in subsequent data sets. Documentation accompanied each instruction to make changes in the raw data set.

Verified Data Set (Data Set 2)

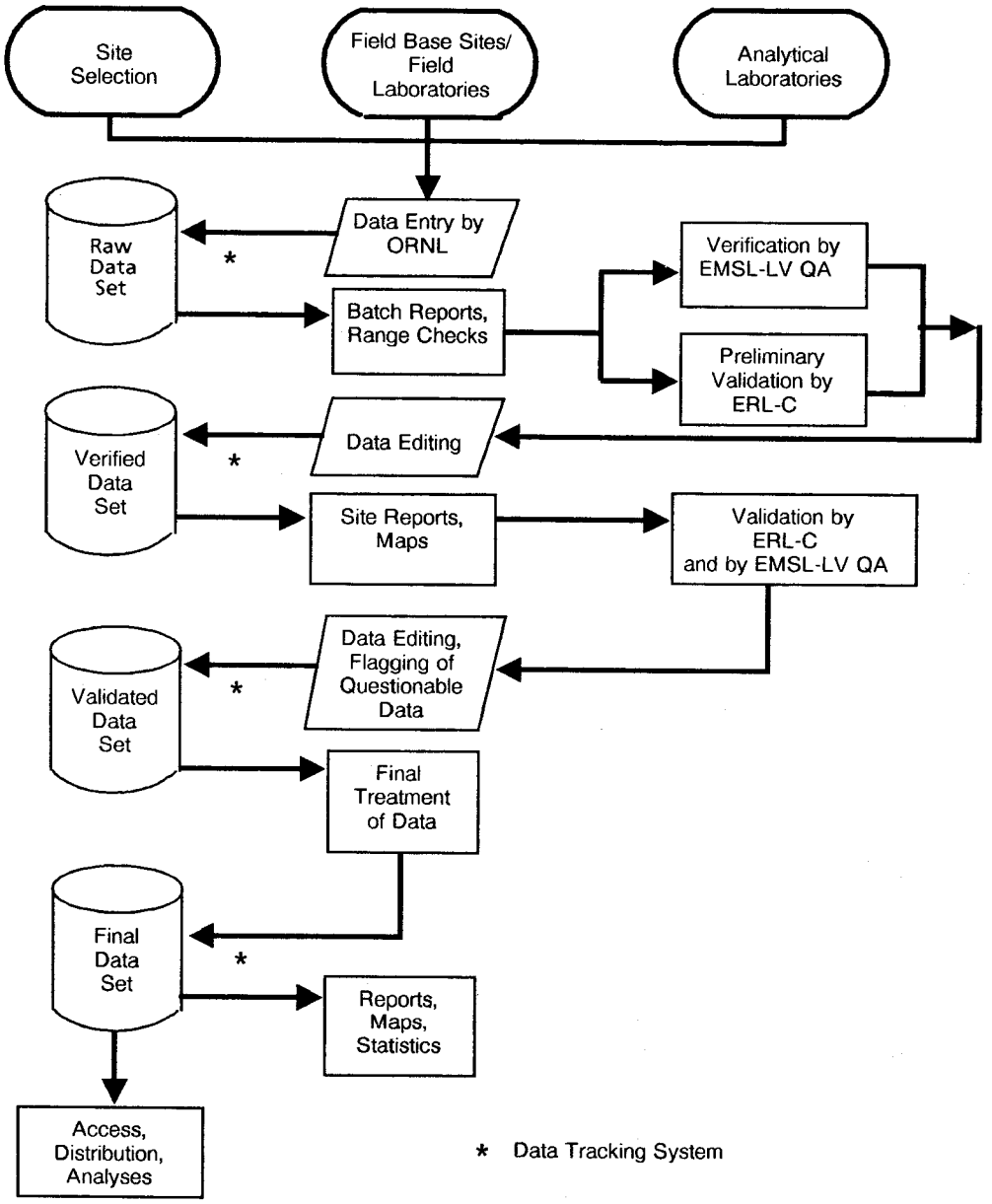
Because the numerical, tag, and flag changes were never applied to the raw data set, a changed data set (the verified data set) was generated. Through magnetic tape transfer to EPA's IBM 3081 computer at the National Computer Center (NCC) in Research Triangle Park, North Carolina, the raw data set was made available to the EMSL-LV QA group for review. To produce the verified data set, the raw data were processed by the Automated Quality Assurance Review, Interactive Users System (AQUARIUS), which is an on-line QA system developed by the EMSL-LV QA staff. AQUARIUS generated "tuples" that directed the flagging of problem data in the raw data set. Tuples are generated by an exception program (a computer program in AQUARIUS that indicates data anomalies) or that are manually created by an auditor. In order to generate the verified data set, the QA computer support staff applied tuples (as SAS observations) generated by the EMSL-LV QA staff to a copy of the raw data set. The data were sent to ORNL via magnetic tapes to be checked for anomalies.

AQUARIUS also generated reports helpful in evaluating intralaboratory biases and field and analytical interlaboratory biases, as well as reports on discrepancies in blanks, duplicates, audits, and other QA and QC samples. The result was a verified data set in which each of the 1,642 samples was inspected carefully and any suspicious value or observation was qualified with appropriate flags. AQUARIUS data qualifier flags and their definitions are given in Silverstein et al. (1987) and in Kanciruk et al. (1987).

Validated Data Set (Data Set 3)

The validation process increased the overall integrity of the data base by evaluating all data for internal and regional consistency and by using data provided by QA and QC information to assess possible analytical inconsistencies. The validation process began in tandem with the verification process. When a computerized version of the verified data set was provided by ORNL to the ERL-C staff through NCC, the validation review process could be completed. After undergoing this review process, the data were transferred to the validated data base. The validation process is discussed further in Landers et al. (1987) and in Silverstein et al. (1987).

Figure 4. Data base management, Western Lake Survey - Phase I.



Final Data Set (Data Set 4)

Linthurst et al. (1986) noted that the calculation of population estimates is difficult if the data set contains missing values. To minimize these difficulties, a final data set was prepared for use in calculating population estimates. This data set was modified by averaging the field duplicate pair values that were within desired precision limits. Negative concentrations that were reported by the analytical laboratory as resulting from instrumental drift (i.e., a negative y-intercept on the calibration curve) were converted to zero (except for ANC and BNC), and analytical values that the validation review had identified as questionable were replaced. The substituted values were determined according to procedures described in Landers et al. (1987) and in Silverstein et al. (1987).

Data Review and Verification

The objectives of the data verification process were to identify, correct, or flag raw data of questionable or unacceptable quality and to identify data that might need to be eliminated during or after validation. The WLS-I verification process was modified considerably on the basis of ELS-I experience and as a result of the need to accommodate the large number of sample types (Table 8) added to the WLS-I sampling design. Many WLS-I QA personnel had prior NSWS experience in QA, field sampling, and field laboratory operations, as well as previous experience in wet chemical and instrumental analysis of water samples in the analytical laboratories. This background expedited the modification of ELS-I field, laboratory, and data verification protocols; the identification and correction of sample collection, processing, and analytical problems; and the identification of data trends.

Preliminary sample data were obtained verbally, by computer, or by telefacsimile, depending on the laboratory. The preliminary data were evaluated by comparing the QA sample data against the acceptance criteria. Responsible parties were notified of problems, and all interactions were recorded in bound notebooks. If necessary, memoranda were sent as documentation.

Data verification began when the field and analytical laboratory data were received by the EMSL-LV QA staff. All data were evaluated on the basis of the QA and QC information and knowledge of lake water chemistry. AQUARIUS computer programs automated much of the verification process. For each analytical data package (representing one batch of samples), the QA audit team performed a sample-by-sample evaluation. The audit team reviewed comments and questions associated with the batch; performed QA checks for data consistency and reasonableness; reviewed QA sample data; obtained confirmation, correction, and reanalysis data from the analytical laboratories; and provided a verified data set to ORNL. For each batch, the audit team prepared a summary of the reporting errors found and of the data confirmation and sample reanalyses required.

Review of Field Data Forms

When the lake data and batch/QC field data forms arrived from the field, the auditor reviewed the forms for data inconsistencies and for adherence to procedures. Data anomalies were reported to the field laboratory coordinator for corrective action, and when possible, data reporting errors were corrected before the data were entered into the raw data set. Changes made to the raw data set were sent to ORNL by telefacsimile for immediate action. A detailed discussion of the field data review procedure appears in Silverstein et al. (1987).

Initial Review of Analytical Laboratory Data Packages

The analytical laboratory submitted a data package to the EMSL-LV QA staff for each batch of samples. The QA staff used the NSWS verification worksheet to review each package for completeness, internal QC compliance, and appropriate use of data qualifiers. The verification worksheet was designed to guide the auditor systematically through the data verification process by explaining how to flag data, track data resubmissions and requests for reanalysis and confirmation, list the steps that lead to identification of QA exceptions, and summarize modifications to the raw data set (prepare records of flag and numeric changes). Written comments submitted with the data package also were reviewed to determine their impact on data quality and to determine any need for follow-up action by the laboratory. Auditors reported problems to the analytical laboratory manager for corrective action.

Final Data Verification

While the EMSL-LV QA staff were conducting the initial review of analytical data packages, the data were also being entered into the raw data set at ORNL. ORNL sent a magnetic tape containing the data to NCC. Through telecommunication, the EMSL-LV QA staff had access to the raw data set and could complete the data verification process.

Each sample was verified individually and by analytical batch. AQUARIUS programs were used to identify or flag results that were classed as exceptions, i.e., results that did not meet the expected QA and QC criteria (Table 10). Additional data qualifiers were added to a given variable when the QA samples (field blanks, field duplicates, or field audit samples) in the same analytical batch did not meet the acceptance criteria. Data also were qualified with flags if internal consistency checks (anion-cation balance, calculated conductance), QC checks, or holding time requirements were not met. The protolyte analysis program flagged field laboratory and analytical laboratory measurements of pH, DIC, ANC, BNC, and DOC when carbonate equilibria, corrected for organic protolytes, were not in internal (within-sample) agreement. A flag was not assigned if the discrepancy could be explained by the presence of organic species (as indicated by the protolyte analysis program) or by an obvious and correctable reporting error.

In all cases, each flag generated by the AQUARIUS system was evaluated by the auditor for reasonableness and consistency before it was entered into the verified data set. These programs automated much of the QA review process and enabled the auditor to concentrate more effort on the substantive tasks of correcting and flagging questionable data. These programs also identified

Table 10. Exception-Generating Programs within the AQUARIUS Data Review and Verification System

Program	Sample (Data) Type
Field Audit Sample Summary	Field Natural (FN), Field Synthetic (FL)
Field/Trailer Blank Summary	Field Blank (BH, BG), Field Laboratory Blank (TB)
Field Duplicate Pair Precision Summary	Routine/Duplicate Pairs (RH/DH, RG/DG)
Instrumental Detection Limit Summary	All Species
Holding Time Summary	All Species
Conductance Check Calculations	All Species
Anion/Cation Balance Calculations	All Species
Batch QA/QC Summary	All Exceptions
Comparison of Form 1 and Form 2	pH and DIC
Comparison of Form 2 and Form 11	pH and DIC
Protolyte Analysis	DIC, DOC, pH, ANC, and BNC (data evaluation)
Comparison of Total Aluminum and Extractable Aluminum	Total Al and Extractable Al
Audit Sample Window Generation	All Species
Raw Data Listing	All Field/Laboratory Data
QA/QC Flag Summary	All Exceptions
Reagent/Calibration Blanks and QCCS	All Species (except pH)
Calculation of Laboratory Penalties	All Species
Matrix Spike Summary	Applicable Species
Gran Analysis	ANC and BNC

outlier data based on QA and QC sample data. The outlier data were the basis for requesting confirmation of data from the analytical laboratories and for requesting reanalysis of suspicious samples. Values were confirmed before reanalysis requests were issued.

The auditor used the output from the AQUARIUS programs (along with original data and field notebooks) to complete the NSWS verification report form (Silverstein et al., 1987).

Modifications to the AQUARIUS System

The QA staff made several changes to the AQUARIUS data verification programs between ELS-I and WLS-I. These changes are summarized in Table 3 (Section 1), and the most significant changes are discussed below.

Determination of Control Limits for Blank Samples--
In ELS-I, contamination levels for field blanks were determined on the basis of previous knowledge of how field sampling and analytical methodology may affect water samples. The WLS-I verification process, however, benefited from the use of historical field blank data generated during ELS-I. The values for the 245 ELS-I field blank samples were used to calculate control limits which, in turn, were used to check for contamination, to determine the necessity of data confirmation or reanalysis, and to generate flags that qualified the data by batch or by sample. Calculation of WLS-I control limits for blank samples and a comparison of ELS-I and WLS-I control limits are given in Appendix B.

Comparison of Extractable Al and Total Al--
The EMSL-LV QA staff developed a computer program to compare the extractable Al and total Al values for each sample. By definition, the extractable Al concentration for a sample could not exceed the total Al concentration. The program generated a flag when the value for extractable Al was higher than the value for total Al by more than 0.010 mg/L (twice the required detection limit; Table 2).

This qualification was intended to account for background noise (especially at low concentrations) and for minor fluctuations in instrument reading and calibration.

Calculation of Percent Ion Balance Difference--
Percent ion balance difference (%IBD) is calculated by

$$\frac{\Sigma\, anions - \Sigma\, cations + ANC}{\Sigma\, anions + \Sigma\, cations + ANC + 2\,[H^+]}\ 100$$

where:

Σ anions = $[Cl^-] + [F^-] + [NO_3^-] + [SO_4^{2-}]$

Σ cations = $[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + [NH_4^+]$

ANC ≈ Alkalinity (the ANC value is included in the calculation to account for the presence of unmeasured ions such as organic ions)

$[H^+] = (10^{-pH}) \times 10^6$ µeq/L

Note: Brackets indicate concentration of an ion in microequivalents per liter.

The anion-cation balance limits are different depending on the total ionic strength (the denominator in the calculation) of the sample. If the sum of the ions were calculated to be less than 50 µeq/L, the difference could be ±60 percent. If the sum were between 50 µeq/L and 100 µeq/L, the difference could be ±30 percent. If the sum were greater than 100 µeq/L, the difference could be ±15 percent. Any routine lake sample or QA sample that did not fall within the applicable criterion was qualified with a flag.

The calculation program was modified so that in all instances where the absolute value of ANC was less than or equal to 10 µeq/L, the value zero was substituted for ANC in the equation. The equation is sensitive to slight variations in ANC for samples that have very low ionic strength.

Calculation of Percent Conductance Balance Difference--

Although no adjustment was necessary for the conductance balance difference (%CD) calculation, the criteria are presented here because of the importance of this internal sample consistency check to the QA program. The formula for determining conductance balance is:

$$\frac{calculated\ conductance - measured\ conductance}{measured\ conductance} 100$$

The ions used to calculate conductance are Ca^{2+}, Cl^-, CO_3^{2-}, H^+, HCO_3^-, K^+, Mg^{2+}, Na^+, NO_3^-, OH^-, and SO_4^{2-}. The limits for the difference between analytical laboratory measured conductance and calculated conductance is ± 50 percent if measured conductance was less than 5 µS/cm, ± 30 percent if measured conductance was between 5 µS/cm and 30 µS/cm, and ± 20 percent if measured conductance was greater than 30 µS/cm. Any routine lake sample or QA sample that did not fall within the applicable criterion was qualified with a flag.

Confirmation and Reanalysis Requests

Completing the verification process often required communication with the analytical laboratory to obtain confirmation or correction of reported data and to request sample reanalyses. The follow-up communication was time-consuming, particularly when the type of request made to the laboratory had not been specified in the original SOW or when the laboratories concerned were involved in other analytical activities at the time of WLS-I verification. Typically, responses to requests for confirmation or correction of reported data were completed within 2 to 4 weeks. Generally, reanalyses were requested when at least three different QA/QC samples generated flags for a particular variable in a particular batch. Three flags were enough to classify a result as suspect.

Preparation and Delivery of Verification Tapes

Constructing the verified data set required a consistent and trackable method for transferring the change records to ORNL. The method chosen to accomplish this transfer employed tuples to identify a change to the data set. Tuples generated by computer programs and those generated by QA personnel were stored in separate data files until the tuple listing was applied to a copy of the raw data set. At that time, a computer program combined all tuple areas (flag, tag, or value changes) and applied the combined tuples to the data set only if the batch ID, sample ID, variable name, and originally reported values matched. Tuples that could not be applied to the data set were reexamined by the QA staff, were corrected, and were reapplied. The final verified data set was generated by the EMSL-LV QA computer support staff. The tape was sent to ORNL where it was checked for consistency before it was used in data validation. ORNL also was responsible for archiving the tape.

At the conclusion of the verification process, a data base audit was performed by an independent firm that did not participate in other WLS-I activities. The audit consisted of reviewing the written verification records, evaluating for accuracy the results generated by AQUARIUS and other computer programs, reviewing the procedures used to substitute for missing values, and determining the error rates associated with each aspect of the verification procedure. The audit identified an error rate of 0.05 percent for data entry at ORNL. In the verified data set no incorrect value changes were detected, and all of the value changes were documented (IS&T, Inc., 1986).

Data Validation

Validation is a functional term for describing the continuing process of defining the quality of the data so that each step results in increased knowledge of and presumably confidence in the data. This is accomplished by reviewing the data for errors; data known to be erroneous are identified so that correct data can be substituted, and possible errors are flagged to alert the user to their questionable status.

The system of data validation used for ELS-I was also used for WLS-I. In the verification step, the quality of the analytical chemical data was determined through a rigorous protocol based on known principles of chemistry. Not all potential sources of error, however, can be evaluated in the verification process. The validation process, then, investigated errors in the chemical analyses not detected in verification and provided a review of the quality of nonchemical variables.

Two aspects of the data validation process were the identification of outliers and the evaluation of possible systematic errors in the measurement process. The methods selected for detecting outliers and systematic errors stressed visual presentations and conservative, subjective selection procedures. They were chosen for their simplicity of implementation and employed pre-existing software whenever possible. An audit performed on the validated data set (IS&T, Inc., 1986) identified an error rate of 0.01 percent for data values.

Data validation procedures are discussed fully in Drousé et al. (1986) and in Linthurst et al. (1986). WLS-I data validation design and results are discussed in Landers et al. (1987).

Section 5

Results and Discussion - Operational Quality Assurance Program

The results presented in Sections 5 through 8 are limited to QA and QC observations and data. A discussion of regional population estimates for WLS-I appears in Landers et al. (1987).

Field Sampling Activities and Protocols

The field auditors conducted on-site evaluations of all field bases and of selected remote sites. The auditors found that all field sampling and laboratory crews performed their duties professionally and cooperatively, in spite of the tight schedules required to complete seasonal sampling activities. In some cases, severe weather conditions contributed to logistical problems, but the crews adapted well, documented problems accurately, and often proposed effective solutions (Bonoff and Groeger, 1987).

Sampling activities commenced on September 11, 1985, and were completed on November 4, 1985. In the WLS-I sampling design, 973 lakes originally were selected for sampling and for use in estimating populations; 95 of those randomly selected lakes were eliminated from the design before sampling began. Forty-two other lakes also were scheduled for sampling because of special interest, but they were not part of the random selection process and they were not used in calculating population estimates. (Landers et al. [1987] details the process of selecting the lakes used in the population estimates and the application of the data derived from those lakes.) Therefore, at the start of field operations, 920 lakes were scheduled to be visited. Sampling crews attempted to sample 912 lakes; they collected 811 routine lake samples from 757 of the 912 lakes. Data from 719 of the lakes were used in calculating population estimates. Some lakes were not sampled because they were frozen, thermally stratified, or too shallow. Other lakes were not sampled because access permission could not be obtained, because weather conditions or hazardous conditions prevented access, or because the lakes had dried up since they were mapped. Some lakes were sampled twice, either by different sampling crews (Section 9) or by the same crew (see below). Bonoff and Groeger (1987) describe sampling activities in detail.

In addition to the changes in field sampling protocol that were made prior to WLS-I (Table 3 in Section 1), some changes were made in response to situations that arose during the survey. These changes are summarized in Table 4 (Section 2); the most significant change is also discussed here.

During WLS-I sampling, some lakes were found to be thermally stratified. When a helicopter crew determined that a lake was stratified, they did not always sample the lake, but returned at a later date to sample when there was a better chance that the lake was isothermal. The field base coordinator incorporated the second visit into the sampling schedule. Ground crews were not constrained by this protocol because of the time and distance involved in returning to the lake; however, they did return to these stratified lakes when possible. The lakes visited twice are categorized in Table 11.

If a lake was sampled twice by the same crew, a "2" was added to the sample code for samples collected on the second visit. For example, RH2 is the code for a routine helicopter sample collected on the second visit (see Table 8 in Section 3). For cases where a lake was stratified on the first visit but not stratified on the second visit, only the analytical results from the sample collected when the lake was unstratified were used in estimating populations.

Field Laboratory Activities and Protocols

In general, WLS-I field laboratory operations were conducted without major difficulties (Bonoff and Groeger, 1987). Numerous field laboratory protocol changes and deviations were instituted in response to WLS-I field situations. These issues are summarized in Table 5 (Section 2); the most significant issues are discussed here also.

Filtration Procedure

Because of residual nitrate contamination, separate filtration apparatuses for the 0.45-µm filters and filtrators rinsed with nitric acid were used in processing certain aliquots during ELS-I. (A nitric

Table 11. Lakes Visited Twice by Sampling Crews, Western Lake Survey - Phase I

	No. of Lakes Sampled on Both Visits		No. of Lakes Sampled on Second Visit Only	
Sampling Crew	Stratified	Other Reasons	Stratified	Other Reasons
Helicopter	5	0	15	2
Ground	2	2	2	0
Total	7	2	17	2

acid solution [5 to 10%] rinse is standard laboratory procedure for washing off residual metals [e.g., Ca, Mg] that may be adsorbed onto filters and onto the walls of filtration apparatuses.) This segregation of filtration apparatuses became standard protocol for the NSS Phase I Pilot and WLS-I.

Receipt of Samples from Sampling Crews

WLS-I protocols established a daily cut-off time for sample receipt. Samples were not incorporated into the daily batch later than 2 hours after field laboratory start-up. Samples that arrived after that time were refrigerated until the next day and were included in the next day's batch. Exceptions were allowed when the following three conditions were met:

- Field communications alerted the laboratory that samples would be received by a specified time.
- The DIC analyzer had not been turned off (recalibration of the instrument would take analyst's time away from normal pH analysis).
- Filtrations and Al extraction were not completed on the other samples.

The Forest Service manager, field base coordinator, and field laboratory personnel evaluated each situation to accommodate delivery-schedule deviations, usually brought about by adverse weather conditions.

During WLS-I, ground crews collected 366 routine samples from 362 lakes (see Table 8). Of the samples collected at these lakes, 62 percent were processed at the field laboratory on the day that they were collected, 28 percent were processed within one day after sampling, 7 percent were processed within two days after sampling, and 3 percent were processed more than two days after sample collection (see Table 12).

Shipment of Samples

Of the 149 batches analyzed during WLS-I, one batch (ID 1117; 14 samples) was detained in transit for three days between the field laboratory and the analytical laboratory. Upon arrival at the analytical laboratory, the internal temperature of the shipping containers was below 10°C, which indicated that the integrity of the samples was maintained and that the shipping container insulation was effective. Subsequent analyses did not exceed specified analytical laboratory holding times by more than two days for any analyte. The data for the samples are flagged appropriately in the data base.

In a second situation, the Carson City field base sent an unscheduled sample shipment to one analytical laboratory. This flexibility had been given to the Carson City field base before routine sampling began. When the field base's regular analytical laboratory (II), which was also used regularly by two other field bases, received too many samples at one time, the Carson City base shipped one batch (ID 1504) to the other analytical laboratory (I) for analysis. This situation illustrates the role that the Communications Center in Las Vegas played in tracking sample flow to ensure that the analytical laboratories were not overloaded with samples on a given day.

Comparison of Lake Site and Field Laboratory pH Measurements

ELS-I and WLS-I field laboratory protocols included a comparison of Hydrolab pH (in situ) measurements and field laboratory pH meter measurements. If the difference between the two measurements was greater than 0.5 pH unit, field laboratory pH was to be remeasured. The majority of Hydrolab versus pH meter readings, however, were within the ± 0.5 pH QC requirement.

Initially, the parallel comparison between field pH (indicator strips) and field laboratory pH (meter) was conducted. At several field bases, a pattern developed among the first few batches. Most pH indicator strip measurements were at least 0.5 pH unit lower than the laboratory pH meter reading, and many readings were at least 1.0 pH unit lower. When

Table 12. Field Laboratory Holding Times[a] for Samples Collected by Ground Crews, Western Lake Survey - Phase I

Number of Days Elapsed Since Sampling Date[b]	Number of Lakes Sampled	Percent (to nearest whole)
0	227	62
1	102	28
2	25	7
3	4	1
4	3	1
5	2	<1
6	1	<1
7	1	<1
8	1	<1
	366	100

[a] These holding times refer to the time differences between sampling and sample preservation. They are not related to holding time requirements for the analytical laboratories.

[b] An estimated 5 to 10 percent of holding time delays beyond the sampling date were because the field laboratories did not operate on some days.

the discrepancies were first noted, field pH indicator strip readings were cross-checked with indicator strip readings taken in the field laboratory. Results of this cross-check confirmed that the ground crews were reading the pH paper color development correctly. Subsequently, the protocol for the pH paper comparison was changed so that reanalysis of only two to four laboratory measurements per batch was necessary when indicator strip pH was outside criteria. In these cases, one measurement was taken at each extreme of the pH readings. Depending on the size of the batch and the pH range, a reading also was taken at reasonable intervals within the range. Theories about the origin of the problem are being explored, but are not within the scope of this report. The data user, however, should note that pH indicator strips provide a coarse reading at best. The data user also should be aware that the only way to distinguish Hydrolab pH measurements from pH indicator strip measurements, both of which are reported on the lake data form (entered into the data base as "PH_TOP"), is to check whether the lake was sampled by helicopter-access or ground-access. The closed-system pH readings determined in the field laboratory provide data most suitable for use in estimating populations.

Analytical Laboratory Activities and Protocols

On-site evaluations were conducted at the analytical laboratories after sample analysis was underway. QA and QC data that had been provided up to the time of the visit were reviewed, and the QA and QC issues were identified and discussed. The on-site evaluations were a contractual part of the QA program used to observe laboratory operations and to check for protocol deviation. The evaluations permitted the QA and analytical laboratory staff to discuss concerns about contract interpretation and questions about sample analysis. Topics of particular interest to the WLS-I laboratories included preliminary QA and QC data, lost samples, contingency plans for unexpected laboratory shut-down, QA and QC acceptance criteria, and improvement and documentation of protocol decisions and procedural changes. The meetings were helpful in solving problems and clarifying previous telephone communications.

At Laboratory I, operations were satisfactory and QCCS control charts were current. To meet analytical holding time requirements, the laboratory was operating two shifts, both of which were observed during the visit. It was noted that reagent bottles needed to be labeled more carefully in accordance with good laboratory practices.

The visit to Laboratory II showed that communication between QA and laboratory staff members was adequate and that sample receipt was progressing smoothly. Sample analysis trends indicated that the laboratory's preliminary data for NH_4^+, total P, and dissolved organic carbon (DOC) were near the detection limits for routine samples, but corresponding synthetic audit sample data did not indicate any analytical problems.

The analytical laboratories implemented several protocol changes during WLS-I. Some of these changes, as well as a contingency plan for sample analysis in the event a laboratory became inoperable, applied to both laboratories. In addition, each laboratory had specific questions and analytical problems that required the direction of the management team and QA staff. These issues are summarized in Table 6 (Section 2). The most significant issues are also discussed here.

Incorrect Reporting of pH Values

After data verification, a consistent data reporting problem was identified concerning the initial pH values for all samples in the 58 batches analyzed by Laboratory I. Instead of reporting the measured pH value as required, the laboratory reported the calculated pH value used in the Gran analysis. In most cases, the calculated pH was approximately 0.05 pH unit less than the measured pH. The calculated pH values appear in the data base. However, population estimates are not affected because only the field laboratory (closed-system) pH measurements are used in their preparation. Modifications to the QA and QC procedures, the SOW, and the data verification process are under consideration to ensure that such misreporting problems are not encountered in future surveys.

Incorrect Use of Calibration Blanks

At Laboratory II, the calibration blanks required for the atomic absorption analysis for Ca, Fe, K, Mg, Mn, and Na were not used properly or were not reported as protocol required. The proper procedure for use of the calibration blank was (1) to analyze calibration standards, (2) to fit the calibration curve and the linear dynamic range to those standards, and (3) to analyze the calibration blank and detection limit QCCS. Instead, after fitting the calibration curve, the laboratory analyst analyzed the calibration blank, then "auto zeroed" the instrument before the detection limit QCCS was analyzed. This fact was not revealed until initial data verification was complete and statistical analyses began. Fortunately, the detection limit QCCSs provided an additional check of the extremely low end on the linear dynamic range of the calibration curve. Because these QCCSs were consistently within the QA limits, the incorrect use of the calibration blank sample appeared to have a negligible effect on data reporting for these metals. Laboratory II did use the calibration blank sample correctly for all other applicable analytes. The NSWS verification process has been modified to ensure that similar situations do not occur in future surveys.

Suspect Silica Values

From a trend indicated in field natural audit lot FN5 during data verification for Laboratory II, all the SiO_2 values that represented concentrations greater than 14 mg/L (i.e., about 80 samples) were suspect. Approximately 75 percent of these values represented reporting errors that resulted from incorrect dilution-factor calculations or data-reporting errors. The remaining suspect samples had to be reanalyzed because the proper dilution and digestion procedures were not implemented when these samples originally were analyzed. This case shows the need for different audit lots with varying concentrations that cover the range of the routine lake sample concentrations.

Data Verification Activities

The QA staff reviewed field data forms and analytical data packages to identify and correct data reporting errors, to evaluate data trends, and to identify which samples needed reanalysis. These reviews resulted in changes to the raw data set and created the verified data set. The types and quantities of changes made to create the data sets are given in Table 13. The results of each data verification step are discussed below and are summarized in Table 7 (Section 2). The QA staff also identified several necessary modifications to the flag-assignment process. These changes also are presented in Table 7.

Review of Field Data Forms

The first step in the confirmation and reanalysis process was to check the lake data forms, batch/QC field data forms, and, for the ground-access samples, the chain-of-custody forms. The QA staff identified more than 1,000 possible field data problems involving analytical values, QA and QC sample values, data tags, and preparation of data forms. The field data review resulted in 770 changes that affected approximately 1.5 percent of the reported data. Because the field personnel responded quickly (usually within one day) to requests for information concerning the field data forms, the changes were made on the forms before the data were entered into the raw data set. Discrepancies that were found in the field data after the raw data set was completed were resolved in the verified data set.

Correction of Data

Review of the sample data packages submitted by the analytical laboratories took much longer than the review of the field data. The analytical laboratory data were more extensive and more complex, and the values for QA and QC samples had to be assessed for each batch. Data for special-studies samples (see Section 9) also were checked for data consistency and outlying values. The analytical laboratories typically took 2 to 4 weeks to confirm questionable data. Therefore, these data could not be corrected before the raw data set was created. The corrections were made in the verified data set.

More than 75 percent of the approximately 1,900 requests for data confirmation were tracked on the

TTable 13. Value Changes Incorporated into the Raw and Verified Data Sets, Western Lake Survey - Phase I

Data Source (Data Set)	Number of Changes Made to Data Set	Percent (approx.) of Changes to Total Number of Values in Data Set	Comments
Field data forms (raw data set)	770	1.5	Changes made to data tags before entry into raw data set
Lake sample data from analytical laboratory measurements			Changes made because of data reporting errors (confirmed data)[a]
confirmed data	451	1.1	
reanalyzed data (verified data set)	141	0.4	
Analytical laboratory quality control data (verified data set)	3,168	5.5	2,229 changes on laboratory duplicates and matrix spike from improper data reporting practices from Laboratory II; 541 data tag changes
EMSL-LV split sample data (split sample data set)	124	6.8	Changes made because of reporting errors
All verified data (verified data set and EMSL-LV split sample data set)	4,654	2.7	Approximate number of changes made to data and data tags (not number of data flags)

[a] This does not include the approximately 1,000 ANC and BNC recalculations that Laboratory II performed before the values were entered into the raw data set.

data confirmation/reanalysis request form (Appendix A). The rest were transmitted by telephone or by letter.

In some cases, the QA staff requested that the analytical laboratories submit raw instrumental data (e.g., instrument readouts, strip charts) with changes in analytical values. As a result of analytical laboratory data verification, 451 sample values (about 1.1 percent of the analyses) were changed. These changes were made to correct transcription, decimal place, and dilution-factor errors, and to include previously omitted data. Approximately 5.5 percent of the QC sample data (3,168 of the 57,000 values) had to be corrected. Most of the changes (70%) to the QC sample data were required because of consistent errors in the method of calculation used to derive some matrix spike and laboratory duplicate data (see Table 6 in Section 2).

Requests for Reanalysis

The purpose of reanalysis was to improve the quality of suspect data or to substantiate the value from the first analysis. If it was not evident that better information on data quality could be obtained from the reanalysis, the request was not made. Before any reanalyses were requested, all suspect values were confirmed by analytical laboratory personnel. If, after confirmation, the values were still suspect, reanalyses were requested. However, the analytical laboratories were not asked to reanalyze samples unless the verification procedure generated three data qualifier flags for either a single variable within a batch or an individual sample. Usually, one request was generated for all reanalyses that pertained to a particular batch so that all reanalyses for the batch could be performed at the same time, but there were exceptions to this policy. The laboratories were not normally asked to reanalyze when all the flags on the batch were related to a single, outlying sample value; nor were reanalyses requested (for analytes that were subject to high variability over time) if analytical laboratory holding times had been exceeded by weeks or months by the time the need for reanalysis was determined.

During WLS-I, 237 reanalyses were requested and 211 were performed. The 26 reanalyses requested but not performed were flagged to indicate that they were highly suspect and that they should not be used in statistical analyses. Of the reanalyses requested, 40 percent were for SiO_2 and 15 percent were for NO_3^-. SO_4^{2-}, Cl^-, BNC, total P, conductance, and air-equilibrated pH together were responsible for 20 percent of the requests. The remaining 25 percent of the reanalysis requests were related to suspect DIC values that had been identified by the use of the protolyte program (see Table 10 in Section 4). The analytical laboratories performed all reanalyses; 141 of the reanalyzed samples (0.4 percent of all sample data) were used in place of the original values.

Seventy reanalyses values were not substituted for the original values because they did not decrease the number of flags; therefore, they would not increase the quality of the data. The new values, however, were relayed to the validation staff for possible future use.

Section 6
Results and Discussion - Precision

Introduction

During WLS-I, 757 lakes were sampled (5 of these later were determined to have been missampled or otherwise were not useful in the survey design); 1,642 lake water and QA samples in 149 batches were analyzed in the analytical laboratories. Figure 5 shows the total number of lakes sampled as compared to the number of QA and calibration study samples taken. Table 8 (Section 3) shows a breakdown of the number of samples collected by sample type. Table K-1 in Appendix K characterizes the distribution of analyte concentrations for WLS-I routine lake samples. For each batch, WLS-I averaged 11 samples associated with 5 lakes, whereas ELS-I batches averaged 19 samples associated with 14 lakes. The smaller number of samples and lakes per batch in WLS-I can be attributed to the greater distance between lakes in the West than between lakes in the East, severe weather conditions, and the fact that ground crews could sample only one or two lakes per day. The percentage of QA samples used during WLS-I was considerably larger than the percentage used during ELS-I because the batch sizes and the number of lakes represented in each batch were much smaller in WLS-I. Of the WLS-I samples collected, 46 percent were routine lake samples, and 54 percent were QA-related or calibration study lake samples. In contrast, 75 percent of ELS-I samples were routine lake samples, and 25 percent were QA-related samples (Best et al., 1987). QC samples and split samples (i.e., matrix spikes, laboratory and trailer duplicates, calibration/reagent blanks, detection limit and low and high QCCS samples) are not included in these QA/routine sample percentages.

QA samples were analyzed during WLS-I so that estimates of precision, accuracy, detectability, and bias could be made. Sampling and analytical variance can arise from three major sources apart from seasonal variations in lake chemistry:

- a field component associated with sample collection or with short-term, localized variability in lake chemistry
- an analytical component associated with aliquot preparation or with variation in instrument response within an analytical batch
- an analytical component associated with batch-to-batch variation in instrument calibration and response

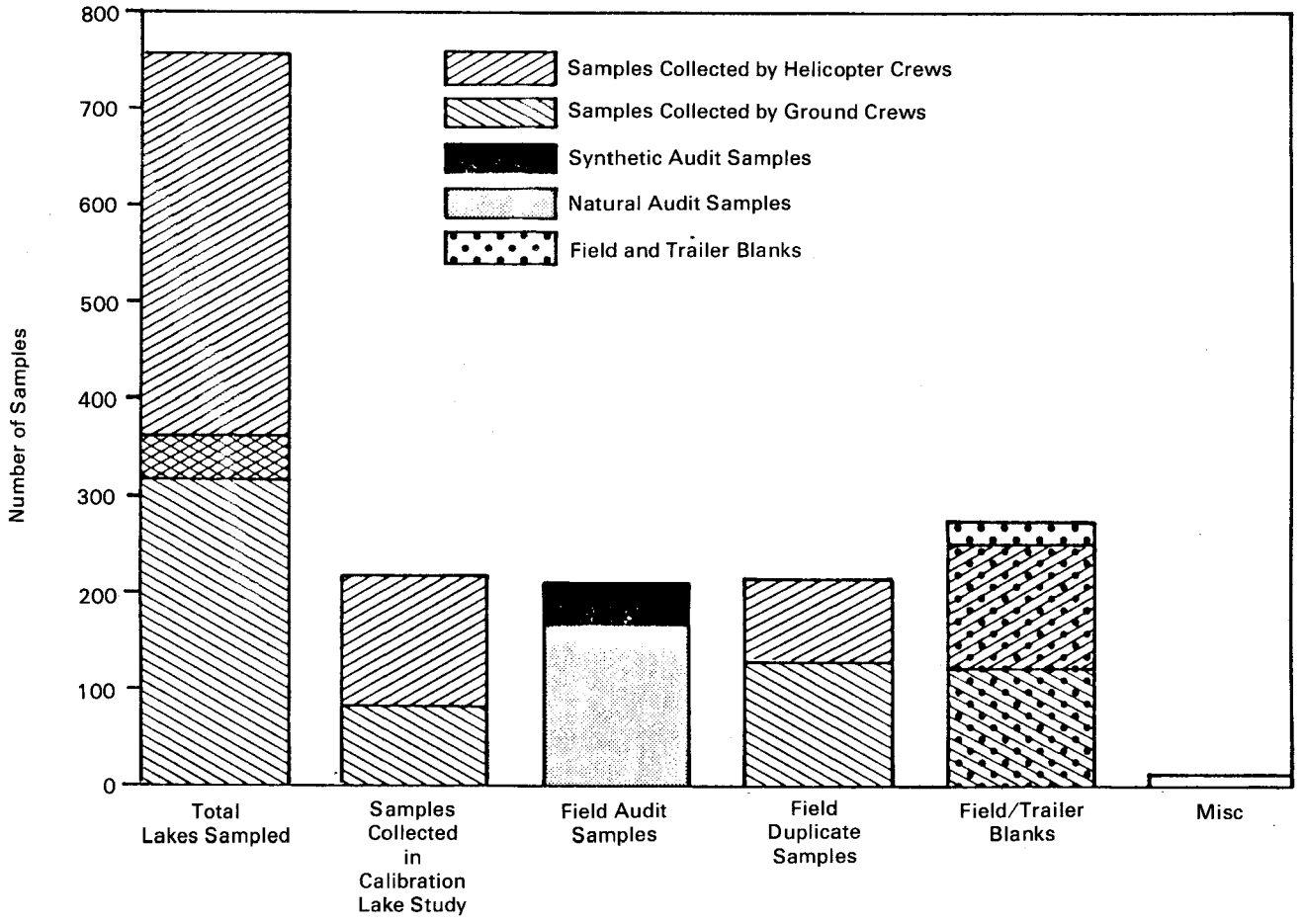
The relative importance of these sources of variation was assessed by comparative statistical evaluations. Evaluations of field audits, field duplicates, trailer duplicates, and laboratory duplicates provided estimates of precision and bias. Field synthetic audit samples were used to estimate accuracy. Field blank samples were used to estimate system detectability and levels of potential contamination introduced at the lake site, during field laboratory processing and sample handling, and during analysis at the analytical laboratory.

Estimating precision and accuracy are important facets in determining WLS-I data quality and reliability of the lake water samples measurements (see Figure 6 for an explanation of the ways in which these estimates are calculated). These estimates, in turn, aid the data user in estimating subregional and regional populations. This section discusses the ways in which precision has been estimated for WLS-I. It provides estimates of precision on the basis of the QA and QC information gathered. Similar discussions in subsequent sections describe accuracy (Section 7), detectability (Section 8), and relative bias (Section 9 and Appendix I).

Method of Estimating Precision

The most important aspect of estimating precision is to determine the overall (system) precision, which accounts for the cumulative effect on analyte concentration of all activities from sample collection to final sample analysis and data reporting. This is the precision estimate of most interest to the data user concerned with calculating population estimates (Landers et al., 1987). Subsets of system precision can be used to segregate total variability into components: sample collection and handling,

Figure 5. Lakes sampled versus sample types, Western Lake Survey - Phase I.



processing and preservation, and analysis. These components, however, cannot be separated easily.

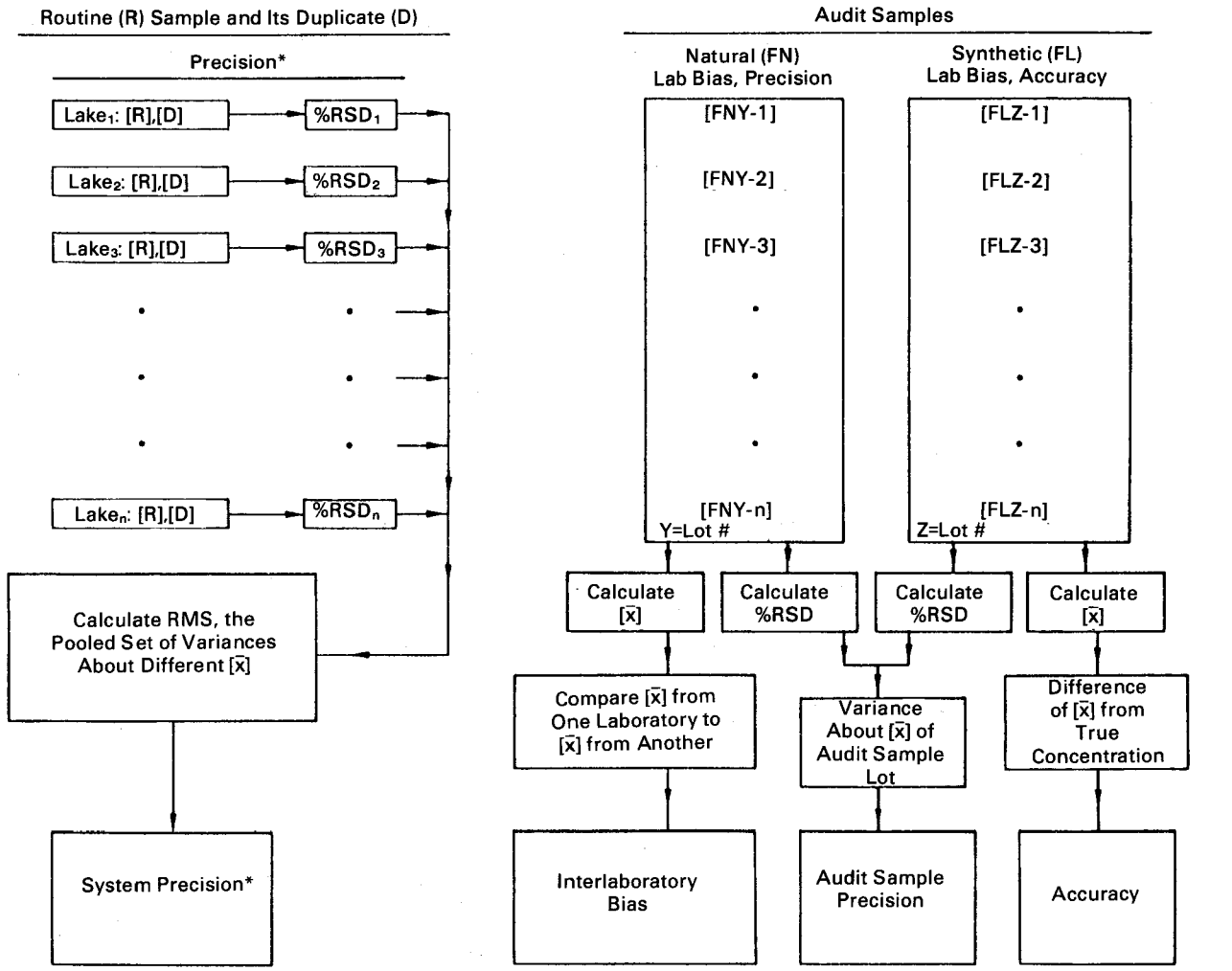
The following discussions describe the ways that the different components of variability are addressed in the WLS-I sampling design. Aspects of variability that the sampling design does not address are discussed also. Where applicable, recommendations are given for refining the methods used to determine the components of variability.

For WLS-I, two principal types of samples (duplicate pairs and audit samples) were used to estimate precision. Figure 7 illustrates the ways in which duplicate pairs (field, trailer, and analytical laboratory) and audit samples (natural and synthetic) were used to estimate precision.

Estimating System Precision from Field Duplicate Pairs

System precision was estimated from data on field duplicate pair samples because (1) they were the only precision-related QA sample type that was carried through the entire system, that is, every process applicable to the routine lake water samples from collection at the lake site to analysis at the analytical laboratory (see Figure 7), and (2) they had varying analyte concentrations, depending on the lake from which they were collected. This system precision estimate differed from the precision estimated from field audit samples, because field audit samples were introduced at the field laboratory; therefore, they did not include the field sampling component of variability. Field audit samples also reflected the "among-batch" variability caused by day-to-day differences introduced at the field laboratory and by instrument calibration, but only at a single concentration for each analyte. (Precision estimates derived from field audit sample data are discussed later in this section.) Because field duplicate pairs were analyzed within one batch (i.e., on the same calibration curve), they do not include the variability of day-to-day instrument calibration. Therefore, the

Figure 6. Methods of estimating precision, accuracy, and bias, Western Lake Survey - Phase I.



*If Laboratory Duplicates are Used Instead of Lake Duplicates, the Estimate is Termed Intralaboratory Precision

[ ]=Concentration

data user should assess the information derived from the field duplicate pair system precision in conjunction with the precision estimates derived from the audit sample data (see Appendix J).

For each analyte, the precision of the field routine sample and its duplicate (termed a field duplicate pair), analyzed in the same batch, represented the precision within that batch. This within-batch variability was expressed as the percent relative standard deviation (%RSD; also known as the coefficient of variation), which is calculated as follows:

$$\%RSD = 100\ \frac{SD}{\bar{X}}$$

where:

SD = standard deviation of the field duplicate pair
$\bar{X}$ = mean concentration of the field duplicate pair

(For pH, the within-batch variability was expressed as the standard deviation of the field duplicate pairs.)

The system precision was calculated by pooling all the %RSD values from all the duplicate pair samples (which represent the unique analyte concentrations of each lake). This "pooling" procedure was accomplished by calculating the root-mean-square (RMS) of the %RSD values of the field duplicate pair

samples. The formula for calculating the $RMS_{\%RSD}$ is:

$$RMS_{\%RSD} = \sqrt{\bar{X}^2 + [SD^2 (n-1/n)]}$$

where:

$\bar{X}$ = the mean of the %RSD values
SD = the standard deviation of the %RSD values
n = the number of duplicate pairs
$RMS_{\%RSD}$ = root-mean-square of the %RSD values

For pH, the precision estimate is calculated as the RMS of the standard deviation of the field duplicate pairs. A statistical discussion on the use of RMS to calculate precision estimates with duplicate pair data is provided by Permutt and Pollack (1986) in Best et al. (1987).

For a given analyte, the RMS is a single value whose square estimates the mean variance for all duplicate pair measurements. Because the %RSDs for all duplicate pairs are used in the RMS calculation, it has become necessary to segregate pairs whose mean concentrations are near the detection limit, as precision is a function of analyte concentration (see Figure 9 later in this section). This segregation process is accomplished with the use of a quantitation limit, which is discussed below.

Although RMS is the calculation for this pooled %RSD, as an aid to the reader all tables and discussions in this report that refer to duplicate pair (field, trailer, laboratory) precision estimates use the term pooled %RSD, not RMS.

To estimate sampling method precision and laboratory precision, the system precision estimates also can be separated by field duplicate pairs collected according to each sampling method and analyzed by each analytical laboratory. Just as the term "system precision" applies to the estimation for all field duplicate pairs, it applies when only laboratory values are pooled, and when only collection methods are pooled. Because samples collected by helicopter crews and by ground crews were distributed to both analytical laboratories, it was not necessary to evaluate each collection method in each laboratory. Therefore, when the collection methods were compared, the laboratories were pooled, and, when the laboratories were compared, the collection methods were pooled.

Estimating Precision of Field Duplicate Pairs Analyzed in the Field Laboratory

Field duplicate pairs can be used to determine precision in the field laboratory for the measurements of pH, DIC, turbidity, and true color. Because field duplicate pairs are analyzed for these variables, precision can be assessed for samples that are analyzed in the field laboratory. This precision estimate, however, does not isolate the precision attributable to the field laboratory alone, because the field sampling variability is included in the estimate. For WLS-I samples, trailer duplicate pairs are the only samples that can be used to quantify precision for field laboratory measurements.

Estimating Field Laboratory Precision from Trailer Duplicate Pairs

The trailer duplicate sample pair is created by splitting a lake water sample in the field laboratory. The precision estimate for the trailer duplicate pair is different from the estimate for the field duplicate pair analysis in the field laboratory, because the effect of sample collection is eliminated from the trailer duplicate pair. This precision estimate, termed the field laboratory precision estimate, is calculated from trailer duplicate pairs. It applies only to the four variables analyzed in the field laboratory (closed-system pH, closed-system DIC, true color, and turbidity) and can be related directly to the DQOs for intralaboratory precision (see Table 2 in Section 1). In order to check the precision for other analytes, especially for those filtered or preserved in the field laboratory, an additional QA step that was not in the WLS-I sample design or QA design would be needed. This step would consist of splitting a routine sample in the field laboratory, processing the split samples, and including them in the batches sent to the analytical laboratory. This design modification would impact other aspects of sample collection and analysis; the volume of sample required for the performance of all analyses would exceed the amount of sample collected according to the WLS-I design (see Figure 8).

As in ELS-I, the design of the QA program provided one trailer duplicate to be run for each sample batch. In fact, 137 trailer duplicates were analyzed for the 149 WLS-I batches. The discrepancy between the number of trailer duplicates and the number of batches resulted from the complex sampling design of the calibration study. Because the trailer duplicate was designed to be a daily check on the variability of analyses within the field laboratory, it was necessary to analyze only one trailer duplicate per processing day. On 12 occasions, the field laboratories processed two separate batches in one day. One was the normal batch that contained a trailer duplicate and one was a batch that contained calibration study samples only. In these instances, a single trailer duplicate was used to check for field laboratory precision in conjunction with the two batches.

Figure 7. Ways in which quality assurance and quality control samples are applied to estimates of precision and accuracy, Western Lake Survey - Phase I.

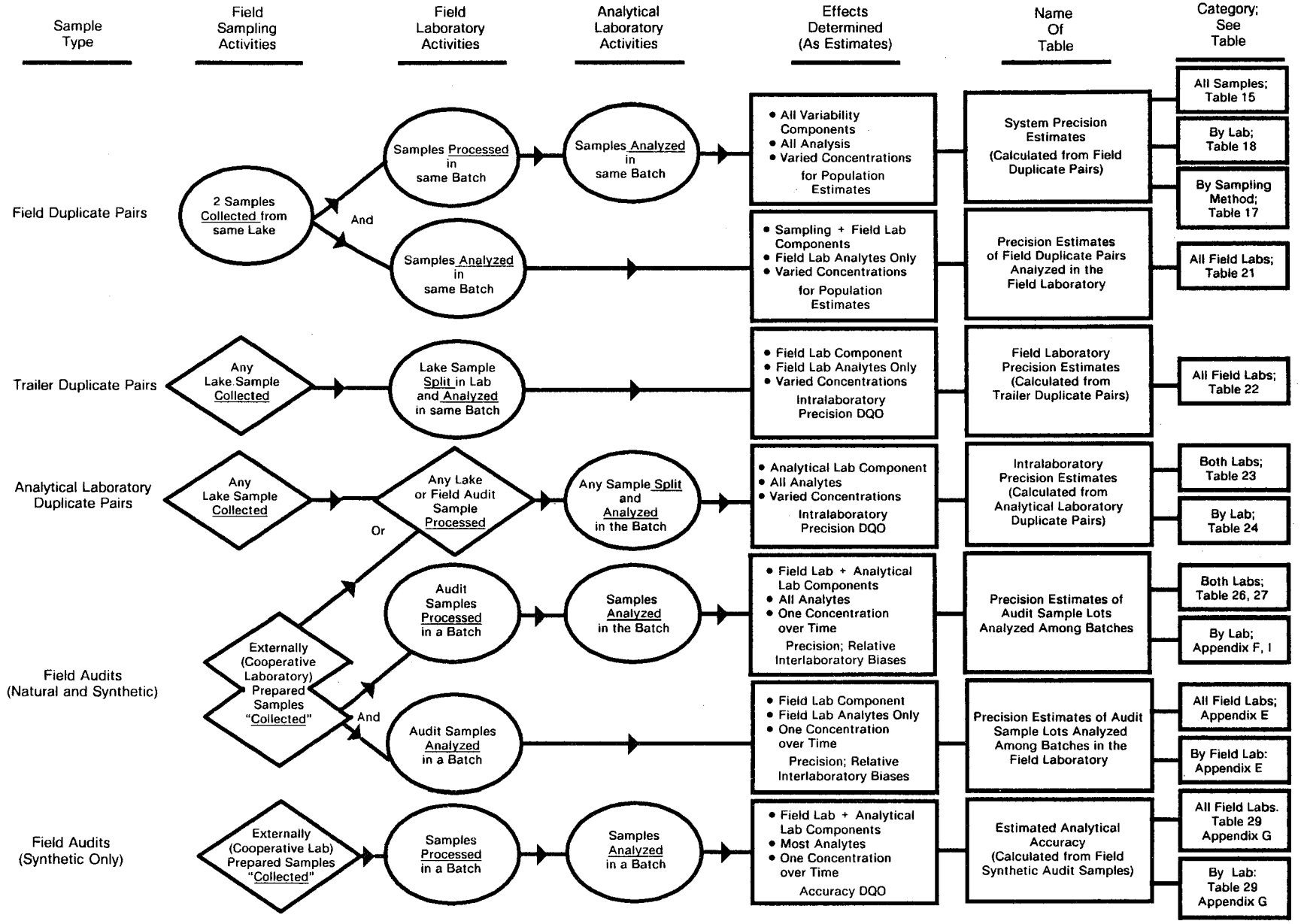
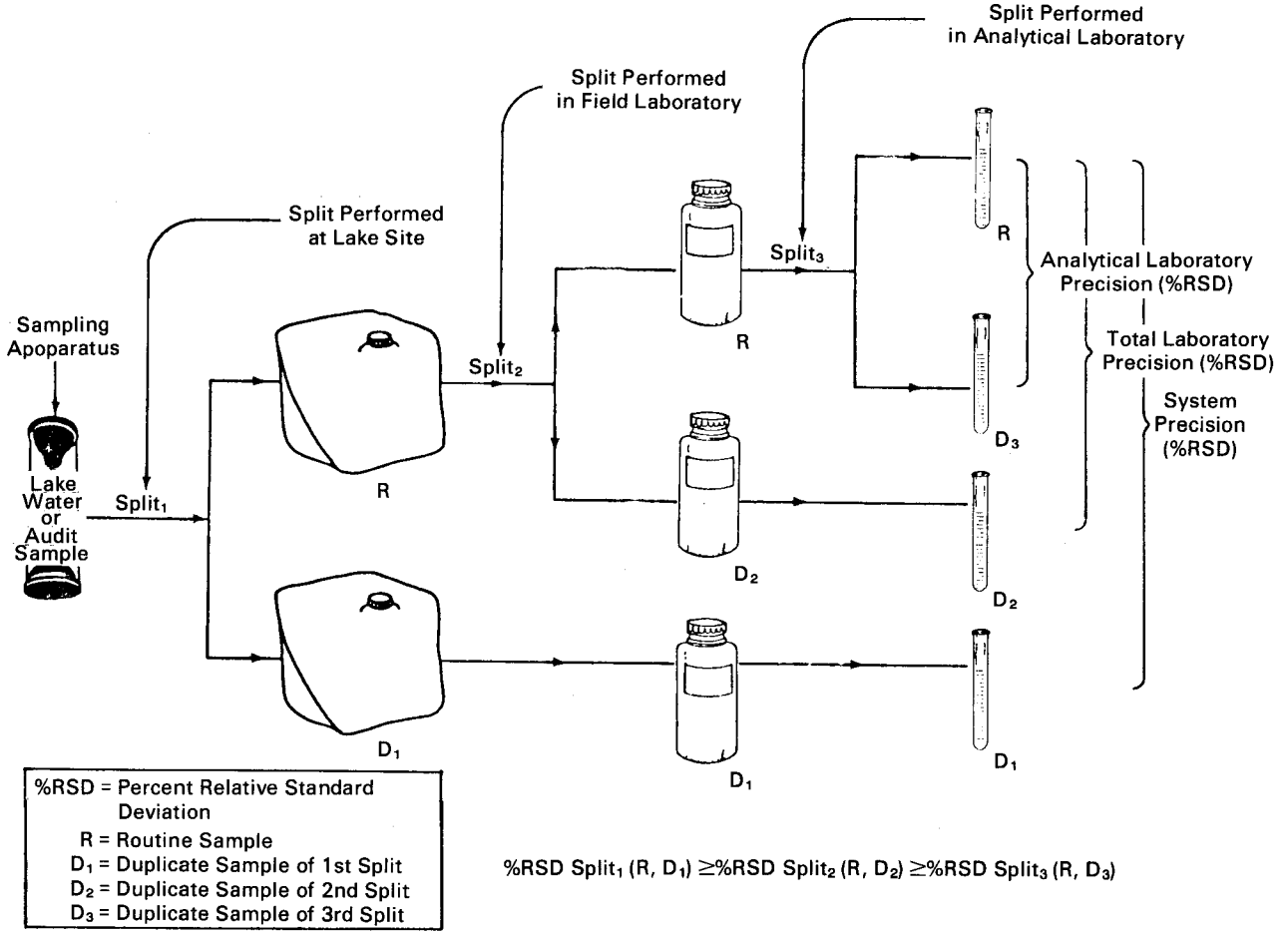


Figure 8. **Proposed procedural steps that would be necessary to quantify the collection, processing, and analytical components of variability.**



Estimating Intralaboratory Precision from Analytical Laboratory Duplicate Pairs

Although field duplicate pairs are analyzed in the analytical laboratory, the precision estimates derived from these samples include the overall effects on the sample (sampling, handling, and analysis at all stages). In order to quantify only the analytical laboratory precision, analytical laboratory duplicate pairs are used. These pairs are created in the analytical laboratory by splitting one sample from each batch. Precision for these pairs is termed intralaboratory precision. It can be compared directly to the intralaboratory precision goal (the DQO).

Statistical manipulation of analytical laboratory duplicate pairs is similar to that for field duplicate pairs. A %RSD is calculated for each pair to represent variability within the batch, and a pooled %RSD is calculated for all duplicate pairs. Estimates can be calculated for the laboratories combined, also termed "pooled," and for each laboratory individually. The interpretation of the results for analytical laboratory duplicate pairs and field duplicate pairs, however, differs significantly: The pooled %RSD for analytical laboratory duplicate pairs estimates intralaboratory precision (a DQO); the pooled %RSD for field duplicate pairs estimates system precision.

Establishing the Quantitation Limit

To ensure that mean sample concentrations of the field duplicate, trailer duplicate, and analytical laboratory duplicate pairs are sufficiently above the level of background contamination to estimate precision reliably, a quantitation limit is used for all variables except pH. For WLS-I, the quantitation limit was calculated as 10 times the standard deviation (10 S_B) of the concentrations of the corresponding blanks (field, trailer, or analytical laboratory). Precision

estimates can be calculated from all sample pairs (pairs that have mean concentration greater than zero). Some of these pairs are affected greatly by background (pairs that have mean concentration near zero, or the detection limit); other pairs are affected minimally by background (those pairs with mean greater than 10 S_B). Therefore, the quantitation limit is the level above which duplicate precision is expected to stabilize. The relationship of duplicate pair samples to quantitation limits and to sample concentrations is illustrated in Figure 9; supporting sample-concentration data are given in Table 14.

System Precision Results

System Precision Estimated from Field Duplicate Pairs

Sampling Methods and Analytical Laboratories Pooled--

System precision estimated from WLS-I field duplicate pairs is shown in Table 15. The intralaboratory precision DQOs that were the check on analytical laboratory precision are inappropriate for rigid application to field duplicate precision, but these DQOs are useful as a gauge for assessing the field duplicate precision estimate. Field duplicate precision estimates that are within these intralaboratory precision goals (using the quantitation limit as a cutoff) should be considered better than the precision that was anticipated before the survey began. For some variables, precision estimates calculated from field duplicate pairs did not meet the intralaboratory precision goals, but they may be reasonable estimates when the additional handling of the samples in the field is considered. Still other variables may be considered to have poor precision based on the intralaboratory precision goals. Table 16 lists variables for which field duplicate pair precision was within or slightly above the DQO for intralaboratory precision. It also lists variables for which field duplicate pair precision was poor (well above the DQO for intralaboratory precision).

Sampling Methods Separated--

The ability to sample lakes in a precise manner was essential to meeting the goals of WLS-I. Duplicate pairs were compared for precision as one way of assessing potential differences between the ability of the helicopter crew and that of the ground crew to collect routine samples. Table 17 separates the two sampling methods and shows quantitation limits that are calculated from the appropriate field blanks (e.g., field blanks collected by the ground crews were used to establish the quantitation limit for precision of the field duplicate pairs they collected). By separating the two methods, the precision of each sampling method and the differences in precision between methods can be assessed. For both sampling methods, most analytes show excellent precision for duplicate pairs that have mean values above the quantitation limit. Precision met or was near the DQO for all analytes that have a large enough sample size (n) to yield reliable precision estimates.

Analytical Laboratories Separated--

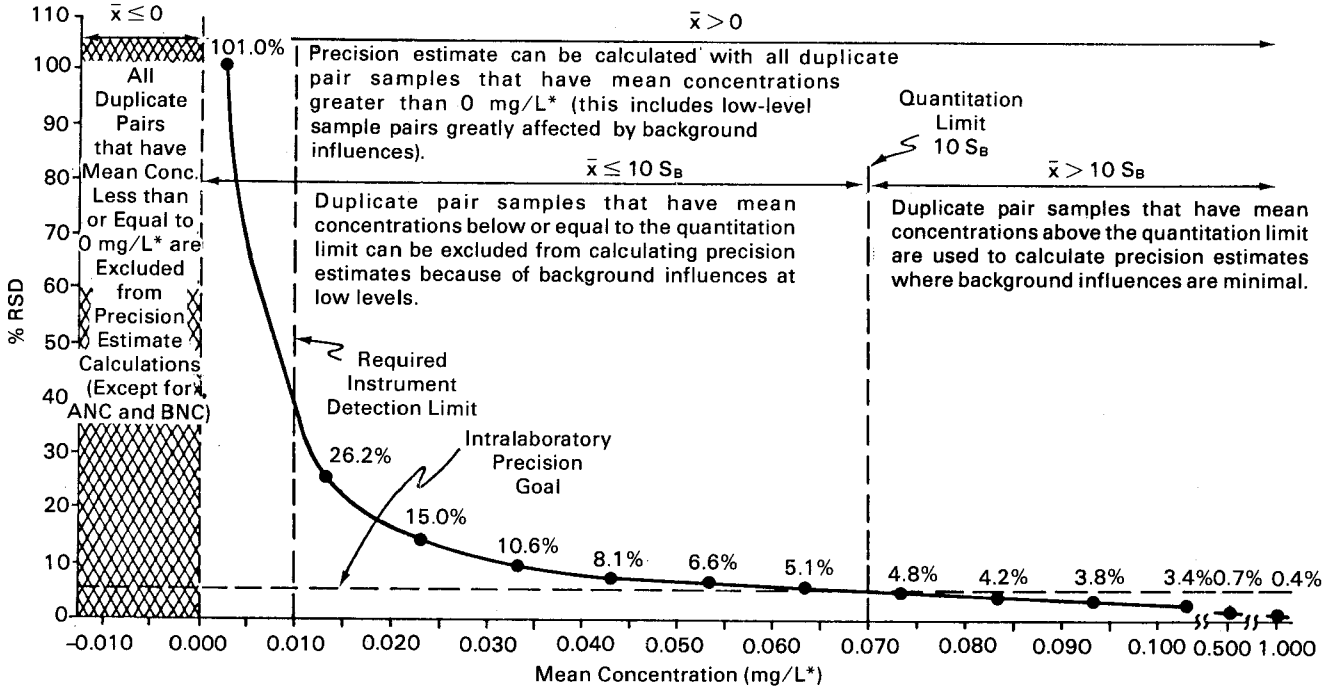
Table 18 presents system (field duplicate) precision separated by analytical laboratory. Comparing these two sets of results may be useful in determining

Table 14. An Example of the Relationship of %RSD to Duplicate Pair Samples for Different Concentrations[a]

Pair Number	Routine Sample Concentration (mg/L)	Duplicate Sample Concentration (mg/L)	Differences between the Routine and its Duplicate: Practical Difference (absolute, mg/L)	Differences between the Routine and its Duplicate: Statistical Difference (relative, %RSD)
1	0.001	0.006	0.005	101.0
2	0.011	0.016	0.005	26.2
3	0.021	0.026	0.005	15.0
4	0.031	0.036	0.005	10.6
5	0.041	0.046	0.005	8.1
6	0.051	0.056	0.005	6.6
7	0.061	0.066	0.005	5.6
8	0.071	0.076	0.005	4.8
9	0.081	0.086	0.005	4.2
10	0.091	0.096	0.005	3.8
11	0.101	0.106	0.005	3.4
12	0.501	0.506	0.005	0.7
13	1.001	1.006	0.005	0.4

[a]These are not actual WLS-I data. They are companion material to Figure 9.

Figure 9. Relationship of duplicate pair samples to quantitation limits and sample concentrations.



● = The mean concentration of a routine sample and its duplicate; each pair has an absolute difference of 0.005 mg/L.

$10\ S_B$ = 10 times the standard deviation of the blank sample concentrations.

*mg/L is used for illustrative purposes; other units can apply.

whether imprecision is associated with sampling technique or with analytical performance.

Tables 15, 17, and 18 must be evaluated with the understanding that, except for calibration study lakes, each laboratory analyzed samples from different subregions (Landers et al., 1987). Thus, the field duplicate pairs for each subregion also were segregated by laboratory. Consequently, because precision is concentration dependent (Figure 9), differences in the precision estimates for the two laboratories may be in part the result of subregional differences in concentrations of some analytes. Precision also may depend on the chemical matrix of the lake water samples, which may be a subregional characteristic. (See Landers et al., 1987, for further discussion of sub- regional lake chemistry.)

Another consideration is the distribution of duplicate pairs sent to each laboratory (see Table 19). Laboratory II analyzed about 60 percent of the WLS-I field duplicate pairs sampled by helicopter crews and by ground crews, and Laboratory I analyzed the other 40 percent. Because the pooled system precision (Table 15) may mask poor precision associated with one laboratory or with one method, it is essential that all of these variability issues are accounted for when field duplicate precision estimates are assigned to particular components of laboratory and method.

Table 20 summarizes the system precision results (pooled and by method or analytical laboratory component) that showed a high degree of variability. This table illustrates that, for a given analyte, isolating a particular source of variability (sampling method, laboratory, lake chemistry, subregion, or quantitation limit) from other potential sources is often difficult. Table 34 (Section 9) illustrates the interactions between the major components that contribute to variability. This table was constructed on the basis of calibration lake sample data.

In a few cases, field duplicate pairs produced results far outside the precision goals across many analytes. For instance, the field laboratory pH readings for the field duplicate pair collected from Lake ID 4A3-044 (Twin Lakes-North) in California were quite different

Table 15. System Precision Estimates Calculated from Field Duplicate Pairs (Sampling Methods and Laboratories Pooled), Western Lake Survey - Phase I

Variable (in mg/L unless noted)	Intralaboratory Precision Goal (in %RSD unless noted)	All pairs (mean > 0)		Quantitation Limit[a]	Pairs that have a mean > Quantitation Limit	
		n	Estimated Precision (Pooled %RSD)[b]		n	Estimated Precision (Pooled % RSD)[b]
Al, extractable	10 (if Al conc. > 0.01 mg/L) 20 (if Al conc. ≤ 0.01 mg.L)	189	299.7	0.021	11	44.2
Al, total	10 (if Al conc. > 0.01 mg/L) 20 (if Al conc. ≤ 0.01 mg/L)	215	33.4	0.085	11	10.2
ANC (μeq/L)	10	215	4.5	24.9	204	4.1
BNC (μeq/L)	10	203	190.4	92.3	3	72.4
Ca	5	215	2.3	0.30	208	2.3
Cl^-	5	215	15.7	0.21	65	8.6
Conductance (μS/cm)	2	215	6.5	6.1	192	6.4
DIC, air equilibrated	10	215	6.9	0.71	173	6.9
DIC, initial	10	215	7.7	1.32	103	2.7
DOC	5 (if DOC conc. > 5 mg/L) 10 (if DOC conc. ≤ 5 mg/L)	215	16.7	2.0	49	12.7
F^-, total dissolved	10	213	24.7	0.016	90	26.2
Fe	5	197	112.5	0.07	16	24.6
K	5	215	9.6	0.08	199	4.5
Mg	5	215	8.1	0.03	212	8.2
Mn	10	137	139.2	0.10	1	N/A
Na	5	215	7.2	0.17	206	7.3
NH_4^+	5	83[c]	324.7	0.13	3	7.9
NO_3	10	205	61.3	0.342	8	1.1
P, total	10 (if P conc. > 0.01 mg/L) 20 (if P conc. ≤ 0.01 mg/L)	210	77.4	0.043	9	37.5
pH, acidity (pH units)	0.05 (pH units)	215	0.08	--	--	--
pH, alkalinity (pH units)	0.05 (pH units)	215	0.08	--	--	--

(continued)

Table 15. (Continued)

Variable (in mg/L unless noted)	Intralaboratory Precision Goal (in %RSD unless noted)	All pairs (mean > 0)		Quantitation Limit[a]	Pairs that have a mean > Quantitation Limit	
		n	Estimated Precision (Pooled %RSD)[b]		n	Estimated Precision (Pooled % RSD)[b]
pH, air equilibrated (pH units)	0.05 (pH units)	214	0.17	--	--	--
SiO_2	5	215	16.1	2.07	119	7.0
SO_4^{2-}	5	215	14.5	0.56	124	4.3

[a] The quantitation limit is 10 S_B (10 times the standard deviation of the field blank measurements). Quantitation limits are not calculated for pH measurements.
[b] Pooled standard deviation used for pH.
[c] Number of observations is smaller because concentrations of NH_4^+ were low in most WLS-I samples and because of instrumental drift (i.e., mean concentrations of $NH_4^+ \leq 0$).
[d] N/A = not applicable.

Table 16. Summary of System Precision Results by Variable (Sampling Methods and Analytical Laboratories Pooled), Western Lake Survey - Phase I

Variable that met or was near DQO; duplicate pairs above the quantitation limit[a]	DQO (in %)[b]	Variables that did not meet DQO; duplicate pairs above the quantitation limit[a]	Comments
	10 or 20	Al, extractable	Low concentrations[c] found in all WLS-I lake samples.
Al, total	10 or 20		
ANC	10		
	10	BNC	Only 3 duplicate pair samples above the quantitation limit.
Ca	5		
Cl^-	5		
	2	Conductance	Mostly low-conductance[c] lakes sampled in WLS-I; even so, precision estimate was 6.4%.
DIC (air equilibrated)	10		
DIC (closed system)	10		
DIC (initial; open system)	10		
	5 or 10	DOC	Low-DOC[c] routine lake samples analyzed in WLS-I.
	5	F^-, total dissolved	Most of the poor precision indicated in Laboratory I; very low (0.016 mg/L) quantitation limit.
	10	Fe	Low concentrations[c] found in WLS-I lake samples.
K	5		
Mg	5		
	10	Mn	Very low concentrations[c] found in WLS-I lake samples.
Na	5		
NH_4^+	5		
NO_3^-	10		
	10 or 20	P, total	Low quantitation limit and very few duplicate pairs that have mean concentrations above that limit.
pH (acidity; open system)	0.05 (pH unit)		
pH (alkalinity; open system)	0.05 (pH unit)		
pH (air equilibrated)	0.05 (pH unit)		
	0.05 (pH unit)	pH (closed system)	Possibly a result of low ionic strength, circumneutral lake samples[c]; no quantitation limit calculated for pH measurements.
SiO_2	5		
SO_4^{2-}	5		
True Color	5 (PCU)		
Turbidity	10		WLS-I lakes very low in turbidity.

[a] Note: The field duplicate pair mean concentrations are often below the quantitation limit; therefore, they are not included when precision goals and estimates are discussed. Figures J-1b to J8b, J-9, J-10b to J-23b, J-24, and J-25b to J-26b present all field duplicate pairs plotted by mean concentration and %RSD. This allows the data user to examine the relationship between precision and concentration and the quantitation limits.

[b] Note: DQO is used as a gauge, but is not directly applicable for field duplicate samples.

[c] Note: Poor system precision probably is attributable to the fact that low concentrations of the analyte were measured for most WLS-I lake samples (see Table K-1 in Appendix K.

(pH 9.55 for the routine and 8.16 for the duplicate). The analytical laboratory results for this pair showed very poor precision for BNC, Cl^-, DOC, initial DIC, pH, and SiO_2 as well. Written comments on the field forms indicated that aquatic vegetation was present at the sampling location. The presence of vegetation could account for the heterogeneity of the sample pair. This situation, which was assessed during data validation and during calculation of population estimates, indicates that thorough, detailed documentation is essential to explaining possible data inconsistencies and anomalies.

Table 17. System Precision Estimates Calculated from Field Duplicate Pairs (by Sampling Method) Western Lake Survey - Phase I

Variable (in mg/L unless noted)	Helicopter					Ground				
	All Pairs (mean > 0)			Pairs that have a mean > Quantitation Limit		All Pairs (mean > 0)			Pairs that have a mean > Quantitation Limit	
	n	Estimated Precision (Pooled %RSD)[b]	Quantitation Limit[a]	n	Estimated Precision (Pooled %RSD)[b]	n	Estimated Precision (Pooled %RSD)[b]	Quantitation Limit[a]	n	Estimated Precision (Pooled %RSD)[b]
Al, extractable	75	150.9	0.022	4	12.2	114	366.0	0.020	7	54.7
Al, total	87	28.7	0.099	5	12.8	128	36.2	0.067	8	10.1
ANC (μeq/L)	87	2.9	19.2	84	2.9	128	5.4	30.2	117	4.7
BNC (μeq/L)	79	300.4	80.0	2	25.0	124	43.3	104.7	1	N/A
Ca	87	1.6	0.28	84	1.7	128	2.6	0.32	124	2.6
Cl^-	87	8.1	0.12	54	7.7	128	19.3	0.28	16	12.5
Conductance (μS/cm)	87	8.0	5.5	81	8.2	128	5.1	6.7	107	4.2
DIC, air equilibrated	87	9.7	0.77	70	9.9	128	3.9	0.58	112	3.7
DIC, initial	87	4.4	0.93	68	4.3	128	9.4	1.61	42	3.7
DOC	87	18.2	2.4	19	17.1	128	15.6	1.40	44	8.3
F^-, total dissolved	87	20.6	0.010	63	23.5	126	27.1	0.021	40	34.9
Fe	81	110.0	0.07	10	29.1	116	114.2	0.07	6	14.2
K	87	13.4	0.09	77	4.1	128	5.7	0.08	121	4.7
Mg	87	1.6	0.03	87	1.6	128	10.4	0.04	124	10.6
Mn	60	152.1	0.11	1	N/A	77	128.3	0.10	0	N/A
Na	87	3.0	0.22	82	2.7	128	9.0	0.09	127	9.1
NH_4^+	39	449.4	0.11	3	7.9	44	141.0	0.14	0	N/A
NO_3	81	72.3	0.334	3	1.2	124	52.9	0.352	5	0.9
P, total	84	58.3	0.040	8	8.2	126	87.8	0.046	1	N/A
pH, acidity (pH units)	87	0.10	--	--	--	128	0.06	--	--	--
pH, alkalinity (pH units)	87	0.10	--	--	--	128	0.06	--	--	--
pH, air equilibrated (pH units)	87	0.09	--	--	--	127	0.20	--	--	--
SiO_2	87	11.4	1.25	70	9.1	128	18.6	2.71	45	4.0
SO_4^{2-}	87	5.7	0.40	62	5.6	128	18.1	0.70	68	3.7

[a] The quantitation limit is 10 S_B (10 times the standard deviation of the field blank measurements [helicopter or ground]). Quantitation limits are not calculated for pH measurements.

[b] Pooled standard deviation was used for pH.

N/A = not applicable.

Table 18. System Precision Estimates Calculated from Field Duplicate Pairs (by Analytical Laboratory) Western Lake Survey - Phase I

Variable (in mg/L unless noted)	Laboratory I					Laboratory II				
	All Pairs (mean > 0)			Pairs that have a mean > Quantitation Limit		All Pairs (mean > 0)			Pairs that have a mean > Quantitation Limit	
	n	Estimated Precision (Pooled %RSD)[b]	Quantitation Limit[a]	n	Estimated Precision (Pooled %RSD)[b]	n	Estimated Precision (Pooled %RSD)[b]	Quantitation Limit[a]	n	Estimated Precision (Pooled %RSD)[b]
Al, extractable	63	507.4	0.024	4	14.2	126	77.9	0.016	10	53.0
Al, total	86	49.2	0.111	2	3.9	129	15.6	0.042	35	17.5
ANC (μeq/L)	86	6.5	34.5	82	5.6	129	2.5	12.8	128	2.5
BNC (μeq/L)	78	302.5	85.4	2	87.0	125	42.6	54.4	7	11.2
Ca	86	1.4	0.23	86	1.4	129	2.7	0.28	122	2.7
Cl^-	86	15.2	0.19	33	13.2	129	16.1	0.22	39	2.6
Conductance (μS/cm)	86	2.3	4.3	86	2.3	129	8.1	5.9	107	8.3
DIC, air equilibrated	86	4.0	0.41	85	4.0	129	8.3	0.7	103	8.4
DIC, initial	86	3.6	1.58	44	3.6	129	9.5	0.94	84	4.3
DOC	86	11.0	2.6	13	20.4	129	19.6	0.8	90	14.9
F^-, total dissolved	84	37.6	0.021	45	36.3	129	9.2	0.009	77	8.5
Fe	76	141.7	0.04	16	20.9	121	89.4	0.07	6	37.1
K	86	14.3	0.06	83	14.1	129	4.1	0.09	113	3.5
Mg	86	12.7	0.03	86	12.7	129	1.4	0.04	125	1.3
Mn	65	70.9	0.01	8	31.4	72	179.9	0.13	1	N/A
Na	86	11.1	0.24	71	12.1	129	2.2	0.08	129	2.2
NH_4^+	29	424.8	0.18	2	9.5	54	255.2	0.05	1	N/A
NO_3	83	56.4	0.196	15	11.5	122	64.4	0.415	1	N/A
P, total	85	99.0	0.063	1	N/A	125	58.3	0.021	3	8.9
pH, acidity (pH units)	86	0.07	--	--	--	129	0.09	--	--	--
pH, alkalinity (pH units)	86	0.07	--	--	--	129	0.09	--	--	--
pH, air equilibrated (pH units)	85	0.05	--	--	--	129	0.21	--	--	--
SiO_2	86	24.9	2.90	20	14.7	129	3.9	1.20	115	3.5
SO_4^{2-}	86	6.4	0.52	77	4.4	129	17.9	0.57	46	4.2

[a] The quantitation limit is 10 S_B (10 times the standard deviation of the analytical laboratory blank measurements). Quantitation limits are not calculated for pH measurements.

[b] Pooled standard deviation was used for pH measurements.

N/A = not applicable.

Table 19. Distribution of Field Duplicate Pairs (Helicopter and Ground) by Laboratory, Western Lake Survey - Phase I

Laboratory	Duplicate Pairs Collected by Helicopter Crews	Duplicate Pairs Collected by Ground Crews	Total Duplicate Pairs
I	31	55	86
II	56	73	129
Total	87	128	215

Precision Estimated from Field Duplicate Pairs and Trailer Duplicate Pairs Analyzed in the Field Laboratory

Precision estimates for field duplicate pairs analyzed in the field laboratory (Table 21) and for trailer duplicate pairs analyzed in the field laboratory (Table 22) are given for pH, DIC, true color, and turbidity. All pH and DIC measurements were within desired precision goals, except that the precision estimate for the pH of field duplicate pairs was calculated at 0.12 pH unit. Although the intralaboratory precision goal was ±0.05 pH unit, on the basis of ELS-I experience, the EMSL-LV QA staff considered ±0.10 pH unit acceptable when assessing daily QA precision for field duplicate pairs (see Table 2). Precision goals for trailer duplicate pairs for turbidity and true color were met for mean values above the quantitation limit. Quantitation limits were not calculated for pH and DIC because field blank and trailer blank samples were not analyzed in the field laboratory for these parameters.

Intralaboratory Precision Estimated from Analytical Laboratory Duplicate Pairs

On the basis of intralaboratory precision estimated from pooled values for analytical laboratory duplicate pairs, the two analytical laboratories exhibited excellent reproducibility. The intralaboratory precision estimated from analytical laboratory duplicate pairs above the quantitation limit met the DQOs for every analyte except Mn (see Table 23). Concentrations of Mn in WLS-I routine lake samples generally were below the levels at which good precision is expected. The median concentration for Mn was 0.001 mg/L (see Appendix K, Table K-1). In addition, 95 percent of the routine lake samples had concentrations less than 0.03 mg/L. The less than acceptable precision estimate (16.6%) for samples above the quantitation limit (0.02 mg/L) should be of little concern to the data user.

Table 24 presents the intralaboratory precision by laboratory. This analysis of individual laboratories reveals results similar to those obtained from the analysis of pooled values, except that for Laboratory II, Fe as well as Mn was outside the DQO.

Mn is the only analyte that had precision estimates higher than the intralaboratory precision goals for duplicate pairs above the quantitation limit. ANC and BNC, however, were not assessed in this manner because a quantitation limit could not be calculated. For the field duplicate determinations, field blanks were used in the calculation of the quantitation limits; however, in the laboratory, calibration blanks were not analyzed for ANC or BNC. Because a quantitation limit was not used for these analytes, precision estimates for all laboratory duplicate pairs are shown in Tables 23 and 24 regardless of how close the mean values are to 0 μeq/L.

Evaluating data from the laboratories separately also revealed a procedural problem with Laboratory II's analysis of the cations (Ca, Fe, K, Mg, Mn, and Na). It was not discovered that Laboratory II reported all of the calibration blanks (n = 91) as 0.000 mg/L until statistical analyses and data verification had been completed on the data for these analytes. In a subsequent discussion, the laboratory manager indicated that the calibration blanks were used to "auto-zero" the spectrophotometer before the detection limit QCCS was analyzed. This procedure was a misinterpretation of the SOW (contract) and a deviation from the laboratory's analytical performance in ELS-I.

Two problems resulted from this action. First, because the true calibration blank was not reported and because the instrument calibration was improper, some concern arose that there might be enough bias to create statistical problems for the data user. Fortunately, the detection limit QCCS provides an additional check for values at or near the detection limit. Because Laboratory II had no difficulty analyzing these QCCSs within the criteria required (±20% of the true value) for any of the metals, it was determined that any bias created was negligible and did not affect the statistical evaluation for population estimates. Second, proper quantitation limits could not be calculated from the calibration blanks for these metals (i.e., the standard deviations of the blanks were all equal to 0.000; therefore, the quantitation limit equalled 0.000). Although quantitation limits could not be calculated, Ca, K, Mg, and Na still met the DQOs when all the pairs that had mean concentrations greater than zero were used; only Fe and Mn did not. To calculate overall intralaboratory precision of the pooled laboratory duplicate data (Table 23), quantitation limits for these six cations were calculated from Laboratory I's calibration blank values only.

In spite of the protocol changes and the procedural and reporting difficulties noted above, the intralaboratory precision goals for WLS-I were met

Table 20. Checklist of Variables for Which System[a] Precision Estimates Calculated from Field Duplicate Pairs Did Not Meet Intralaboratory Precision Goals (Pooled and Separated by Sampling Method and by Laboratory), Western Lake Survey - Phase I (Note: X indicates high variability above the quantitation limit.)

Variable	DQO (%)[b]	Pooled	Heli-copter	Ground	Lab. I	Lab. II	Comment
Al,extract-able	10 or 20	X		X		X	Only 1 duplicate pair sample had poor precision.
Al, total	10 or 20						
ANC	10						
BNC	10	X	X		X		Very few samples above the quantitation limit.
Ca	5						
Cl-	5			X	X		Only 1 duplicate pair sample had poor precision.
Conductance	2	X	X	X		X	WLS-I samples had low conductance.
DIC (air equilibrated)	10						
DIC (initial)	10						
DOC	5 or 10	X	X	X	X	X	Low DOC in WLS-I lakes.
F^-, total dissolved	5	X	X	X	X		Poor precision result of Laboratory I performance.
Fe	10	X	X	X	X	X	WLS-I samples had low Fe concentrations.
K	5				X		Only 1 duplicate pair had poor precision.
Mg	5			X	X		Only 1 duplicate pair had poor precision.
Mn	10				X		Low Mn in WLS-I lakes.
Na	5			X	X		
NH_4^+	5						
NO_3	10						
P, total	10 or 20	X					Only 1 duplicate pair had poor precision.
pH (acidity)	0.05 (pH unit)						
pH (alkalinity)	0.05 (pH unit)						
pH (air-equilibrated)	0.05 (pH unit)	X		X		X	Only 1 duplicate pair had poor precision.
SiO_2	5				X		Two duplicate pair samples had poor precision.
SO_4^{2-}	5						

[a] System precision includes variability from lake sampling, sample processing, and sample analysis.
[b] DQO is for intralaboratory precision and is not directly applicable to system precision.

(see Table 25). This observation indicates that any lack of precision in sample analysis was likely to have come from sources outside the analytical laboratories. However, even the small amount of imprecision (expressed as intralaboratory precision estimates) shown by the analytical laboratory must be considered as a component of the (system) precision estimates.

Method of Estimating Precision Among Batches

Estimating Precision Among Batches from Field Audit Samples

Field audit samples (natural and synthetic) were used to estimate precision at specific concentrations over time (i.e., among batches) in WLS-I. Field audit sample precision estimates (as %RSD or, for pH, as standard deviation) also indicate variability of the

Table 21. Precision Estimates for Field Duplicate Pairs Analyzed in the Field Laboratory, Western Lake Survey - Phase I

		All Pairs (mean > 0)			Pairs that have a mean > Quantitation Limit[a]	
Variable	Intralaboratory Precision Goal	n	Estimated Precision (Pooled %RSD)	Quantitation Limit[a]	n	Estimated Precision (Pooled %RSD)
pH	±0.1 pH unit	208	0.12[b]	--	--	---
DIC	10 %RSD	208	6.8	--	--	---
True Color	±5 PCU	165	61.3[c]	32	6	4.7[d]
Turbidity	10 %RSD	206	24.4	0.8	37	16.5

[a] The quantitation limit is 10 S_B (10 times the standard deviation of the field blank measurements). Quantitation limits cannot be calculated for pH and DIC because field blanks were not analyzed.
[b] Pooled standard deviation was used for pH.
[c] This value is equivalent to an average standard deviation of ± 6.0 PCU.
[d] This value is equivalent to an average standard deviation of ± 2.2 PCU.

analytical and sample preparation methods; they exclude variability associated with lake sampling. Data from field audit samples play a key role in maintaining a credible data base. Such samples are useful in estimating relative biases between laboratories (interlaboratory bias).

Description of Field Natural Audit Samples-- The field natural audit sample is obtained by sampling a natural lake system in bulk (200 to 400 L). The bulk sample receives a unique lot number which distinguishes it from audit samples collected at other lakes and from audit samples collected at the same lake but at other times. The bulk sample is filtered and is apportioned into 2-L subsamples.

As in ELS-I and the NSS Phase I Pilot Survey, EPA contracted with Radian Corporation to prepare and distribute the field audit samples. To ensure that all audit samples of a particular lot were uniform, Radian was instructed by EMSL-LV to follow a specified protocol (see Appendix C) for preparing the 2-L field natural audit aliquots. The procedure called for preparing all aliquots from the sample lots at the same time.

In contrast, ELS-I field audit samples were prepared just before daily shipment to the field laboratories. It can be argued that preparing aliquots for an entire lot of a natural audit sample by separating the lot into 2-L bottles at one time (as many as 100 aliquots, depending on the bulk volume) creates separate populations (i.e., each container) over time. For instance, biological action may occur in one aliquot, changing the chemical composition, yet may not occur in all aliquots. WLS-I field activities had a 2-

Table 22. Precision Estimates for Trailer Duplicate Pairs Analyzed in the Field Laboratory, Western Lake Survey - Phase I

		All Pairs (mean > 0)			Pairs that have a mean > Quantitation Limit[a]	
Variable	Intralaboratory Precision Goal	n	Estimated Precision (Pooled %RSD)	Quantitation Limit[a]	n	Estimated Precision (Pooled %RSD)
pH	±0.1 pH unit	132	0.03[b]	--	--	---
DIC	10 %RSD	134	3.4	--	--	---
True Color	±5 PCU	99	25.1[c]	15	25	3.8[d]
Turbidity	10 %RSD	134	11.8	0.4	65	7.8

[a] The quantitation limit is 10 S_B (10 times the standard deviation of the field blank measurements). Quantitation limits cannot be calculated because field blanks were not analyzed.
[b] Pooled standard deviation was used for pH.
[c] This value is equivalent to an average standard deviation of ± 2.7 PCU.
[d] This value is equivalent to an average standard deviation of ± 0.8 PCU.

Table 23. Intralaboratory Precision Estimates Calculated from Analytical Laboratory Duplicate Pairs (Laboratories Pooled), Western Lake Survey - Phase I

Variable (in mg/L unless noted)	Intralaboratory Precision Goal (in %RSD unless noted)	All pairs (mean > 0)		Quantitation Limit[a]	Pairs that have a mean > Quantitation Limit	
		n	Estimated Precision (Pooled %RSD)[b]		n	Estimated Precision (Pooled % RSD)[b]
Al, extractable	10 (if Al conc. > 0.01 mg/L) 20 (if Al conc. ≤ 0.01 mg/L)	140	13.3	0.014	22	4.3
Al, total	10 (if Al conc. > 0.01 mg/L) 20 (if Al conc. ≤ 0.01 mg/L)	148	3.3	0.029	64	3.3
ANC (μeq/L)		139	121.6	--	--	--
BNC (μeq/L)	10	148	16.4	--	--	--
Ca	5	149	0.7	0.04[c]	148	0.7
Cl^-	5	149	2.3	0.06	145	2.3
Conductance (μS/cm)	2	149	1.1	3.4	147	1.1
DIC, air equilibrated	10	149	6.4	0.33	126	5.8
DIC, initial	10	149	4.3	0.26	131	2.7
DOC	5 (if DOC conc. > 5 mg/L) 10 (if DOC conc. ≤ 5 mg/L)	146	11.1	0.6	119	4.1
F^-, total dissolved	5	148	2.7	0.008	148	2.7
Fe	10	144	56.1	0.04[c]	63	4.9
K	5	149	1.4	0.08[c]	147	1.4
Mg	5	149	0.6	0.02[c]	148	0.6
Mn	10	120	105.1	0.02[c]	45	16.6
Na	5	149	1.1	0.13[c]	147	1.0
NH_4^+	5	59[d]	95.3	0.07	6	0.9
NO_3^-	10	148	8.8	0.052	118	2.8
P, total	10 (if P conc. > 0.01 mg/L) 20 (if P conc. ≤ 0.01 mg/L)	137	41.7	0.010	46	7.2
pH, acidity (pH units)	0.05 (pH units)	149	0.03	--	--	--
pH, alkalinity (pH units)	0.05 (pH units)	149	0.03	--	--	--

(continued)

Table 23. (Continued)

Variable (in mg/L unless noted)	Intralaboratory Precision Goal (in %RSD unless noted)	All pairs (mean > 0)		Quantitation Limit[a]	Pairs that have a mean > Quantitation Limit	
		n	Estimated Precision (Pooled %RSD)[b]		n	Estimated Precision (Pooled % RSD)[b]
pH, air equilibrated (pH units)	0.05 (pH units)	149	0.02	--	--	--
SiO_2	5	148	25.9	0.28	125	2.9
SO_4^{2-}	5	149	1.8	0.12	143	1.7

[a] The quantitation limit is 10 S_B (10 times the standard deviation of the calibration or reagent blank measurments). Quantitation limits are not calculated for ANC, BNC, or pH measurements.
[b] Pooled standard deviation values were used for pH measurements.
[c] Quantitation limit calculated from Laboratory I's calibration blanks only.
[d] Reported concentrations of many NH_4^+ pairs were ≤ 0. As a result, the n for this variable is small relative to the n for other variables.

Table 24. Intralaboratory Precision Estimates Calculated from Analytical Laboratory Duplicate Pairs (by Laboratory), Western Lake Survey - Phase I

Variable (in mg/L unless noted)	Laboratory I					Laboratory II				
	All Pairs (mean > 0)			Pairs that have a mean > Quantitation Limit		All Pairs (mean > 0)			Pairs that have a mean > Quantitation Limit	
	n	Estimated Precision (Pooled %RSD)[b]	Quantitation Limit[a]	n	Estimated Precision (Pooled %RSD)	n	Estimated Precision (Pooled %RSD)[b]	Quantitation Limit[a]	n	Estimated Precision (Pooled %RSD)[b]
Al, extractable	52	21.2	0.021	12	5.3	89	12.5	0.007	32	20.0
Al, total	57	5.0	0.026	34	4.7	91	1.4	0.013	77	1.4
ANC (µeq/L)	48	206.9[c]	--	--	--	91	2.2	--	--	--
BNC (µeq/L)	57	10.6	--	--	--	91	19.2	--	--	--
Ca	58	0.7	0.04	58	0.7	91	0.7	--	--	--
Cl^-	58	2.5	0.09	54	2.4	91	2.2	0.03	91	2.2
Conductance (µS/cm)	58	1.3	1.0	57	1.4	91	0.9	1.8	91	0.9
DIC, air equilibrated	58	4.3	0.29	50	2.9	91	7.5	0.22	82	7.4
DIC, initial	58	5.9	0.25	50	2.9	91	3.0	0.13	91	3.0
DOC	58	3.0	0.4	58	3.0	88	14.1	0.5	67	5.5
F^-, total dissolved	57	3.0	0.002	57	3.0	91	2.5	0.010	91	2.5
Fe	53	74.1	0.04	25	4.0	91	42.3	--	--	--
K	58	1.4	0.08	58	1.4	91	1.4	--	--	--
Mg	58	0.6	0.02	58	0.6	91	0.5	--	--	--
Mn	49	43.7	0.02	12	1.9	71	131.8	--	--	--
Na	58	1.3	0.13	58	1.3	91	0.9	--	--	--
NH_4^+	16[d]	44.3	0.11	1	N/A	43[d]	108.3	0.03	6	0.9
NO_3^-	57	2.2	0.068	52	2.1	91	11.0	0.037	71	3.4
P, total	55	10.7	0.013	27	6.1	82	53.2	0.006	25	15.8
pH, acidity (pH units)	58	0.02	--	--	--	91	0.04	--	--	--
pH, alkalinity (pH units)	58	0.02	--	--	--	91	0.04	--	--	--
pH, air equilibrated (pH units)	58	0.02	--	--	--	91	0.02	--	--	--
SiO_2	57	34.9	0.43	47	2.5	91	18.2	0.08	80	3.1
SO_4^{2-}	58	1.9	0.11	57	1.8	91	1.8	0.06	90	1.8

[a] The quantitation limit is 10 S_B (10 times the standard deviation of the calibration or reagent blanks). Quantitation limits are not calculated for ANC, BNC, and pH because blanks were not analyzed. Nor were blanks analyzed at Laboratory II for Ca, Fe, K, Mg, Mn, or Na.

[b] Pooled standard deviation values were used for pH measurements.

[c] If eight pairs that have means < +3 µeq/L are removed from the precision estimate calculation the estimate would be 8.0 percent.

[d] Reported concentrations of many NH_4^+ pairs were ≤ 0. As a result, the n for this variable is small relative to the n for other variables.

N/A = not applicable.

Table 25. Summary of Intralaboratory Precision Results by Variable, Western Lake Survey - Phase I

Variables that met DQO	DQO (%)	Variables that did not meet DQO	Comments
Al, extractable	10 or 20		
Al, total	10 or 20		
	10	ANC	Quantitation limits were not calculated for ANC. If a quantitation limit of 0 ± 3 μeq/L were applied to the data, the precision estimate would meet the DQO.
	10	BNC	Quantitation limits were not calculated for BNC; even so, the precision estimate is close to the DQO.
Ca	5		
Cl^-	5		
Conductance	2		
DIC (air equilibrated)	10		
DIC (closed system)	10		
DIC (initial; open system)	10		
DOC	5 or 10		
F^-, total dissolved	5		
	10	Fe	Only the precision estimate for Laboratory II did not meet the DQO, because a quantitation limit could not be calculated.
K	5		
Mg	5		
	10	Mn	Very low concentrations in most WLS-I samples (95% of routine lake samples < 0.030 mg/L); only one duplicate pair value was above quantitation limit.
Na	5		
NH_4^+	5		
NO_3^-	10		
P, total	10 or 20		
pH (acidity; open system)	0.05 (pH unit)		
pH (alkalinity; open system)	0.05 (pH unit)		
pH (air equilibrated)	0.05 (pH unit)		
pH (closed system)	0.05 (pH unit)		
SiO_2	5		
SO_4^{2-}	5		
True Color	5 (PCU)		
Turbidity	10		

month duration, which would have been long enough to produce significant biochemical changes in the 2-L subsamples. However, the initial homogeneity of each bulk audit sample lot was ensured by filtering the bulk sample lot and by storing it in the dark at 4 °C until the 2-L aliquots were prepared. Therefore, it was determined that having aliquots of all field audit samples prepared at one place and time by the same technician (or the same team of technicians) would provide better overall audit sample consistency than would preparing aliquots as needed.

When the mean analyte concentrations of the FN4 samples analyzed during WLS-I (see Appendix F) are compared to those analyzed during the NSS Phase I Pilot Survey (Drousé, 1987), no significant difference is observed between the analytical results from the two surveys. Like FN4, FN3 and FN5 have

been used as audit samples in more than one NSWS survey. The FN3 sample collected from Lake Superior (see Appendix F), was used in the ELS-I audit program (Best et al., 1987) and was stored for almost one year before it was used for WLS-I. The mean analyte concentrations between the two surveys show excellent agreement across all analytes, in spite of the potential laboratory bias and time factors involved. There are some differences in these audit samples between surveys, but determining whether time factors and laboratory bias contribute to these differences is not within the scope of this report.

Observing differences in analyte concentration for the same audit sample lot across surveys, however, can be a useful daily QA tool. FN5, for example, was used for the NSS Phase I Pilot Survey as well as for WLS-I, and it showed very good agreement across surveys. One change, however, was of concern to the QA staff. The FN5 mean nitrate concentration during the NSS Phase I Pilot Survey was 0.085 mg/L (Drousé, 1987). Through daily QA communications during the WLS-I sample analysis phase, preliminary analytical laboratory data showed routine lake sample concentrations of approximately 0.140 mg/L. The higher concentrations were of concern to the QA staff because nitrate contamination had been a problem during ELS-I (Linthurst et al., 1986). A check of field blank values and of other QA samples did not indicate systematic contamination from nitrate. Continual monitoring of FN5 nitrate concentrations indicated a possible increase in concentration in the bulk sample over time, but did not indicate contamination. A slight decrease in ammonium levels indicates that oxidation of nitrogen may have been responsible for converting ammonium to nitrate and may account for the elevated nitrate concentrations. There is no conclusive evidence, however, that explains why the NO_3^- concentrations increased between surveys for this natural audit sample.

Midway through the survey, the reserve amounts of natural audit samples were critically low, so a new Bagley Lake sample (approximately 80 gallons) was collected, shipped to Radian, and prepared as aliquots of FN6. Radian also analyzed three FN6 samples before initial shipment to the field bases so that the EMSL-LV QA staff could compare them to the field laboratory and analytical laboratory values. It was assumed that the chemical composition of the two Bagley Lake samples (FN5 and FN6) would be similar, even though they were collected during different seasons of 1985. FN5 was collected in January and FN6 was collected in September; therefore, temporal differences between the two sample types were expected. The concentrations of FN5 and FN6 are given in Table 26 (later in this section) and in Appendix E.

Description of Field Synthetic Audit Samples--

The lakes selected as the sources of field audit samples contain a matrix of analytes considered to be important in acid precipitation research. It is useful to select a suite of audits that contain different concentrations that bracket the predicted ranges of concentrations for the key variables to be analyzed in a survey. Because it was difficult to find lakes that contained all the desired concentration levels of all the variables measured in the analytical laboratories, field synthetic audits also were employed during WLS-I. A synthetic audit is ASTM Type I reagent-grade water spiked with analytes at a specific concentration. Field synthetic audit samples simulate natural lake systems, but the analyte concentrations in them can be artificially adjusted. Because analytical results could be compared immediately to the theoretical concentrations of the analyte, field synthetic audit samples also gave the QA staff rapid feedback on analytical performance during the analytical phase of the survey.

Two low-concentration synthetic field audit lots (FL11 and FL12) were used in WLS- I. No major problems were encountered with the use, preparation, or stability of these audit samples. These samples, which were ionically balanced to simulate natural lake water, were prepared by Radian at the predetermined concentration ranges specified in Silverstein et al. (1987). The two audits had the same theoretical concentrations for all analytes.

The four stock concentrates used during WLS-I comprise one synthetic lot (see Section 2 of Appendix C for description). Each concentrate volume was designed to last only as long as the volumes of the other concentrates of that lot. When the concentrate volumes were depleted, a new set of stock concentrates was prepared. The new set was given a sequential lot number to indicate that it was from different stock and that it was prepared at a later date.

Use of Field Audit Samples in Estimating Precision

At least one field audit sample was to be incorporated into each batch of WLS-I lake samples, and the precision of the audits was calculated after all of the audits from all of the batches had been analyzed. The cumulative field audit precision estimates are calculated as %RSD among all the batches for each audit lot. For field audits, the precision is calculated for many measurements of a single concentration.

Field audit samples are processed and analyzed in the field laboratory in the same manner as routine samples. The precision estimates calculated from field audit samples are used to estimate the variability of the field laboratory measurements over time. Precision also can be estimated by the variability of the field audit sample in the analytical laboratory. This

Table 26. Precision Estimated from Field Natural Audit Samples Analyzed Among Batches (Analytical Laboratories Pooled), Western Lake Survey - Phase I[a]

Variable (in mg/L unless noted)	Field Natural Lot 3 (FN3, Lake Superior)		Field Natural Lot 4 (FN4, Big Moose Lake, NY)	
	Mean Concentration	Estimated Precision as %RSD (n = 38)	Mean Concentration	Estimated Precision as %RSD (n = 37)
Al, extractable	0.002	116.1	0.195	31.1
Al, total	0.012	51.8	0.352	13.2
ANC (μeq/L)	846.1	5.0	-24.1	10.2[b]
BNC (μeq/L)	21.9	59.5	119.8	10.9
Ca	13.84	4.8	2.10	3.6
Cl^-	1.43	6.9	0.54	6.1
Conductance (μS/cm)	95.5	1.9	32.2	3.6
DIC, air equilibrated	9.90	9.7	0.32	80.9
DIC, initial	9.86	10.7	0.51	30.4
DOC	1.4	20.6	8.1	2.1
F^-, total dissolved	0.035	21.5	0.074	11.7
Fe	0.005	155.8	0.07	10.2
K	0.52	4.4	0.68	2.7
Mg	2.90	2.6	0.36	1.3
Mn	-0.002	439.2[b]	0.078	9.9
Na	1.36	2.5	0.74	3.7
NH_4^+	-0.010	221.2[b]	-0.001	1770.4[b]
NO_3	1.418	4.7	2.351	4.8
P, total	0.001	296.7	0.002	141.4
pH, acidity (pH units)	7.86	0.08[c]	4.68	0.03[c]
pH, alkalinity (pH units)	7.85	0.07[c]	4.68	0.02[c]
pH, air equilibrated (pH units)	8.13	0.09[c]	4.70	0.03[c]
SiO_2	2.51	18.3	4.45	11.0
SO_4^{2-}	3.24	6.4	6.68	5.5

(continued)

estimate includes the effect of sample processing in the field laboratory. These precision results can be compared to the DQOs for precision shown in Table 2 (Section 1); however, they should be used only as a gauge in that comparison of data quality because the DQOs apply directly to analytical laboratory performance only and do not apply to the other components (sources) of variability.

Among-Batch Precision Results

Among-Batch Precision Estimated from Field Audit Samples Analyzed in the Field Laboratory

Tables E-1 through E-4 in Appendix E show the precision estimates that are based on all the audit sample types for each field laboratory. These tables show the precision estimates separately and pooled for DIC, pH, turbidity, and true color. The tables also present the comparable values for DIC and pH from the analytical laboratory. (Turbidity and true color were not analyzed in the analytical laboratory.) Across all six lots of audit samples for all four field determinations, where population and concentration were high enough to determine statistical confidence, the precision for each field laboratory was acceptable. The pooled values for the five field laboratories show good precision across audit lots and measurements. The only exception to good pooled precision is the true color value for the FN4 Big Moose lake audit sample; however, the values are sufficiently low that this imprecision should not be of concern to the data user.

Among-Batch Precision Estimated from Field Audit Samples Analyzed in the Analytical Laboratory

Table 26 presents precision data for the field natural audit samples and Table 27 presents precision data for the pooled field synthetic audit samples. It is legitimate to pool the data for the two field synthetic

Table 26. (Continued)

Variable (in mg/L unless noted)	Field Natural Lot 5 (FN5, Bagley Lake, WA, lst Sampling)		Field Natural Lot 6 (FN6, Bagley Lake, WA, 2nd Sampling)	
	Mean Concentration	Estimated Precision as %RSD (n = 68)	Mean Concentration	Estimated Precision as %RSD (n = 37)
Al, extractable	0.002	120.4	0.006	39.1
Al, total	0.010	43.1	0.015	18.6
ANC (μeq/L)	146.7	3.5	121.3	1.6
BNC (μeq/L)	37.1	16.1	28.5	20.3
Ca	1.99	3.2	1.59	2.6
Cl^-	0.24	11.8	0.16	5.7
Conductance (μS/cm)	17.8	6.4	14.2	3.5
DIC, air equilibrated	1.83	11.3	1.48	5.9
DIC, initial	1.91	13.3	1.47	7.0
DOC	0.4	79.2	0.2	50.4
F^-, total dissolved	0.025	8.0	0.021	9.9
Fe	0.004	177.8	0.01	75.6
K	0.36	5.5	0.29	2.9
Mg	0.24	2.0	0.17	2.0
Mn	0.003	351.7	0.003	261.0
Na	1.06	5.2	0.81	2.1
NH_4^+	0.011	106.1	-0.001	629.6[b]
NO_3	1.147	23.1	0.016	234.2
P, total	0.004	197.2	0.002	191.6
pH, acidity (pH units)	7.00	0.10[c]	7.07	0.08[c]
pH, alkalinity (pH units)	7.02	0.09[c]	7.09	0.07[c]
pH, air equilibrated (pH units)	7.29	0.13[c]	7.25	0.15[c]
SiO_2	11.37	8.6	9.36	7.2
SO_4^{2-}	0.97	7.6	0.63	4.5

[a] The among-batch precision estimate represents the variability introduced in the field laboratory, the analytical laboratory, and the audit-sample preparation laboratory. It cannot indicate variability introduced during sampling.
[b] The absolute value of the percent relative standard deviation (%RSD).
[c] Standard deviation (SD) values were calculated for pH measurements.

lots (FL11 and FL12) because their theoretical concentrations are the same. Appendix F (Tables F-5 and F-6), present the field synthetic audit data separated by lot. For the field synthetic audits, separate sets of values for each analytical laboratory can be evaluated also (Table 27). These laboratory subsets of among-batch precision indicate whether or not an analytical method problem was inherent throughout the survey, or if a problem resulted from the number of audit samples analyzed by each analytical laboratory. It is also important to check the precision of each analytical laboratory separately because all samples from each subregion were analyzed by only one of the analytical laboratories. Bias in one laboratory's measurements, therefore, could affect population estimates (see Appendix I). For all audit sample lots, the precision estimates for most analytes met or were near the DQOs. The tables in Appendix J provide detailed information about each audit lot and are useful for the data user who is interested in the components of variability for each audit sample.

Table 28 summarizes among-batch precision data for only those analytes that did not meet the DQOs or that had concentrations so close to the detection limit that the precision estimates have little meaning.

It is evident that both laboratories had high variability in measuring initial and air-equilibrated DIC, DOC, NH_4^+ and, at a low concentration, total P. All pH precision estimates are about 0.1 pH unit. These estimates did not meet the DQO of 0.05 pH unit for intralaboratory precision, but they should still be considered reasonable because the 0.05 pH unit goal does not apply to field audit sample precision. Laboratory I's variability contributed significantly to the higher precision estimate for the pooled Ca, K, Na, and SiO_2 measurements. Laboratory II was the major contributor to the high variability of the pooled Mn values. For FL11, Laboratory II's mean value was 0.077 mg/L; for FL12 the mean was 0.109 mg/L (see Appendix F). This shows variability over time for Laboratory II, whereas for Laboratory I the means were 0.097 (FL11) and 0.092 (FL12). Conductance imprecision for Laboratory II (5.0%) was greater than that for Laboratory I (3.3%). For extractable Al, total

Al, BNC, and Fe, the concentrations were too low for determining precision estimates confidently.

Audit samples and duplicates are used in calculating precision estimates. Audit samples also are used to assess intralaboratory bias and accuracy. Figure 6 shows the relationship of precision, bias, and accuracy in the assessment of data quality. A discussion at the end of Section 7 summarizes the overall performance of the audit sample program and discusses suggestions for modifying the use of these samples in future surveys.

Table 27. Precision Estimated from Pooled Field Synthetic Audit Sample Lots, (Analytical Laboratories Pooled and Separated), Analyzed Among Batches, Western Lake Survey - Phase I[a]

Variable (in mg/L unless noted)	Theoretical Concentration	Laboratories Pooled		Laboratory I		Laboratory II	
		Mean Concentration	Estimated Precision (%RSD) (n = 47)	Mean Concentration	Estimated Precision (%RSD) (n = 17)	Mean Concentration	Estimated Precision (%RSD) (n = 30)
Al, extractable	0.020	0.005	48.0[b]	0.005	32.7[b]	0.004	56.2[b]
Al, total	0.020	0.027	29.3	0.020	26.5	0.031	20.0
ANC (μeq/L)	c	111.0	6.1	110.6	6.4	111.3	6.0
BNC (μeq/L)	c	30.0	29.6	21.3	18.8	35.0	19.5
Ca	0.194	0.22	16.1	0.25	15.5	0.20	4.6
Cl^-	0.343	0.36	5.6	0.36	7.5	0.36	4.4
Conductance (μS/cm)	c	19.7	4.4	19.6	3.3	19.7	5.0
DIC, air equilibrated	c	1.44	18.3	1.26	17.7	1.54	15.0
DIC, initial	0.959	1.54	20.4	1.42	22.8	1.60	18.3
DOC	1.0	1.0[d]	25.0	1.1[e]	20.9	1.0	26.4
F^-, total dissolved	0.042	0.043	7.1	0.044	7.9	0.042	5.9
Fe	0.059	0.006	153.3[b]	0.001	465.8[b]	0.009	112.2[b]
K	0.203	0.21	8.7	0.22	9.7	0.21	6.7
Mg	0.447	0.45	3.8	0.46	3.2	0.45	3.9
Mn	0.098	0.097	14.0	0.095	3.4	0.098	17.1
Na	2.74	2.77	8.5	2.78	13.5	2.77	3.7
NH_4^+	0.168	0.16[d]	16.2[b]	0.15[e]	21.2[b]	0.16	13.5[b]
NO_3^-	0.464	0.483	6.5	0.468	5.7	0.492	6.3
P, total	0.027	0.025	22.0	0.025	18.1	0.024	24.2
pH, acidity (pH units)	c	6.94	0.13[f]	6.99	0.13[f]	6.92	0.12[f]
pH, alkalinity (pH units)	c	6.95	0.11[f]	6.96	0.13[f]	6.94	0.10[f]
pH, air equilibrated	c	7.24	0.14[f]	7.19	0.08[f]	7.27	0.16[f]
SiO_2	1.07	1.10	10.5	1.07	14.6	1.12	7.5
SO_4^{2-}	2.28	2.30	5.4	2.23	5.0	2.34	4.8

[a] The among-batch precision estimate represents the variability introduced in the field laboratory, the analytical laboratory and the audit-sample preparation laboratory. It cannot indicate variability introduced during sampling.
[b] Poor precision may be the result of sample instability, sample mixing error, or both (Best et al., 1987).
[c] Although theoretical values can be calculated, the theoretical value depends on the concentration of chemicals added to the synthetic audit sample.
[d] n = 45.
[e] n = 15.
[f] Standard deviation (SD) values were calculated for pH measurements.

Table 28. Summary of Analytes That Showed High Variability Among Batches for Field Audit Samples, Western Lake Survey - Phase I

Audit Sample	Variables Not Within or Near DQO for Precision			Variables with Extremely Low Mean Concentrations[b]
	Laboratories Pooled	Laboratory I[a]	Laboratory II[a]	
FN3 Lake Superior	DOC, total dissolved F^-, SiO_2	Cl^-, total dissolved F^-, SiO_2	DOC, total dissolved F^-, SiO_2	Extractable Al, total Al, BNC,' Fe, Mn, NH_4^+, total P
FN4 Big Moose Lake	Extractable Al, total Al, total dissolved F^-, SiO_2	Extractable Al, SiO_2	extractable Al, total Al, total dissolved F^-, Mn	DIC (initial and air equilibrated) , NH_4^+, total P
FN5 Bagley Lake (Ist sampling)	Cl^-, Conductance, DIC (initial), NO_3^-, pH (air equilibrated)	Cl^-, Conductance, DIC (initial and air equilibrated), NO_3^-, pH (air equilibrated), SiO_2	Conductance, NO_3^-, pH (air equilibrated), SiO_2	Extractable Al, total Al, BNC, DOC, total dissolved F^-, Fe, Mn, NH_4^+, total P
FN6 Bagley Lake (2nd sampling)	pH (air equilibrated)	---	pH (air equilibrated)	Extractable Al, total Al, BNC, DOC, total dissolved F^-, Fe, Mn, NH_4^+, NO_3^-, total P
FL11 (Synthetic)	Ca, DIC (initial and air equilibrated), DOC, K, Na, $NH4^+$	Ca, DIC (initial and air equilibrated), K, Na, NH_4^+	DIC (initial and air equilibrated), NH_4^+	Extractable Al, total Al, BNC, Fe
FL12 (Synthetic)	Ca, Conductance, DIC (air equilibrated), total P, pH (air equilibrated), SiO_2	Ca, DIC (air equilibrated), total P, SIO_2	Conductance, DIC (air equilibrated), total P, pH (acidity, alkalinity, air equilibrated)	Extractable Al, total Al, BNC, Fe
FL11 and FL12 (Synthetics Pooled)	Ca, Conductance, DIC (initial and air equilibrated), DOC, NH_4^+, total P, pH (acidity and air equilibrated), SiO_2	Ca, K, Na, SiO_2	Conductance, Mn	Extractable Al, total Al, BNC, Fe

[a] See Appendix F.

[b] These variables had concentrations that were too low to allow precision to be compared confidently to the DQO. Not applicable for pH measurements.

Section 7
Results and Discussion - Accuracy

Introduction

Accuracy is a measure of the bias in a system. It is the degree of agreement of a measurement (or, as used in this report, an average of measurements of the same variable, $\bar{X}$) with an accepted reference or true value, T. Accuracy usually is expressed as the difference between the two values, $\bar{X}$-T, or the difference as a percentage of the reference or true value, [($\bar{X}$-T)/T] 100. This percentage value is used in this report to relate accuracy to the WLS-I DQOs.

Method of Estimating Accuracy from Field Synthetic Audit Samples

In the WLS-I sampling design, field synthetic audit samples were used to estimate accuracy (expressed as absolute bias) for the analytical laboratory measurements (see Figures 6 and 7). Although there may be several ways to analyze the two field synthetic audit samples for accuracy, there is only one formula for estimating accuracy as percent, as specified in the DQOs (see above). For the statistical analyses presented here, the theoretical concentrations of the field synthetic audit samples are considered to be true values (T); the average of the measurements for the same variable ($\bar{X}$) is the mean concentration of the synthetic audit samples. [Note: In the WLS-I QA program, natural audit samples could not be used in determining accuracy because a theoretical concentration for each analyte could not be confirmed.] These synthetic audit samples are as close in composition to the WLS-I lake water samples as could be anticipated before sampling began. The WLS-I field synthetic audits are not certified standards (e.g., by NBS). In addition, NBS prepares only certain standards; none covers in a single sample the entire range of analytes required for WLS-I.

Accuracy Results Estimated from Field Synthetic Audit Samples

Because the theoretical concentrations of FL11 and FL12 are identical (see Appendix C), and because once each week each field laboratory incorporated synthetic audit samples into its batches, accuracy data for the two synthetic audit samples can be pooled to determine an overall estimate of accuracy across the survey. The FL11 and FL12 audit stock concentrates were prepared on different days, about one month apart. As a result, there may be slight differences in lot composition that can be attributed to chemical degradation or to preparation variability. Because subsets of each audit lot were analyzed by each analytical laboratory, evaluating the FL11 and FL12 values pooled by laboratory and separately by laboratory provides an indication of whether or not laboratory differences or lot differences significantly affected accuracy estimates. Accuracy estimates, like those for precision, depend on sample concentration; therefore, the data user should observe the theoretical concentration of the analyte when assessing the accuracy estimates.

Table 29 presents the estimated analytical accuracy for FL11 and FL12 synthetic audit samples pooled and shows the accuracy by laboratory pooled and separate. [Note: Data for FL11 and FL12 separated are given in Appendix G.] The only analytes for which accuracy estimates exceeded their DQOs were Ca at +11.3 percent and total Al at -35.5 percent. Laboratory I's accuracy of +28.7 percent for Ca, compared to Laboratory II's value of +1.6 percent, identifies the apparent cause of the inaccuracy. Similarly, the +55.5 percent bias of Laboratory II for total Al overshadows the +0.5 percent bias of Laboratory I. No other pooled data showed this inaccuracy. However, Laboratory II's value was slightly outside the DQO for total P (-11.1%), as was Laboratory I's value for DOC (+13.5%). The accuracy of DOC suggests another source of variability: Although the theoretical DOC concentration is 1.0 mg/L added in the form of $C_6H_4(COOH)_2$ and $KHC_8H_4O_4$, there may have been as much as 0.3 mg/L DOC as background in even ASTM Type I reagent-grade water used in the synthetic audit preparation (personal commun. to Silverstein from David Lewis, Radian Corporation). These background concentrations were also observed in field blank data (see Section 8). Table 30 summarizes the analytes that did not meet the DQOs for accuracy.

Ten variables that were measured in synthetic audits as part of the WLS-I protocol either have no

Table 29. Estimated Analytical Accuracy for Field Synthetic Audit Samples Pooled, Western Lake Survey - Phase I

Variable[a]	Theoretical Concentration	Laboratories Pooled		Laboratory I		Laboratory II	
		FL11 and FL12 Combined Mean Concentration (n = 47)	Accuracy[d] (%)	FL11 and FL12 Combined Mean Concentration (n = 17)	Accuracy[d] (%)	FL11 and FL12 Combined Mean Concentration (n = 30)	Accuracy[d] (%)
Al, extractable	0.020	0.0046	-77.0	0.0054	-73.0	0.0042	-79.0
Al, total	0.020	0.0271	+35.5	0.0201	+0.5	0.0311	+55.5
ANC (μeq/L)	--	111.1	--	110.6	--	111.3	--
BNC (μeq/L)	--	30.1	--	21.3	--	35.0	--
Ca	0.194	0.216	+11.3	0.250	+28.7	0.197	+1.6
Cl^-	0.343	0.358	+4.4	0.356	+3.8	0.359	+4.7
Conductance (μS/cm)	--	19.7	--	19.6	--	19.72	
DIC, air equilibrated	--	1.435	--	1.258	--	1.536	--
DIC, initial	0.959	1.537	+60.3	1.424	+48.5	1.600	+66.8
DOC	1.0	1.042[b]	+4.2	1.135[c]	+13.5	0.955[c]	-4.5
F^-, total dissolved	0.042	0.0429	+2.1	0.0443	+3.1	0.0421	+0.2
Fe	0.059	0.0059	-90.0	0.0012	-98.0	0.0085	-85.6
K	0.203	0.211	+3.9	0.221	+8.9	0.205	+1.0
Mg	0.447	0.449	+0.4	0.455	+1.8	0.445	-0.3
Mn	0.098	0.097	-1.0	0.095	-3.0	0.098	+0.1
Na	2.74	2.772	+1.2	2.780	+1.5	2.770	+1.1
NH_4^+	0.168	0.155[b]	-7.7	0.154	-8.4	0.156	-7.3
NO_3	0.464	0.483	+4.1	0.468	+0.8	0.492	+6.1
P, total	0.027	0.0245	-9.3	0.0255	-5.6	0.0240	-11.1
pH, acidity (pH units)	--	6.94	--	6.99	--	6.92	--
pH, alkalinity (pH units)	--	6.95	--	6.96	--	6.94	--
pH, air equilibrated	--	7.24	--	7.19	--	7.27	--
SiO_2	1.07	1.100	+2.8	1.067	-0.3	1.118	+4.5
SO_4^{2-}	2.28	2.300	+0.9	2.228	-2.3	2.342	+2.7

[a] All variables are measured in mg/L unless otherwise noted. Mean concentrations are presented in as many significant figures as possible for the purpose of calculating accuracy estimates.
[b] n = 45.
[c] n = 15.
[d] A plus sign (+) indicates that the mean concentration was higher than the theoretical concentrations; a minus sign (-) indicates that the mean concentration was lower than the theoretical concentration.

Table 30. Summary of Variables[a] that did not Meet Data Quality Objectives for Estimated Analytical Accuracy, Western Lake Survey - Phase I

	Components of Inaccuracy (Source)		
Audit Lot	Laboratories Pooled	Laboratory I	Laboratory II
FL11	Total Al, Ca, Mn, NH_4^+, Total P	Ca, NH_4^+, total P	Total Al, DOC, Mn, NH_4^+
FL12	Total Al, DOC	Ca, DOC, SiO_2	Total Al, Mn, Total P
FL11 and FL12 pooled	Total Al, Ca	Ca, DOC	Total Al, total P

[a]Not included in accuracy determinations because of sample matrix problems are ANC, BNC, conductance, DIC, and pH. Not included in accuracy determinations because of sample chemical instability are Fe and extractabale Al.

theoretical concentration or are subject to inherent methodological problems that result in poor accuracy or in the inability to measure for accuracy reliably. Six of the ten variables (ANC, BNC, conductance, DIC [air equilibrated], and pH [initial and air equilibrated]) have no reliable, theoretical concentrations, and thus no reliable accuracy determinations can be made. The concentrations of each of these analytes depends on the concentrations and identities of all the analytes that comprise the audit sample matrix. ANC, for example, is not spiked into the audit in the same manner that Ca or other ions are, but the level of ANC is affected directly by the anions, cations, and other components of the audit matrix and is calculated from the acid titrated into this matrix. Consequently, if the volume of Ca added to the audit sample was inaccurate, the accuracy of the ANC measurement (and of other measurements such as conductance) could be affected.

Initial DIC does have a theoretical concentration (0.959 mg/L). Accuracy for initial DIC was poor overall, by laboratory, and by lot. The matrix effect is a factor for this analyte as well. The theoretical concentration of the sample is based on the assumption that the deionized water and all the additives were pure and were mixed properly; therefore, the theoretical concentration assumes no matrix effect. DIC was added to the synthetic sample in the form of HCO_3^-, as part of the audit sample preparation protocol (see Appendix C). Equilibration of the sample also was expected to minimize variability of initial DIC, but because the sample was not natural lake water, complete equilibration was difficult to achieve.

For two of the ten variables, Fe and extractable Al, accuracy DQOs were not met for either lot or by either laboratory (Table 30). This is consistent with the results found in ELS-I (Best et al., 1987) and in the NSS Phase I Pilot Survey (Drousé, 1987). In the presence of oxygen, these analytes precipitate out of solution within 24 hours. Therefore, they were not totally soluble and were often filtered out or were adsorbed onto filtrator walls during the aliquot preparation process in the field laboratory. As a result, accuracy for Fe and total Al was expected to be poor. The accuracy has been calculated for these two analytes, but any results should be considered with caution.

In summary, the accuracy results exhibit the following characteristics:

- Where calculation was applicable, overall accuracy estimates for most analytes were within the DQOs. Where analytes did not meet the DQOs, the inaccuracy generally is attributable to one laboratory's measurement error.

- Of the 14 analytes for which accuracy can be calculated reliably, only Ca and total Al are outside the DQOs when laboratories and audit sample lots are pooled. In each case, the inaccuracy can be attributed to one laboratory or the other, not to both. Laboratory II showed some measurement variability with Mn and total Al for both audit samples and with DOC for one audit sample; Laboratory I showed some measurement variability with Ca for both audit samples and with DOC and $Si0_2$ for one. Each laboratory showed a bias for total P for one audit sample but not for the other; when the audit sample values were pooled, this bias was within the DQO for the analyte.

- NH_4^+ accuracy estimates for both laboratories met the DQO for FL12; the laboratories had similarly poor accuracy estimates for FL11 (about -20%). The FL11 inaccuracy may be the result of NH_4^+ degradation in the lot overtime; that is, the result of inconsistency in the sample rather than inconsistency or inaccuracy in the analytical procedure (see Appendix G). When the NH_4^+ values for the FL11 and FL12 were pooled, however, overall accuracy was within the ± 10 percent DQO.

- For 8 of 24 variables (ANC; BNC; air-equilibrated and initial DIC; acidity, alkalinity, and air-equilibrated pH; and conductance) accuracy cannot be reliably calculated because the analytical methods for these variables are subject to matrix effects.

- Two variables, Fe and extractable Al, are subject to physicochemical problems inherent in the analytical method; thus, reliable accuracy calculations cannot be derived from field synthetic audit data for these variables.

Summary of Audit Sample Data for Precision and Accuracy

Data for all audit sample lots (FN3, FN4, FN5, FN6, FLII, and FL12) contribute to the understanding of the precision, accuracy, and laboratory biases associated with the WLS-I data base. When these data are used to help interpret regional and subregional characteristics or to characterize one lake or a subset of lakes sampled, the data user must consider the proposed use of the data. For example, the data user interested in precision at a certain concentration range must consider that concentrations and precision estimates are specific to the audit sample type and to each analyte in that audit sample. Thus, the user should determine which analytes are of interest, should evaluate the mean sample concentration of the field audit lots, should assess the analytical laboratory involved in a particular subregion, and should select for review those audits that cover the concentration range of interest. The selected subset of field audit data then can be used in conjunction with the accuracy data provided by the synthetic audits (also at the concentrations of interest only) to yield a degree of confidence for a particular subset of the data.

The confidence assigned to subregional population estimates can be supported by the audit sample results. In any application of audit data, however, the user must be aware that there are nuances associated with precision estimates for laboratory data, whether the data are pooled or separated by laboratory. Often, where precision estimates are well outside the DQOs, one or a few outlying sample values are responsible. For example, of the 68 FN5 samples, 44 were analyzed in Laboratory II. The %RSD for the 44 samples analyzed for NO_3^- is 26.5 percent at a mean concentration of 0.151 mg/L. When four unusually high sample values are removed from the %RSD calculation, the n of 40 yields a %RSD of 9.6 percent. This example illustrates the profound effect that a few unusual values may have on the overall precision of the audit lot analyzed in one of the analytical laboratories. In this example, removing 9 percent (4 of 44) of the audit samples from the population improves the precision from 26.5 percent to 9.6 percent. This illustration suggests that the four data points that were removed did yield unusual results. The data user may wish to identify such data as outliers by applying appropriate statistical tests when analytes yield high precision estimates.

Specific examinations of data subsets, such as the NO_3^- example given above, will continue to generate questions concerning the WLS-I data base:

- What are the causes of outlier values?

- Was contamination introduced by the analytical laboratory, by the field laboratory, by the audit sample supplier laboratory, by the supplier of the aliquot bottles, or by a combination of these components?

- Does this variability affect the primary survey goal of subregional lake characterization?

Audit data alone cannot answer these questions. Field duplicate pairs, which are the only QA samples that reflect all components of system variability that can affect the routine lake samples, must be used to estimate overall system variability. Audit sample data, however, can isolate variability that is related to the controlled environment of the laboratory from the variability associated with the field sampling component (sampling procedures and uncontrollable lake-site environmental factors such as high winds). Audit samples cannot measure system variability because they are not collected at each lake site and they are not processed through the Van Dorn samplers as are field blanks and field duplicate pairs. Consequently, field audits are most useful in identifying method and daily analytical problems related to the field laboratories and analytical laboratories, in detecting and quantifying laboratory bias, and in estimating the accuracy of the analytical measurements with the aid of synthetic audits.

Thus, the WLS-I QA audit samples can be used to make only certain inferences about data variability, and these inferences are limited to the realm of analytical measurements. The usefulness of audits in the daily QA and data verification aspects of the program, however, is certain. Initially, the field audit samples gave the QA staff immediate feedback on daily performance in the field laboratory and in the analytical laboratory. Monitoring daily laboratory performance through telephone calls and obtaining hard-copy, raw data results for audit samples identified trends or problems in sample analysis, sample handling, and data reporting. Subsequent evaluation and statistical analysis of the full suite of audit sample results provided a basis for determining whether or not requests for reanalysis of sample batches were necessary. Evaluation of the FN5 audit sample data, for example, identified a silica dilution

error: a suspicious trend indicated by a few samples resulted in value changes for 80 samples from one analytical laboratory; 60 of these samples had dilution calculation errors and 20 were reanalyzed because of incorrect dilution procedures.

For the analytical laboratory audit sample results, 168 precision estimates could be calculated (7 audit lots times 24 variables per audit lot). Of the 168 estimates, 90 percent (1) were reasonable in comparison to the survey precision goals, (2) represented a mean concentration that was too low to provide a meaningful estimate, or (3) had high %RSD values as a result of one or a few aberrant sample values. In cases where the aberrant sample values may have influenced the %RSD greatly, statistical outlier tests should be applied. Only 17 of the 168 estimates did not fit one of these three categories; 7 of the 17 were pH, DIC, and DOC determinations for synthetic audits and reflected sample instability or analytical problems. The NH_4^+ measurement for FLII indicated decomposition over time, which is confirmed in poor precision and accuracy. Ca exhibited similar precision and accuracy estimates for FLII. Precision for K was less than desirable for FLII, but accuracy was acceptable (+6.4%) at a concentration of 0.22 mg/L.

Only six variables among the four lots of field natural audits exhibited high variability (imprecision) that was difficult to explain; however, accuracy cannot be determined reliably from natural audit sample data. For FN5, initial and air-equilibrated DIC, conductance, and NO_3^- were highly variable (see Table 26). For conductance, the 6.4 %RSD is well above the intralaboratory precision DQO; however, because the standard deviation is only 1.1 µS/cm, a high precision estimate should be of little concern to the data user. For FN4, extractable Al values ranged from 0.106 to 0.315 mg/L, which is a large spread in the data for a sample size of 20. The sources of variability are not known, but they could be contamination, poor laboratory technique (i.e., extraction), problems with instruments or problems with methods. Fortunately, 99 percent of the WLS-I lake samples collected had extractable Al concentrations below 0.050 mg/L; therefore, imprecise measurements at the extractable Al concentrations found in FN4 should not be of concern to the WLS-I data user. Of all the analytes, SiO_2 appears to be the most variable. SiO_2 values for FN3 and FN4 had less than desirable precision (see Table 26), and the FL12 accuracy value for Laboratory I is slightly outside the desired range (see Appendix G, Table G-2).

Field audit precision data for the field laboratory determinations of pH, DIC, true color, and turbidity indicate no systematic problems in any of the five field laboratories. In most cases, even the pH and DIC precision estimates for synthetic audits are acceptable, which indicates that the variability of these measurements for synthetic audits increases with time; specifically, the difference can be attributed to the time elapsed between analysis in the field laboratory and in the analytical laboratory.

General conclusions that can be drawn regarding the audit sample data are as follows:

1. The field audits are essential to daily QA operations and laboratory monitoring, and they provide evidence on which to base requests for reanalysis.

2. Most of the precision estimates are at or near the DQOs for precision, are too low in concentration to allow precision to be estimated reliably as %RSD, or had one or a few values that were responsible for the poor precision estimates.

3. The analyte that shows the most variability in precision and in accuracy is SiO_2. Whether this variability is attributable to method, procedure (e.g., poor digestions), or contamination is not known. Extractable Al also shows poor precision, but levels of extractable Al were extremely low in WLS-I lake samples.

4. Synthetic audits are useful in estimating accuracy and precision, but the precision and accuracy values for some synthetic audit variables may not be reliable. DIC and pH seem to be unstable over time, even after equilibration; conductance, ANC, BNC, and DOC also have inherent problems when theoretical or true values are determined. Precision and accuracy for Fe and extractable Al are in question because of the instability of these analytes in the audit solution. The accuracy data for the remaining 14 analytes are acceptable overall when compared to the DQOs; however, total Al and total P are exceptions (see Table 29). The inaccuracy estimated for these two analytes, however, may be a function of their low theoretical concentrations. Ca values suggest inaccuracy for one laboratory but not for the other, and not for the data pooled. This evidence may relate to a laboratory bias problem.

5. The results and conclusions regarding relative interlaboratory bias are discussed in Permutt et al. (Appendix I of this report). In general, these results indicate statistically significant bias between analytical laboratory measurements for most analytes. An analyte-by-analyte inspection of the audit sample data (Appendix I) shows that it is difficult to interpret these biases in terms of quantifying the differences over the range of concentrations for the routine samples. In many cases, the percentage of bias between the analytical laboratories is large only because the mean analyte concentration is small for the

audit lot. In other cases, the percentage of bias is different at different mean concentrations. In some cases, the percentage of bias is different at the same mean concentration; and, in some cases, one laboratory is biased high at one audit lot mean concentration and low at a different mean concentration. In addition, one laboratory may have analyzed a larger percentage of the audit sample lot population, thus weighting the results. Depending on the analyte, such situations can confound the ability to quantify interlaboratory bias. Because these biases are relative and often are lot-specific, data calibration between laboratories was not performed. The WLS-I QA audit sample program was not designed to do this *a priori*. This report provides the statistical data (Appendix I) in the event that the data user wishes to assess biases for individual laboratories or for analytes within specific concentration ranges or subregions.

6. Audit sample preparation appears to have added only minimal variability to the analytical precision, and the procedure of preparing natural audit aliquots en masse appears to be effective; however, within the scope of the QA program, there is no effective way of quantifying the contribution that audit sample preparation makes to variability. Designers of future surveys may want to include a mechanism for determining such variability. Accuracy calculated from synthetic audit data indicates that the stock concentrates were prepared properly and that the subsequent dilution procedure was performed correctly.

7. Field laboratory performance shows negligible variability across all audit lots. The estimated precisions for DIC and pH were as good as or better than the counterpart measurements in the analytical laboratories. This observation regarding DIC and pH indicates that time, increased handling, and exposure to the atmosphere may have a small but detectable effect on the amount of CO_2 in a sample, especially for the synthetic audits. Measuring precision for true color and turbidity is hindered by inherent problems. Because turbidity is measured on unfiltered samples for lake water analysis, a direct comparison (with the use of filtered natural lake water audits or with synthetic audits using reagent-grade water) raises questions about the validity of the precision estimates. Duplicate sample pairs are a more appropriate tool for estimating the precision of turbidity measurements. Meaningful quantification of the true color precision estimates was hindered by the fact that only one audit (FN4) has a mean value above 5 PCU, at about 20 PCU. Because color determinations are quantified in increments of 5 PCU, variability of 1 or 2 increments can indicate poor precision when, in fact, the incremental precision is good. With this in mind, precision of the true color measurements was reasonable in comparison to the DQO for this determination.

A key concept is that precision is dependent on concentration. Once the concentration levels of interest for each variable have been established, the composition of the audit samples must be scrutinized. The precision for a variable from one audit sample lot can be used in conjunction with the precision for the same variable from a different lot if the concentration levels carry different importance for specific applications. Combining this information with the precision estimates provided from duplicate sample analysis gives a more complete picture of overall data quality (see Appendix J).

Pooling the data from the analytical laboratories is useful for an overview of survey analytical precision. Looking at the precision separated by laboratory, on the other hand, is helpful in quantifying bias. For example, Laboratory I analyzed most of the samples from subregions 4D and 4E, and Laboratory II analyzed the samples from subregions 4A, 4B, and 4C. If the audit samples showed significant interlaboratory bias, the bias would indicate biases in the subregional population estimates as well. No adjustment was made for bias in part because of some limitation in the data to do so (see Permutt et al., Appendix I). A synthetic audit program that employs samples that are more representative of the entire routine sample concentration range is needed to better quantify the interlaboratory bias in terms of accuracy (the deviation from a theoretical or true value) so that the data can be adjusted confidently. This process can be accomplished by varying analyte concentration in the synthetic aduit sample lots so that they represent the range of routine sample concentrations. Natural audit samples cannot be used for this purpose because they can only be used to estimate relative biases. The more intensive programs implemented in subsequent NSWS programs (i.e., ELS-II Fall Chemistry Survey) employ synthetic audit sample lots that have different concentration increments for each analyte to cover the expected range of routine samples. These synthetic audits are laboratory audit samples, which are more useful in assessing interlaboratory bias in absolute terms than are field audit samples.

Field audit samples include the variability introduced in the field laboratory as a result of sample processing. In WLS-I, the field laboratory variability was spread among five field laboratories. Laboratory audits, which were not used in WLS-I, were not subject to the field laboratory variability; therefore, they were more appropriate for determining analytical laboratory bias. Laboratory synthetic audits also did not exhibit instability with extractable Al and Fe, as

field synthetic audits did, because the holding time between sample preparation and preservation was reduced from about 24 hours to 2 hours (Best et al., 1987).

The final step in evaluating the success of the audit sample programs used in ELS-I and WLS-I is to establish DQOs specific to these QA samples. These DQOs can be determined only when the needs of the individual data user are known. These needs are based on the answers t o several questions: Do the data generated from the audit programs suit the needs of the data user? That is, are the precision and accuracy adequate for the intended data interpretations? If the precision and accuracy are adequate, are they adequate at all the concentrations of interest, or are "sliding-scale" DQOs required for different concentration ranges? If the precision and accuracy are not adequate, what methodological or procedural changes are necessary to produce data of the necessary quality?

Section 8
Results and Discussion - Detectability

Introduction

To answer questions related to detectability and sample contamination, the WLS-I sampling design employed three types of blank samples: field blanks, trailer blanks, and calibration or reagent blanks (see Figure 3 in Section 3). Data from these blanks were used to establish three major statistical limits: the system detection limit, the system decision limit, and the instrument detection limit. Together, the blank data and these limits, calculated from that data, provide information on detectability. A fourth statistical limit, the quantitation limit, can be derived from blank data as well, but this limit is used in estimating precision (see Section 6). Plots showing blank sample data results for each analyte are given in Appendix J.

All types of blank measurements are compared to the required detection limits (see Table 2), which are the DQOs for laboratory detectability. The required detection limit is the highest instrument detection limit allowable in the analytical laboratory contract. Laboratory blanks, which are used to calculate instrument detection limits, are the only blank samples that apply directly to required detection limit criteria. The relation of blank sample data to the associated statistical limits and the required detection limits is discussed below and is illustrated in Figure 10. The discussion also shows how blank sample data relate to lake sample data.

Method of Estimating System Detectability from Field Blank Measurements

During WLS-I, 236 field blanks were used in estimating cumulative (system) background noise and contamination levels that were inherent in WLS-I sampling and analytical methods (i.e., all the components of variability or contamination that can affect a routine lake sample from the time it is collected until the final data are reported; see Figure 3). Contamination is most often caused by the extensive sample handling that field blanks (and lake samples) undergo.

Field blanks also can be used to detect positive and negative bias that results from analytical drift associated with poor instrument calibration. A negative instrument response derived from a field blank or routine sample directly relates to analytical instrument calibration, not field contamination (except for ANC and BNC). Field blanks, however, cannot indicate degradation of an analyte in a water sample (e.g., precipitation or oxidation-reduction); it is necessary to rely on field duplicate pairs and on field audit samples (see Sections 6 and 7) for this purpose.

System Decision Limit

One method of evaluating analytical detectability and levels of contamination in the field samples is to calculate the system decision limit, which uses a nonparametric statistical analysis of all the WLS-I field blank samples. The system decision limit is defined as the 95th percentile (P_{95}) of the distribution of field blank values (see Permutt and Pollack, 1986, Appendix A in Best et al., 1987; see also Figure 10). The system decision limit provides an estimate of the level of an analyte that potentially can be introduced during sample collection, handling, processing, and analysis. For measured values below this limit, it cannot be known with certainty (i.e., 95% confidence) whether the analyte was present in the lake or was introduced at some stage of handling. Thus, when the analyte concentration of a routine sample is at or below the system decision limit, it cannot be distinguished confidently from the system background shown in the field blanks. Analyte at a concentration above the system decision limit is not system background noise. The system decision limit for each WLS-I analyte, based on the analysis of the 236 WLS-I field blanks, is given in Table 31. Field blank measurement data are presented by analytical laboratory in Appendix D, Table D-1, and are illustrated in Appendix J.

System Detection Limit

The system detection limit is the highest concentration of an analyte that could be present in a lake water sample in which the analyte was not detected. Any measured concentration less than the system decision limit should be considered "not

Figure 10. Relation of statistical limits to data derived from blank samples, Western Lake Survey - Phase I.

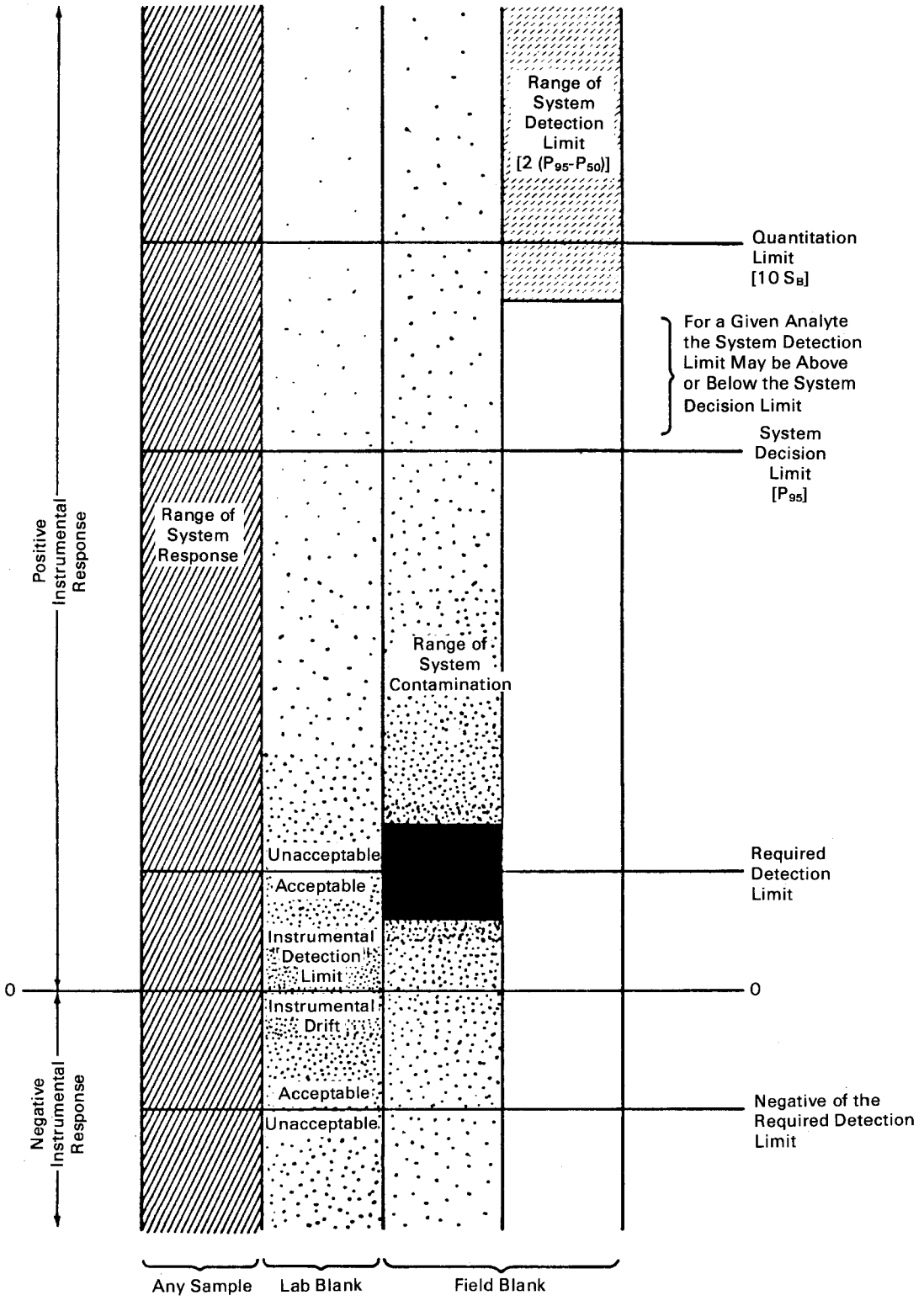


Table 31. Required Detection Limits, System Decision Limits, and System Detection Limits for all Variables, Western Lake Survey - Phase I

Variable[a]	Required Detection Limit	System Decision Limit (P_{95})[b]	System Detection Limit 2 (P_{95} - P_{50})[b]
Al, extractable	0.005	0.004	0.006
Al, total	0.005	0.019	0.020
ANC (μeq/L)	10.0	3.9	5.2
BNC (μeq/L)	10.0	29.8	22.2
Ca	0.01	0.07	0.12
Cl^-	0.01	0.04	0.08
Conductance (μS/cm)	c	1.6	2.0
DIC, air equilibrated	0.05	0.33	0.26
DIC, initial	0.05	0.43	0.50
DOC	0.1	0.3	0.3
F^-, total dissolved	0.005	0.003	0.004
Fe	0.01	0.01	0.03
K	0.01	0.01	0.02
Mg	0.01	0.01	0.01
Mn	0.01	0.01	0.03
Na	0.01	0.01	0.03
NH_4^+	0.01	0.01	0.02
NO_3^-	0.005	0.071	0.126
P, total	0.002	0.006	0.010
pH, acidity	N/A	N/A	N/A
pH, alkalinity	N/A	N/A	N/A
pH, air equilibrated	N/A	N/A	N/A
SiO_2	0.05	0.18	0.26
SO_4^{2-}	0.05	0.07	0.11

[a] All variables were measured in mg/L unless otherwise noted.
[b] P_{95} is the 95th percentile of 236 field blank measurements; P_{50} is the 50th percentile of 236 field blank measurements.
[c] The mean of six nonconsecutive blank measurements was required to be < 0.9 μS/cm.
N/A = not applicable.

detected." The true concentration, in such a case, could be as low as zero and as high as but no higher than the system detection limit at the 95 percent confidence level. The system detection limit is calculated as 2 (P_{95}-P_{50}), where P_{50} is the 50th percentile of the distribution of field blank measurements. Permutt and Pollack (1986) in Best et al. (1987) discuss further the statistical basis of the system detection limit calculation. System detection limits for WLS-I variables are given in Table 31. The system decision limit (P_{95}) is most useful in estimating background contamination. The system detection limit, however, can aid the data user in determining whether or not background contamination greatly affects precision (Section 6) and accuracy estimates (Section 7) for audit lots that have low analyte concentrations.

Detectability Results Estimated from Field Blank Measurements

Results of the field blank analyses indicate that there was no significant contamination for any variable that would affect population estimates; however, each data user must assess the contamination levels to suit the specific purpose. Random contamination as a result of sampling, processing, or analytical error may have caused the system decision limit to exceed the required detection limit for some variables. For most variables, the system decision limit was less than or near the required detection limit. Variables for which the system decision limit was higher than the required detection limit include total Al, BNC, Cl^-, initial and air-equilibrated DIC, and DOC. For these variables, however, the system decision limits are comparable

to the field blank values from ELS-I (see Best et al., 1987).

For three other variables (Ca, NO_3^-, and SiO_2), the system decision limits were outside the acceptable ranges. The system decision limit for NO_3^- was 0.071 mg/L. The system decision limit for Ca was 0.07 mg/L; for SiO_2 it was 0.18 mg/L. Therefore, there is at least a 5 percent chance of introducing contamination at concentrations above these limits for NO_3^-, Ca, and SiO_2.

Possible explanations for the high background concentrations for these three analytes include:

- High concentrations of Ca and SiO_2 could have been caused by (1) incomplete rinsing of the sampling apparatus, (2) incomplete rinsing of the filtration apparatus, or (3) instrument response (carryover) from one sample to the next.
- Nitrate concentrations (a mean of 0.105 mg/L) in WLS-I routine lake samples were relatively low. Therefore, carryover was probably not a significant factor in field blank sample concentrations. There is an indication that elevated NO_3^- concentration levels might have been introduced in the field laboratory (see Appendix J, Figure J-19a).

The concentrations of Ca and SiO_2 in the WLS-I lakes (each with a mean of about 3.7 mg/L) indicate that field blank sample contamination (0.07 and 0.18 mg/L, respectively) was relatively insignificant; therefore, the effect that the background concentrations have on population estimates should be negligible. Nitrate, in contrast, was not abundant in WLS-I lake samples; therefore, the high NO_3^- field blank sample concentrations could be significant in relation to the routine lake samples. Since NO_3^- was not a major contributor to the anion sum, the background concentration levels should be insignificant in determining population estimates. The significance of these concentrations, however, should be assessed by the individual data user (see Appendix K).

Comparison of Results for Field Blank Samples Collected by Helicopter Crews and Ground Crews

The differences between the sampling methods used by the helicopter crews and the ground crews were of great interest and concern. (See Section 9 for a discussion of calibration study results.) Also of interest were ways in which contamination levels introduced into the lake samples might have differed between methods. Table 32 shows the mean and standard deviation of the field blanks collected by the helicopter crews and the ground crews. The data indicate that there was no practical difference in the level of contamination or in the variability in blank collection between methods for any analyte measured. The data are also consistent with the results for system detectability for all field blanks combined. The comparability of blank values for the two sampling methods is excellent considering the number of individuals who were involved in collecting samples (60 ground crews and 7 helicopter crews). Therefore, regardless of sampling method, the blank collection procedure appears to be highly efficient.

Method of Estimating Detectability from Trailer Blank Sample Measurements

Trailer blanks were not used regularly as QA samples in WLS-I. Although useful information on analytical performance can be obtained from the standard use of trailer blanks, for WLS-I these samples were used only when deviations from the normal sampling and batch design occurred (e.g., when the ground crew did not collect a field blank and the helicopter crew did not sample on that day). For comparison, 236 field blanks were collected during WLS-I; only 22 trailer blanks were used. Because WLS-I employed only 22 trailer blanks, separate statistical criteria were not used for field blanks and trailer blanks when trends and systematic contamination were evaluated during data verification.

Trailer blank samples have a purpose similar to that of field blank samples. The difference between the two blank sample types is that contamination levels detected from trailer blanks do not include the effects that the entire system has on variability because they originate at the field laboratory rather than at the lake site. Consequently, they are not carried through any of the steps in the sample collection procedure and are expected to have lower background levels. Any statistical conclusion derived from the trailer blanks relates solely to analytical detectability, i.e., variability contributed by field laboratory and analytical laboratory activities combined. It follows that any negative response is an instrument calibration problem (bias) rather than a contamination problem because negative analyte contamination cannot exist (except for ANC and BNC).

Detectability Results Estimated from Trailer Blank Sample Measurements

The results for trailer blank sample analyses are presented in Appendix D, Table D-2 and in Appendix J as the median (P_{50}) and 95th (P_{95}) percentile of the measurements. Trailer blank samples indicated background contamination above the required detection limit for six of the variables studied. Slight contamination was indicated for BNC, Ca, and total P. However, the only analytes that showed systematic contamination at levels well above the required detection limit were Cl^-, NO_3^-, and SiO_2. For Cl^-, 95 percent of the lakes sampled had analyte concentrations above the P_{95} of the trailer blanks.

Table 32. Evaluation of Field Blank Data by Sampling Method, Western Lake Survey - Phase I

Variable[a]	Field Blank Samples Collected by Helicopter Crews (n = 124)		Required Detection Limit	Field Blank Samples Collected by Ground Crews (n = 112)	
	Mean Concentration	Standard Deviation[b]		Mean Concentration	Standard Deviation[b]
Al, extractable	0.000	0.0022	0.005	0.001	0.0020
Al, total	0.009	0.0099	0.005	0.008[c]	0.0067
ANC(μeq/L)	1.1	1.92	5.0	1.2[c]	3.02
BNC(μeq/L)	17.4	8.00	5.0	17.7[c]	10.47
Ca	0.022	0.028	0.01	0.026	0.032
Cl^-	0.008	0.012	0.01	0.014	0.028
Conductance (μS/cm)	0.7	0.55	0.9	0.8	0.67
DIC, air equilibrated	0.22	0.077	0.05	0.19	0.058
DIC, initial	0.18	0.093	0.05	0.22	0.161
DOC	0.15	0.24	0.1	0.15	0.14
F^-, total dissolved	0.001	0.00097	0.005	0.001	0.0021
Fe	0.003	0.0071	0.01	0.002	0.0070
K	0.002	0.0085	0.01	0.002	0.0077
Mg	0.002	0.0026	0.01	0.002	0.0042
Mn	-0.001	0.011	0.01	-0.002	0.0096
Na	0.001	0.022	0.01	-0.001	0.0086
NH_4^+	-0.005	0.011	0.01	-0.007	0.014
NO_3^-	0.015	0.033	0.005	0.018	0.035
P, total	0.001	0.0040	0.002	0.001	0.0046
pH, acidity (pH units)	5.67	0.058	--	5.66	0.084
pH, alkalinity (pH units)	5.66	0.053	--	5.63	0.079
pH, air equilibrated (pH units)	5.72	0.151	--	5.70	0.058
SiO_2	0.08	0.125	0.05	0.076	0.271
SO_4^{2-}	0.02	0.040	0.05	0.030	0.070

[a] All variables were measured in mg/L unless otherwise indicated.
[b] Although nonparameteric tests are useful in determining contamination effects on samples, means and standard deviations are useful in comparing the sampling ability of one method with that of the other method.
[c] n = 111

SiO_2 was found at relatively high concentrations in the routine lake samples. Therefore, the slight contamination should have little effect on the routine sample concentrations or on subsequent population estimates for Cl^- and for SiO_2. The contamination of NO_3^- in the field and trailer blanks may have resulted in part from field laboratory activities. This is plausible, because HNO_3 is used as a standard laboratory preservation and cleaning reagent. Some aerosol or vapor generated from processing laboratory procedures may have affected some blank measurements.

Method of Estimating Detectability from Calibration Blank and Reagent Blank Sample Measurements

The third type of blank sample employed in WLS-I was the calibration blank. Analytical laboratory calibration blank analyses are useful in determining instrument performance capability and instrumental drift. Their use is limited to evaluating performance in the laboratory only. Calibration blanks were analyzed after daily instrument calibration and before analysis of lake water samples as a check on instrumental

drift. In the field laboratory, calibration blanks were used in the calibration of the carbon analyzer. In the analytical laboratory, calibration blanks were analyzed for every variable except ANC, BNC, air-equilibrated DIC, and all pH measurements. Digestion procedures were performed before analysis of total Al and SiO_2; this procedure required that reagent blanks be analyzed and used in the same capacity as calibration blanks.

Determining Instrument Detection Limit

Calibration and reagent blanks were used in two facets of analytical instrument detection. The first facet, dictated by the SOW, required the analytical laboratory to determine and report instrument detection limits at periodic intervals during the survey. This exercise consisted of analyzing 10 nonconsecutive, replicate calibration blanks, then determining the value for three times the standard deviation of the 10 measurements. These 10 measurements were taken on one day (i.e., on one calibration curve). The result had to equal or be less than the required detection limit (see Table 31 and Figure 10). Drousé et al. (1986) provide a detailed discussion of the instrument detection limit calculation. The instrument detection limit is useful in determining the lowest possible concentration at which an instrument can detect the analyte. Attaining instrument performance at this level indicates that contamination introduced at the analytical laboratory could be minimal if the conditions under which the instrument was calibrated remained constant. (Appendix D presents the instrument detection limit data.)

The second facet required that the analytical laboratory assess the laboratory blank data by observing the distribution, the median (P_{50}, 50th percentile), and the 95th percentile (P_{95}) of the daily calibration blank data. These data characterize the distribution of calibration blanks that were analyzed day-to-day, once per batch, during the course of the survey. Comparison of these data to the required detection limit differs from similar comparisons for the instrument detection limit in two ways: (1) each calibration blank was analyzed on a different calibration curve; day-to-day variability is expected to be higher than the variability of blanks analyzed on the same curve, and (2) the concentration for each calibration blank used in daily instrument calibration could be as high as two times the required detection limit according to the SOW.

Like the measurements of field and trailer blanks, the P_{95} of the calibration blank measurements can alert the data user to contamination or instrumental drift that could affect the routine lake sample concentrations. The P_{95} also provides detectability data that eliminate the effects of sample collection, processing, and shipping on the routine samples. Because field blanks were subject to more handling (and thus to more sources of error) than were calibration blanks, variability in field blanks was expected to be higher than in calibration blanks. The data user may find it informative to refer to the P_{95} of the calibration blanks as an "analytical decision limit" in a comparison with the P_{95} of the field blanks (the system decision limit). (See Appendix J for a comparison of the distribution of all blank sample types.)

Detectability Results Estimated from Calibration and Reagent Blank Sample Measurements

In all cases for all analytes, the DQO for instrument detectability was met by each WLS-I analytical laboratory. The instrument detection limit was consistently at or below the required detection limit, which indicates that the analytical laboratory instrumental response did not contribute significantly to the background levels, and, therefore, had little or no effect on the routine samples.

The concentration levels of the daily calibration blanks from each analytical laboratory were always within the criteria (two times the required detection limit) set forth in the SOW. This indicates that daily instrument calibration resulted in negligible background contamination.

Matrix Spike Sample Results

A final component of detectability in the QA analysis of WLS-I data is the evaluation of matrix spike samples. The criterion for the matrix spike QC check, which was applied to 15 variables, was 100 ± 15 percent spike recovery, which was calculated as follows:

$$\frac{\textit{concentration of spiked sample} - \textit{spike concentration}}{\textit{original sample concentration}} 100$$

The overall results (Table 33) indicate that matrix effects produced minimal, if any, interference with routine sample analysis. This indicates that sample matrix did not affect instrumental detection of analytes.

Table 33. Results of Matrix Spike Percent Recovery Analysis[a], Western Lake Survey - Phase I

Variable	Number of Batches for which Criteria Not Met (n = 149)	% of Batches	Number of Samples Affected (n = 1,642)	% of Samples
Al, total	1	< 1%	10	< 1%
Ca	2	1.5%	25	1.5%
Cl^-	0	0	0	0
DOC	0	0	0	0
F^-, total dissolved	0	0	0	0
Fe	0	0	0	0
K	0	0	0	0
Mg	0	0	0	0
Mn	7	4.6%	117	7.1%
Na	0	0	0	0
NH_4^+	8	5.4%	102	6.2%
NO_3^-	1	< 1%	17	1.0%
P, total	0	0	0	0
SiO_2	0	0	0	0
SO_4^{2-}	0	0	0	0

[a] Matrix spike recovery analysis was applied only to the 15 variables listed above.

Section 9
Special Studies

Calibration Study

Introduction

As a part of the overall WLS-I sampling and analytical strategy, a subset of WLS-I lakes was sampled in a calibration study. The study included 50 of the 455 wilderness-area, roadless-area, and national park lakes that were selected for study in WLS-I and that were targeted to be sampled by ground crews only. The 50 calibration study lakes represented a random sample of the WLS-I wilderness-area lakes. 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 50 lakes so that the established sampling method (helicopter access) could be compared to the new method (ground access). A detailed discussion of calibration study lake selection can be found in Landers et al. (1987).

Data derived from the chemical analyses conducted during the calibration study were used to perform calibration by linear regression (see Appendix A in Landers et al., 1987). These calibration data were intended to be applied to analytical values reported for all WLS-I samples that were collected by the ground crews. The calibrations by regression were designed to eliminate value differences that resulted from variations in sampling protocol, sample holding time, or laboratory bias. The regression analyses and the significance of those analyses are discussed in Landers et al. (1987); the goals and design of the calibration study are presented in Silverstein et al. (1987) and are summarized below.

The calibration study was designed to meet three goals:

1. Detect differences between two sampling methods.
2. Evaluate the effects of holding samples for different lengths of time before they were processed (preserved) and analyzed.
3. Detect interlaboratory bias between the two contract analytical laboratories that analyzed WLS-I samples.

Sampling Design

Comparison of Sampling Methods--

For the WLS-I calibration study, an established sampling method (helicopter-access sampling protocols used during ELS-I) was compared to a new sampling method (ground-access sampling protocols not previously tested for NLS). Each calibration lake was sampled by one helicopter crew and by one ground crew. The two crews collected samples from approximately the same location (the perceived deepest spot) on the lake. The plan called for the ground crew to sample the lake first, and the helicopter crew to sample the lake as soon as possible thereafter (optimally, within 1 hour). The ground crew collected a routine sample and a duplicate sample; the helicopter crew collected a routine sample, a duplicate sample, and a triplicate sample. Both types of sampling crews used sample collection techniques standard for all WLS-I lakes.

To ensure that each ground crew's sampling procedure would be representative of all WLS-I lakes sampled, the ground crews were not told which lakes were calibration lakes. Because the helicopter sample collection procedure was tested and proven in ELS-I, there was no need to conceal the identity of calibration lakes from the helicopter crews. Some minor modifications were made to the ELS-I helicopter sampling protocol for WLS-I (Bonoff and Groeger, 1987), but these modifications did not affect the method used to collect lake samples (collecting lake water through a Van Dorn sampler).

When the sampling scenario was designed, there was an indication that the samples collected by the ground crews might arrive at the field laboratory from 1 to 5

days after they were collected. As a result of this indication, the possible effects of delayed sample preservation (or "holding time") were of interest. Processing procedures were designed to account for possible delays in delivering samples from the lake site to the field laboratory and were used to observe the effects of different holding times. Each procedure assumed a different relationship of the sampling time to the arrival time of the helicopter crew's samples and the ground crew's samples at the field laboratory.

The field laboratory personnel preserved the ground crew's samples on the date they were received and preserved two of the helicopter crew's samples on the date they were received. The third sample collected by the helicopter crew was not preserved immediately. Instead, this sample, which was selected randomly from among the helicopter crew's three samples, was held at the field laboratory at 4°C in the dark for a specified length of time before it was processed and preserved. The holding time for the withheld sample depended on which processing procedure applied (See Figure 11). Sample processing and preservation procedures used for calibration lake samples are discussed further in Silverstein et al. (1987) and in Kerfoot and Faber (1987).

Comparison of Analytical Laboratories--
The calibration study also was designed to provide data that could be used to evaluate differences between the analyses performed by the two analytical laboratories. To meet this goal, the survey design called for the field laboratories to randomly assign all calibration-lake samples for shipment to the analytical laboratories. The assignments were designed to ensure that, for each calibration lake, one of the two samples collected by the ground crew and one of the three samples collected by the helicopter crew would be sent to each analytical laboratory. The results of analyses of potential bias are presented in the following discussion and in Table 34 (later in this section); a more detailed discussion concerning the effect that these results may have on population estimates appears in Landers et al. (1987).

Design Modifications

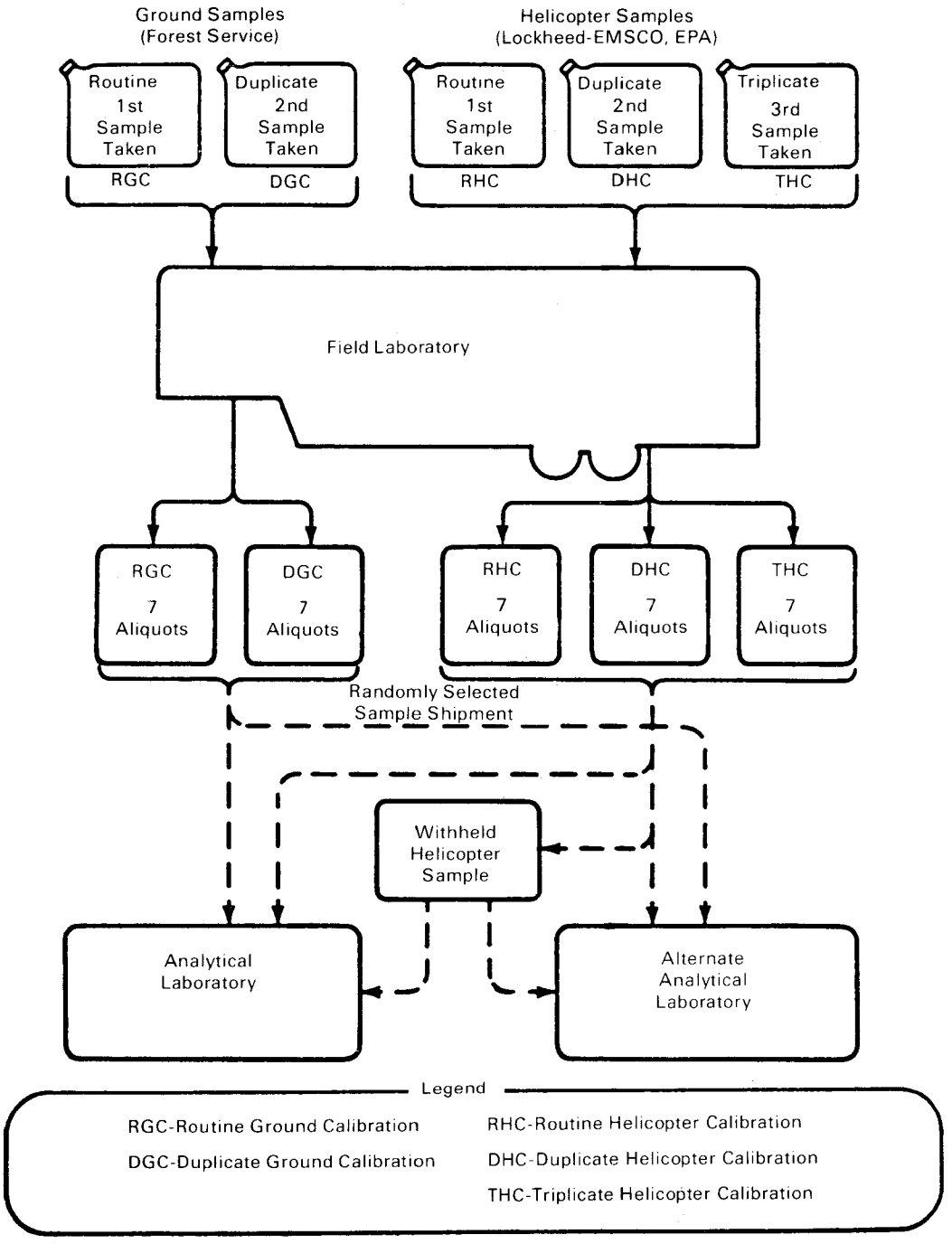
The calibration study originally was called the comparability lakes study. During the survey, the lakes to be sampled were referred to as comparability lakes, a term that appears in many of the early internal documents. After the survey, the official name of the study was changed to describe correctly the purpose of the study. Although the study did compare two sampling methods, the primary purpose was to determine whether or not there were systematic differences in the sampling methods or in the analytical laboratory performance and, if so, to develop factors that would allow the data from the two ground-access samples to be calibrated to the data from the helicopter-access samples.

Modifications to the sampling design and survey protocols limited the number of calibration lake samples that could be used for statistical comparisons. The design of the calibration study called for 50 lakes (9 to 12 per subregion) to be sampled. Of these 50 lakes, 5 were not sampled. All five of the lakes were in subregion 4D (Bozeman, Montana, field base). Three of these lakes were frozen, one was too shallow, and one was inaccessible from the ground. The inaccessible lake (Red Rock Lake; ID 4D2-006), was sampled by a helicopter crew, but weather and trail conditions prevented the lake from being sampled by the ground crew. Because no comparison could be made between sampling methods, data for this lake were deleted from calibration study statistics; however, they were included in the routine statistics for WLS-I samples collected by helicopter.

Ground crews at the Carson City field base (subregion 4A) were told inadvertently which lakes were part of the calibration study. As a result, some new lakes had to be selected for the study, and seven of those lakes were not sampled in duplicate. However, all helicopter crews collected all three samples as per original protocol. The loss of these seven lakes from the statistical analysis was not considered as crucial as ensuring that the ground crews could not identify lakes as calibration study lakes. Therefore, of the 45 calibration lakes sampled, only 38 were used in the determination of calibration for sampling method or for laboratory bias (Landers et al., 1987). In most cases (23 of the first 28 lakes sampled), samples collected by the ground crews arrived at the field base on the day they were collected, so there was no holding-time consideration. As a result, an artificial holding time was used for some subsequent samples so that sufficient data would be available to allow comparison of differences in sample concentration as a result of different lengths of time before preservation.

All of the combinations of sample collection dates, holding times, and different analytical laboratories took considerable coordination among personnel at each field base and among field bases. Scheduling dates for helicopter crew and ground crew sampling was a difficult and intricate task. Because the calibration lakes were in wilderness areas, many of the lakes were difficult for ground crews to reach. Ensuring that helicopter and ground crews could sample the same lake on the same day was difficult, especially when weather conditions were poor. Successful timing required constant radio communication and constant rescheduling of daily sample itineraries. Two-thirds of the lakes sampled (30 of 45) were sampled on the same day by both crews. In many of the remaining cases, the weather

Figure 11. Sample flow for the calibration study, Western Lake Survey - Phase I.



was such that the helicopter could not fly, yet the ground crew was already on its way to the lake. In these cases, the ground crew could not be called back without identifying the lake as a calibration lake and thereby jeopardizing the integrity of the study. Consequently, 14 of the lakes were sampled one or more days earlier by the ground crews than by the helicopter crews (see the detailed discussion on sampling times later in this section). Close communication between field bases also was essential to ensure that calibration lake samples were inserted in the proper batches and were sent to the proper analytical laboratories. The laboratory coordinator had to maintain daily contact with the

communication center and the QA staff in Las Vegas to coordinate protocol changes and shipment of the calibration study samples to the appropriate analytical laboratory.

Verification of Calibration Lake Data

Calibration lake samples were tracked and evaluated as a separate data set because there was concern that these samples could not be used to check precision in the same way that field duplicate pairs were used. The calibration lake study provided five samples from each lake (routine, duplicate, and triplicate samples collected by the helicopter crew and routine and duplicate samples collected by the ground crew). Duplicate samples taken for the calibration study were not used as QA samples because sampling methods, holding times, and batches often differed for the five comparable samples collected from one lake. Therefore, flags were not generated from calibration lake samples the way flags were generated for standard duplicate pairs. All five samples from each lake were compared to each other visually, however, to check for outlier values or reporting errors. In addition, the QA staff performed standard verification checks for ion balance, conductance, and protolytes for each calibration lake sample. In that regard, calibration study lake samples were treated like any other individual sample in the survey. These samples also received tags and flags applicable to the batch in the same manner as routine samples received tags and flags.

Determination of Sampling Method Bias

A primary objective of the calibration study was to determine whether data collected by the ground crews, in either the calibrated or the unadjusted form, were accurate enough to be included in the WLS-I data base. This determination was intended to show that these data could be used in estimating populations for wilderness-area lakes. The management team was concerned that if variables with large systematic error were included in the data base, they would bias the overall survey results significantly.

Preliminary statistical analyses showed that the data on samples collected by the ground crews were of suitable quantity and quality to permit calibration analyses to be performed (Landers et al., 1987).

Sampling method, lake sampled, analytical laboratory, and 2-way interactions of these three factors were tested with an analysis of variance (ANOVA) with interaction. The null hypothesis of no difference is expected to be rejected when it is in fact true 1 time in 20 (Snedecor and Cochran, 1967). The ANOVA results are given in Table 34. For 1 of 24 analytes ($N0_3^-$) the data collected by ground crews were significantly different from the data collected by helicopter crews. Samples showed such low concentrations for NO_3^- that precision was poor for both sampling methods. The relative error for NO_3^- was large; however, the absolute error was small. Therefore, the method of sample collection did not have an overall significant effect on WLS-I data. Analysis of the calibration study data is also presented in Appendix A of Landers et al. (1987). On the basis of that interpretation of the data, and decision criteria outlined there, it was determined that the ground-access data were as acceptable and usable as the helicopter data without performing calibrations for any analyte. Although some differences in the two sampling methods were detected, the practical differences between the two methods were not significant (i.e., slope of 0.99 versus 1.00). When a large relative difference was detected, the absolute difference was small, usually as a result of low sample concentrations that confounded the results. Differences that predicted helicopter-access data from ground-access data could not be detected when the imprecision of the measurement of the analyte was greater than the difference in the sampling method. Therefore, although decision criteria indicate that some statistical benefit may have been shown, there was no practical benefit to calibrating the data.

Determination of Relative Bias Between Analytical Laboratories

The calibration study also was used to determine whether or not a bias between analytical results reported by the two analytical laboratories existed and, if so, to what extent this laboratory bias would affect the WLS-I data base. The effect of laboratories can be evaluated with the same ANOVA with interaction (Table 34) that was used to analyze sampling method differences.

The analytical laboratories had significantly different values for 12 variables. Of those 12 analytes, the interaction between lake and laboratory was significant for all but Fe, Mn, and SO_4^{2-}. Overall, the interaction between lake and laboratory was significant for 14 analytes. Analyte concentration is site-specific. This was reflected by the fact that there was a significant difference among lakes for the concentration of 24 analytes. Only Mn did not have a significant lake effect. The low concentrations observed for Mn in all lakes in this study may account for this situation. These observations suggest that laboratory bias changed with analyte concentration.

Landers et al. (1987) analyzed the calibration lake data for relative bias between the analytical laboratories with standard and weighted regression techniques. Relative bias was found to be statistically significant for some analytes. It was concluded, however, that relative bias between laboratories was not meaningful in the context of the survey objectives for most variables. Because it is difficult to establish

Table 34. Calibration Study Regression With and Without 2-Way Interactions of Its Components, Western Lake Survey - Phase I

Variable	Laboratory (F1,37)[a]	Method (F1,37)[a]	Lake (F37,37)[a]	Laboratory by Method (F1,37)[a]	Lake by Laboratory (F37,37)[a]	Lake by Method (F37,F37)[a]
Al, extractable	198.91[b]	0.002	53.75[b]	0.004	5.89[b]	5.05[b]
Al, total	51.41[b]	0.767	54.17[b]	1.62	2.41[b]	1.18
ANC	1.40	0.09	7497.77[b]	0.10	9.91[b]	1.84[b]
BNC	36.45[b]	2.33	3.51[b]	0.74	2.80[b]	0.775
Ca	22.46[b]	0.18	26593.73[b]	0.25	48.40[b]	2.87[b]
Cl^-	1.547	0.523	62.20[b]	0.85	1.31	1.08
Conductance	1.61	0.016	1408.00[b]	2.62	1.62[d]	1.46
DIC, air equilibrated	0.915	0.669	844.89[b]	0.06	8.35[b]	0.73
DIC, initial	2.03	0.147	1999.60[b]	0.30	22.75[b]	0.82
DOC	1.40	2.57	147.53[b]	1.38	1.66[d]	1.08
F^-, total dissolved	0.306	0.067	17.97[b]	2.97[d]	1.09	1.11
Fe	24.33[b]	0.009	93.52[b]	0.00	1.36	1.55[d]
K	0.308	1.16	728.72[b]	1.18	1.22	1.16
Mg	13.81[b]	0.003	11160.91[b]	0.24	10.34[b]	2.16[c]
Mn	8.16[b]	0.465	1.31	3.21[d]	1.10	1.09
Na	0.843	1.98	2117.52[b]	1.92	2.33[b]	2.15[c]
NH_4^+	11.47[b]	4.08[d]	3.64[b]	1.78	2.18[c]	1.07
NO_3^-	0.771	6.57[c]	26.53[b]	0.63	1.36	0.88
P, total	0.21	1.14	3.59[b]	1.11	1.00	1.09
pH, acidity	98.10[b]	0.000	203.37[b]	8.34[b]	1.90[c]	1.74[c]
pH, alkalinity	29.89[b]	0.033	207.08[b]	4.59[c]	2.59[b]	1.52
pH, air equilibrated	4.28[c]	0.102	59.27[b]	0.68	2.04[c]	0.98
SiO_2	0.177	0.835	54.85[b]	1.16	3.12[b]	0.97
SO_4^{2-}	6.597[c]	0.615	473.75[b]	0.05	0.85	1.09
$P < 0.05$	12	1	24	2	14	6

[a] F-ratio is the statistical test of analysis of variance; 1,37 = degrees of freedom.
[b] $p < 0.01$.
[c] $p < 0.05$.
[d] $0.05 < p < 0.10$.

the absolute bias (accuracy) for an analyte (because neither laboratory is considered the standard), Landers et al. (1987) concluded that accounting for the observed relative bias in WLS-I requires more information than is currently available. Permutt et al. (Appendix I of this report) present similar conclusions from an analysis of data from WLS-I field audit samples.

Determination of Calibration by Linear Regression

The second objective of the calibration study was to determine whether the data on the samples collected by the ground crews could be entered directly into the final data set, or if the data needed to be calibrated before population estimates were calculated. To address this objective, linear regression techniques were used.

For 22 analytes, the difference in the bias measurements is very small. Consequently, the data were comparable, and no correction for sampling bias was applied. This conclusion also was supported by the results of field blank and field duplicate data analyzed by sampling method (see Section 6 and Section 8). For two analytes (NO_3^- and extractable Al) to which regression analysis was applied, both types of samples showed such low concentrations that precision was poor for both sampling methods. The relative error for these two variables was large; however, the absolute error was small. Therefore, there is little risk in using the ground crew sample

data for NO_3^- and extractable Al. No correction for sampling bias was applied.

Holding-Time Effects on Sample Concentration

As a part of the sampling design of the calibration study, one of the three samples collected by the helicopter crew was selected randomly to be stored (in the dark at 4°C) at the field laboratory for as long as 4 days before it was processed and preserved. The length of time that the withheld sample was kept at the field laboratory depended on the amount of time required to transport the corresponding samples collected by the ground crew from the lake site to the field laboratory. This element of the sampling design was intended to evaluate the impact of delayed sample processing and preservation that could result if the ground crews did not deliver their samples to the field laboratory on the day that the lake was sampled. The Forest Service ground crews, however, were extremely efficient in providing same-day sample delivery, even from lakes that were difficult to reach. Consequently, the number of samples for which delivery was delayed (and thus the number of corresponding withheld samples) was much smaller than had been anticipated. The number of withheld samples assigned to each holding time (i.e., the number of days it took to process the sample after collection) and the analytical laboratories to which the samples were sent are summarized in Table 35.

Table 35. Holding Times for Calibration Study Samples Analyzed by Analytical Laboratories, Western Lake Survey - Phase I

Holding Time[a] (days)	Laboratory I (No. of Samples)	Laboratory II (No. of Samples)	Total (No. of Samples)
0[b]	19	6	25
1	1	2	3
2	4	6	10
3	1	3	4
4	3	0	3
Total	28	17	45

[a] Holding time here refers to the time between sample collection and sample processing.
[b] Zero indicates that the sample was processed on the same date that the sample was collected.

For each analyte, the effects of holding time on the concentration were tested with standard linear regression. The difference between the concentration for each variable in the withheld sample and that in the other sample collected by the helicopter crew and analyzed by the same analytical laboratory was calculated. The differences were analyzed as a function of holding time by using standard linear regression. The number of days that the withheld sample was stored before it was processed and preserved was the independent variable in each regression. The dependent variable was the difference between the concentration of the withheld sample and the concentration of the other sample analyzed at the same analytical laboratory (see Figure 11).

The results of the regression analyses are presented in Table 36. A significant effect of holding time was demonstrated in only three cases: extractable Al in samples analyzed at Laboratory II ($p \leq 0.032$), air-equilibrated DIC in samples analyzed at Laboratory II ($p \leq 0.010$), and air-equilibrated pH in samples analyzed at Laboratory I ($p \leq 0.001$). For extractable Al, the effect probably was due to one exceptionally low concentration from one sample held for three days. Because values for all sample pairs in this study were near the detection limit, no conclusions can be drawn about the effect of holding time on extractable Al concentrations. For air-equilibrated DIC, the effect probably was due to one exceptionally low value for this variable analyzed in one sample held for three days. Removal of the results of the analysis on this sample, and the fact that the initial DIC regression showed no statistical significance, indicate that holding time did not affect air-equilibrated DIC concentrations. For air-equilibrated pH, the effect was due to a relatively large difference in this variable in three samples held for four days. Two of these sample pairs had differences of 0.1 pH unit. Because a difference of 0.1 pH unit is acceptable even for field duplicate pairs processed on the same day (see Table 2), it has no practical significance. The third sample pair showed a difference of 0.5 pH unit; of 45 samples, this was the only one that showed a large difference. This difference probably is attributable to random error. Therefore, a practical difference in holding time for this variable cannot be concluded from calibration study data.

Relation of Calibration Study Sampling Times and Locations

Of the 45 lakes sampled in the WLS-I calibration study, 14 were sampled one or more days earlier by the ground crew than by the helicopter crew, 1 was sampled four days earlier by the helicopter crew than by the ground crew, and 30 were sampled by both crews on the same day. Of these 30 lakes, 23 were sampled by the ground crew first. The ground crews sampled these 23 lakes 1 hour 20 minutes to 4 hours 55 minutes earlier than the helicopter crews, with a mean difference of 2 hours 57 minutes. Of the 7 times a helicopter crew sampled before a ground crew, the range was from 25 minutes to 3 hours 45 minutes, with a mean difference of 2 hours 3 minutes.

The spatial variability cannot be assessed with confidence. It is not always possible to determine that a lake was sampled in precisely the same location by both sampling methods. Nor is it certain in some cases (i.e., where several lakes were in immediate

Table 36. Regression Statistics for the Differences Between Routine and Withheld Samples Versus Holding Time by Laboratory, Western Lake Survey - Phase I

	Laboratory I		Laboratory II	
Variable	r^2	p	r^2	p
Al, extractable	0.102	0.103	0.243	0.032[a]
Al, total	0.0004	0.912	0.033	0.451
ANC	0.002	0.823	0.062	0.304
BNC	0.094	0.119	0.001	0.890
Ca	0.070	0.182	0.054	0.335
Cl^-	0.046	0.281	0.085	0.226
Conductance	0.105	0.098	0.051	0.350
DIC, air equilibrated	0.029	0.398	0.364	0.006[a]
DIC, initial	0.024	0.443	0.126	0.136
DOC	0.012	0.582	0.045	0.385
F^-, total dissolved	0.027	0.417	0.003	0.819
Fe	0.013	0.566	0.005	0.770
K	0.001	0.871	0.093	0.205
Mg	0.133	0.062	0.010	0.685
Mn	0.018	0.504	0.001	0.878
Na	0.069	0.186	0.059	0.318
NH_4^+	0.011	0.610	0.013	0.642
NO_3^-	0.004	0.754	0.055	0.332
P, total	0.008	0.667	0.083	0.231
pH, acidity	0.039	0.326	0.003	0.830
pH, alkalinity	0.024	0.440	0.005	0.781
pH, air equilibrated	0.349	0.001[a]	0.005	0.779
SiO_2	0.047	0.275	0.0003	0.945
SO_4^{2-}	0.0004	0.920	0.090	0.210

r^2 = fraction of total variance explained by the linear model.
p = statistical probability of occurrence using standard linear regression procedure.
[a] holding times with significance at $p < 0.05$.

proximity to the lake targeted for sampling) that the helicopter crew and the ground crew sampled the same lake. The analytical data indicate, however, that the correct lakes were sampled.

Summary

In general, analyses of the calibration study samples showed no significant effects of sample holding time on analyte concentration. Possible effects of holding time, however, were not adequately tested for samples with low analyte concentration (i.e., extractable Al, NO_3^-, and NH_4^+) because concentrations for these samples were near the detection limits.

Nitrate-Sulfate Stability Study

Introduction

From the onset of WLS-I, there was concern that the samples collected by the ground crews would arrive at the field laboratory days after the samples were taken. The calibration study was designed to determine the effect of the late arrival. However, there also was concern about the possible instability of nitrate and sulfate in these samples. For example, the instability could be caused by biological activity in the unpreserved samples between the time of collection and the time of processing. Therefore, a special study was conducted in which split samples were collected directly from the Van Dorn sampling apparatus to compare sample preservation methods and to study the effects of holding samples for different lengths of time before preserving them. These split samples (annotated with the code "L" on the field data forms) were analyzed for nitrate and sulfate content at EMSL-LV. The data provided an auxiliary check on sampling, processing, and analytical performance for these analytes.

Sample Processing, Preservation, and Analysis

The nitrate-sulfate split sample consisted of one 125-mL aliquot taken directly from the Van Dorn sampler after the sample syringes and Cubitainers had been filled. The aliquot was preserved with 0.1 mL of 5 percent $HgCl_2$ at the lake site. The preservative was added to stop biological activity that might occur within the split after sampling. These nitrate-sulfate aliquots were prepared by ground crews for all samples they collected (including calibration lake samples, field blanks, and field duplicates). These split samples were collected by helicopter crews at calibration study lakes only. The procedure for collection and preparation of split samples is given in Appendix L.

When the split samples arrived at the field laboratory, the laboratory coordinator assigned and recorded the batch and sample ID numbers on the upper portion of each aliquot label. The upper portion of the label was removed and was taped into the nitrate-sulfate logbook (by batch). The aliquots were then stored at 4°C in the dark until they were shipped to EMSL-LV the following day.

The field laboratory also prepared aliquots of field natural audit samples for the nitrate-sulfate study (see Appendix L). For each field natural audit sample (FN3, FN4, FN5, and FN6) the field laboratory received extra 2-L samples from Radian Corporation. For nitrate-sulfate aliquot batches, the laboratory coordinator substituted the nitrate-sulfate audit aliquots for the regular field natural audits being processed that day. Because of volume limitation and

sample instability, synthetic audit samples were not employed in this study.

On a daily basis, the nitrate-sulfate aliquot batches were shipped to EMSL-LV for analysis by ion chromatography. Samples were shipped in coolers that contained enough frozen freeze-gel packs to maintain the samples at 4°C during shipment.

Analytical Results

Systems Applications, Inc. (SAI), in San Rafael, California, performed statistical analyses to compare results for the samples preserved with $HgCl_2$ with results for the samples that were analyzed by the analytical laboratories, which used standard NSWS preservation techniques.

SAI compared the pairs of sulfate measurements and the pairs of nitrate measurements. For each comparison, the analytical laboratory sample concentration was compared to the split sample concentration. For each pair, two values were computed: (1) the signed difference between the analytical laboratory sample value and the split sample value and (2) the mean of the two values. The signed difference and the mean were used to compute the relative difference:

$$\frac{analytical\ laboratory\ value - split\ sample\ value}{mean\ of\ the\ two\ values}$$

The relative differences for both analytes are summarized in Table 37.

Table 37. Summary Statistics for Relative Differences[a] in Analyte Concentrations for the Nitrate-Sulfate Stability Study, Western Lake Survey - Phase I

	Nitrate	Sulfate
Number of Sample Pairs	918	919
Mean	1.002	-0.308
Standard Deviation	5.315	2.885
Signed Rank	139125	-39322
Median	0.628	-0.007
Lower Quartile	0.015	-0.216
Upper Quartile	1.914	-0.093
Low Extreme	-32	-50
High Extreme	91.333	9.143

[a] Relative difference equals the analytical laboratory value minus the $HgCl_2$ preserved EMSL-LV split sample value, divided by the mean of the two values.

Sulfate Stability Results--
In this study, 919 pairs of sulfate measurements were compared. The moments (e.g., mean and standard deviation) in the first part of Table 37 are not very useful because of the presence of extreme values. For example, in one pair, one negative value and one equally positive value combine to yield a small mean, and therefore, a relative difference of 50. The percentiles in the second part of the table, however, are not significantly affected by the few extreme cases.

The median relative difference is negative, about 0.7 percent, whereas the upper quartile is 9 percent and the lower quartile is -22 percent. Thus, there are considerable random differences in the pairs; the analytical laboratory value exceeds the split sample value by 9 percent or more 25 percent of the time, and the split sample value is as much as 22 percent greater 25 percent of the time. Nevertheless, the systematic difference, represented by the median, is less than 1 percent. Overall, therefore, it appears to make little difference whether or not the sulfate samples are treated with $HgCl_2$, or whether they are analyzed by the analytical laboratory or the EMSL-LV laboratory. For a given sample, however, the difference can be considerable.

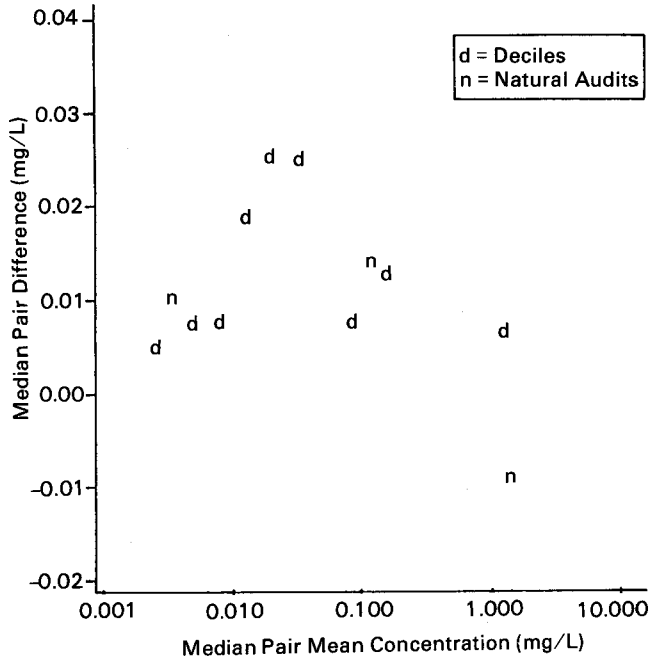
The systematic difference is statistically significant (signed-rank test, $p < 0.0001$) even though it is small. There is either a sample-handling effect or an interlaboratory bias of a fraction of a percent. Furthermore, the direction of the effect is that the split sample results are systematically higher. The effect probably has no practical significance, however, given its size and the much larger random variation. Therefore, it should not affect calculation of population estimates.

Nitrate Stability Results--
For nitrate, 918 sample pairs were compared (see Table 37). The median relative difference for nitrate is about 63 percent. Thus, 50 percent of the time, analytical laboratory measurements of nitrate concentration exceeded the split sample measurements by nearly or more than a factor of two.

Many of the measured concentrations of nitrate were near the detection limits, and even a large relative difference may not be of practical significance at very low concentrations. It is therefore desirable to explore the difference in sample concentration between the sample analyzed by the analytical laboratory and the split sample analyzed by EMSL-LV. The pairs are divided into 10 groups, or deciles. These are deciles of the distribution of the pair means. The median pair difference and the median pair mean for each decile are plotted with a "d" in Figure 12. The horizontal scale is logarithmic for convenience; therefore, the first decile, which consists mainly of blanks and has a very slight negative median pair mean, is eliminated from the graph.

In every decile except the first and the last, the nitrate concentrations measured by the analytical laboratories were significantly higher than those

Figure 12. **Relative differences in nitrate concentrations, nitrate-sulfate stability study, Western Lake Survey - Phase I. Note that two observations were out of range.**



measured by the EMSL-LV laboratory ($p < 0.0001$, signed-rank test). The median differences are largest, about 0.02 mg/L, at concentrations between 0.01 mg/L and 0.1 mg/L, where differences this large represent a substantial fraction of the concentration.

It is not easy to distinguish an effect of the $HgCl_2$ preservation from a possible relative bias between the analytical laboratories and the EMSL-LV laboratory because neither laboratory analyzed both types of samples. The natural audit samples, however, may help somewhat. These samples were stored for several weeks before they were processed and preserved. As a result, it is likely that microbiological activity had reached a steady state. Thus, the effect of preserving these audit samples with $HgCl_2$ a day or two later is of little concern when the audit sample may have been collected months earlier. Therefore, these audit samples were used as a tool to assess interlaboratory bias; their primary purpose did not include the study of the stability of nitrate over time.

A systematic difference between the analytical laboratory values and the EMSL-LV values for natural audit samples might be ascribed to bias rather than to actual change in nitrate concentrations. Furthermore, if the difference for routine lake samples were about the same as for natural audit samples, the difference in the routine samples might be ascribed to bias also.

The median pair means and median pair differences for natural audit lots FN3, FN5, and FN6 are represented in Figure 11 by the letter n. (Lot FN4 is not shown because the median difference, -0.11 mg/L, is so large that it would compress the graph severely. The median pair for lot FN4, however, is 2.35 mg/L; the apparent bias of -0.11 mg/L is an acceptably small fraction of the concentration.)

Interlaboratory bias does appear to account for some of the difference between the analytical laboratory and split sample measurements. For example, the measurements in the eighth and ninth deciles, where most of the FN5 audit values fall, were not significantly different for natural audit samples than for other samples ($p = 0.11$, rank-sum test). In the tenth decile, the FN3 and FN4 audits were significantly different from the other samples, but only by a few percent of sample concentration. In the second and third deciles, the FN6 audits were significantly different from the other samples ($p = 0.012$, rank-sum test), but these concentrations may be too low (i.e., near the instrument detection limit) to be of much interest.

None of the natural audit samples had concentrations between 0.01 mg/L and 0.10 mg/L, where the differences between the analytical and EMSL-LV laboratory measurements were greatest. The possibility that the differences were entirely due to bias cannot be ruled out on the basis of the data.

It seems likely that concentrations of nitrate near 0.02 mg/L can be produced in lake samples during an extended storage before preservation. If it is important to measure concentrations in this range accurately, special precautions such as preservation with $HgCl_2$ are indicated. In future studies, if a 0.02-mg/L difference is of concern, an additional study accounting for laboratory bias at the concentration levels of interest must be employed. The results of the WLS-I stability study indicate that sample holding time before preservation had minimal effect on population estimates.

Section 10
References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Best, M. D., S. K. Drousé, L. W. Creelman, and D. J. Chaloud, 1987. National Surface Water Survey Eastern Lake Survey (Phase I - Synoptic Chemistry) Quality Assurance Report. EPA/600/4-86/011. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

Bonoff, M. B., and A. W. Groeger, 1987. National Surface Water Survey, Western Lake Survey - Phase I (Synoptic Chemistry) Field Operations Report. EPA 600/8-87/018. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

Drousé, S. K., 1987. National Surface Water Survey, National Stream Survey Phase I - Pilot Survey, Summary of Quality Assurance Data Results. In press. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

Drousé, S. K., D. C. Hillman, L. W. Creelman, and S. J. Simon, 1986. National Surface Water Survey, Eastern Lake Survey (Phase I - Synoptic Chemistry) Quality Assurance Plan. EPA/600/4-86/008. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

Eilers, J. M., P. Kanciruk, R. A. McCord, W. S. Overton, L. Hook, D. J. Blick, D. F. Brakke, P. E. Kellar, M. D. DeHaan, M. E. Silverstein, and D. H. Landers, 1987. Characteristics of Lakes in the Western United States. Volume II. Data Compendium for Selected Physical and Chemical Variables. EPA/600/3-86/054b. U.S. Environmental Protection Agency, Washington, D. C.

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

International Science Technology, Inc, 1986. Data Base Audit - National Surface Water Survey, Phase I - Western Lake Survey (IS&T 10067.) Internal Report for the U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, Oregon.

Kanciruk, P., M. Gentry, R. McCord, L. Hook, J. Eilers, and M. D. Best, 1987. National Surface Water Survey: Western Lake Survey - Phase I, Data Base Dictionary. Oak Ridge National Laboratory, Environmental Sciences Division Publication No 2838. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Kanciruk, P., R. J. Olson, and R. A. McCord, 1986. Quality Control in Research Data Bases: The U.S. Environmental Protection Agency National Surface Water Survey Experience. pp. 193-207 *in* W. K. Michener (ed.) Research Data Management in the Ecological Sciences. Belle W. Baruck Library in Marine Science, Number 16. University of South Carolina Press, Columbia, South Carolina.

Kerfoot, H. B., and M. L. Faber, 1987. National Surface Water Survey, Western Lake Survey (Phase I - Synoptic Chemistry) Analytical Methods Manual. EPA/600/8-87/038. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

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

Landers, D. H., J. M. Eilers, D. F. Brakke, W. S. Overton, P. E. Kellar, M. E. Silverstein, R. D.

Schonbrod, R. E. Crowe, R. A. Linthurst, J. M. Omernik, S. A. Teague, and E. P. Meier, 1987. Characteristics of Lakes in the Western United States. Volume I. Population Descriptions and Physico-Chemical Relationships. EPA/600/3-86/054a. U.S. Environmental Protection Agency, Washington, D.C.

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

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

Permutt T. J., and A. K. Pollack, 1986. Analysis of Quality Assurance Data for the Eastern Lake Survey. Prepared by Systems Applications, Inc., for Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada.

Appendix A *in* Best, M.D., S. K. Drousé, L. W. Creelman, and D. J. Chaloud. 1986. National Surface Water Survey, Eastern Lake Survey (Phase I - Synoptic Chemistry) Quality Assurance Report (1987). EPA/600/4-86/011. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

SAS Institute, 1982. The Statistical Analysis System, SAS Institute, Cary, North Carolina.

Silverstein, M. E., S. K. Drousé, J. L. Engels, M. L. Faber, and T. E. Mitchell-Hall, 1987. National Surface Water Survey, Western Lake Survey (Phase I - Synoptic Chemistry) Quality Assurance Plan. EPA/600/8-87/026. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

Snedecor, G. W., and W. G. Cochran, 1973. Statistical Methods. The Iowa State University Press, Ames, Iowa.

U.S. Environmental Protection Agency, 1979. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. EPA/600/4-79/019. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

Appendix A

National Surface Water Survey Form 26
Data Confirmation/ Reanalysis Request Form

The NSWS Form 26 was created to document data changes. The form was used to track reported analytical laboratory results from the raw data set to the verified data set.

National Surface Water Survey Form 26
Data Confirmation/Reanalysis Request Form

Date Sent___________
Date Received________

National Surface Water Survey
Form 26
Data Confirmation/Reanalysis Request Form

Batch #_______________ Contract Analytical Laboratory________________ Laboratory Supervisor_________________

The following values require: _______ Confirmation (See I) _______ Reanalysis (See II)

Variable	NSWS Form #	Sample I.D.	Suspect Original Value	Reconfirmed/ New Value	Explanation	
					Contract Analytical Laboratory	LEMSCO

I. Confirmation Request: Did ANY values change: _____Yes _____No
If yes, reason (note above in explanation column):
- (A) Reporting Error
- (B) Calculation Error
- (C) Original reported value did not change
- (D) Data Previously Omitted
- (E) Other - Explain

If values changed, submit supporting raw data AS REQUIRED.

Additional Comments Regarding Confirmation: ____

____

____

II. Reanalysis Requested Due to:*

_____ External QA Data

_____ Internal QC Data Indicated Below:

- _____ IC Resolution
- _____ IDL > CRDL
- _____ Blank > 2 × CRDL (Reagent: Calibration)
- _____ QCCS Outside Criteria (DL; Low; High)
- _____ Sample Concentration Outside Calibration Range
- _____ QCCS Not in Mid-Range of Calibration Range
- _____ Duplicate Precision (% RSD) Outside Criteria; Insufficient Number of Duplicates Analyzed

Additional Comments Regarding Reanalysis: ____

____

____

* An abbreviated version of NSWS Forms 11, 18, 19, and 20 must be submitted for all reanalyzed data. NSWS Forms 13, 17, and 22 must be submitted when applicable.

FOR LEMSCO USE ONLY: INITIAL REVIEW ______________ NUMBER OF VALUES SUBMITTED______________
VERIFICATION ______________ NUMBER OF VALUES CHANGED ______________

Appendix B
Calculation of Field Blank Sample Control Limits

Criteria for determining contamination were needed in order to check for systematic contamination problems during sample collection and analysis and before preparing a verified data set. These criteria, termed control limits, were determined by a variety of nonstatistical methods during ELS-I. Some control limits were established on the basis of specifications provided by the instrument manufacturer; others reflected DQOs (i.e., the level of detectability needed to meet the goals of the survey). Control limits for some analytes could be defined only in terms of analytical experience and intuitive assumptions based on that experience, because there were not any acceptable precedents.

Upper control limits for WLS-I blank samples were determined statistically, on the basis of ELS-I experience and the analytical results obtained for ELS-I field blanks. The 95th percentile (P_{95}) nonparametric test used to calculate the system decision limit in ELS-I (Best et al., 1987) was selected for the WLS-I control limits for the following reasons:

1. Although negative response values can be valid and were required to be reported, one of the ELS-I analytical laboratories, which analyzed almost 50 percent of all ELS-I samples, reported all negative values as zero. This biased any negative values and further skewed the field blank distribution toward positive values.
2. A field blank is subjected to handling, shipping, and preservation effects at the lake site, in the field laboratory, and in the analytical laboratory. Contamination may result at any or all of these locations. A field blank can yield a positive value as a result of contamination; however, it cannot yield a negative value as a result of contamination. Consequently, the distribution of values may be skewed toward the contaminated levels, and the associated curve will represent a nonnormal distribution about 0. Contamination could reduce a negative bias that resulted from calibration error.
3. Negative values can be reported for an analysis, but they will not result from contamination or from the presence of analyte. Negative values are caused by instrumental drift, analytical error, and standard regression curves with negative y-intercepts. Therefore, negative values are created in the analytical laboratory and do not result from field activities.

Two methods of calculating blank windows were considered in the WLS-I survey design. One calculation was the prediction interval:

$$\overline{X} \pm (t)\, s\sqrt{1 + 1/n}$$

which is the standard 95 percent confidence interval about the mean and assumes a normal distribution. This calculation was rejected because the distribution of ELS-I blanks was not normal; most of the ELS-I blanks showed a skewed distribution to positive values, and one ELS-I laboratory had adjusted all negative values to zero. To accommodate the nonnormal distribution, the non-parameteric P_{95} statistic was used in determining the field blank acceptance criteria. As long as at least 5 percent of the blank values were above zero, this calculation was not affected by distribution or by the number of negative values set to zero.

The P_{95} statistic was used to calculate the upper limit at which blank values would be flagged. The lower limit, however, was designated as the negative value of the required detection limit. Anything less than this negative value was unacceptable and was attributed to excessive instrumental drift or to inaccurate calibration of the instrument.

Table B-1 presents the field blank control limits for ELS-I and WLS-I. Field blank concentrations that were outside these limits were considered suspect and were flagged. Establishing these limits prior to a full-scale statistical analysis was essential to identifying contamination trends as they occurred. The detailed statistical analysis of the WLS-I field blank values was performed after data verification was completed.

Table B-1. Comparison of Field Blank Control Limits, Eastern Lake Survey - Phase I and Western Lake Survey - Phase I

	Low Limit		High Limit	
Variable[a]	ELS-I	WLS-I	ELS-I	WLS-I
Al, extractable	-0.005	-0.005	0.009	0.008
Al, total	-0.005	-0.005	0.009	0.033
ANC (μeq/L)	-10.0	-10.0	10.0	7.18
BNC (μeq/L)	0.00	-10.0	40.0	22.45
Ca	-0.005	-0.010	0.050	0.034
Cl^-	-0.010	-0.010	0.050	0.094
Conductance (μS/cm)	-0.01	-0.9	2.0	1.31
DIC, air equilibrated	0.10	-0.05	0.30	0.294
DIC, initial	0.20	-0.05	0.40	0.426
DOC	-0.20	-0.1	0.6	0.45
F^-, total dissolved	-0.005	-0.005	0.009	0.005
Fe	-0.005	-0.010	0.05	0.023
K	-0.005	-0.010	0.05	0.018
Mg	-0.005	-0.010	0.05	0.008
Mn	-0.005	-0.010	0.010	0.012
Na	-0.005	-0.010	0.050	0.031
NH_4^+	-0.010	-0.010	0.030	0.039
NO_3^-	-0.010[b]	-0.005	0.020[b]	0.023
pH, acidity (pH units)	5.40	5.50[c]	5.90	5.87[c]
pH, alkalinity (pH units)	5.40	5.50[c]	5.90	5.87[c]
pH, air equilibrated (pH units)	5.40	5.41	5.90	5.90
P, total	-0.005	-0.002	0.005	0.008
SiO_2	-0.050	-0.050	0.050	0.117
SO_4^{2-}	-0.01	-0.050	0.10	0.094

[a] Units are in mg/L unless otherwise noted.
[b] NO_3^- limits were calculated by using only the last 99 blanks processed during ELS-I; earlier ELS-I blanks were contaminated.
[c] ELS-I pH (acidity) and pH (alkalinity) values were pooled to calculate WLS-I limits.

Appendix C
Preparation of Audit Samples

1.0 Preparation of Field Natural Audit Samples

To ensure that all field natural audit samples of a particular lot were uniform, EMSL-LV instructed the preparation laboratory (Radian Corporation in Austin, Texas) to follow the protocol specified below.

1. Clearly label the field natural (FN) stock barrels with the lot number.

2. Label the 2-L bottles to be filled.

3. Operating in a clean environment, flush the Tygon tubing lines with lake water. Discard the water.

4. Pump 20 to 25 mL lake water into the audit bottle, cap the bottle, rinse the bottle to get complete coverage, and discard the rinse.

   NOTE: The Tygon tubing must not touch the sidewalls of the bottle.

5. Perform step 4 two more times. Discard the rinse water each time.

6. Fill the bottle to the top (no head space) and cap the bottle.

   NOTE: The bottle must be capped immediately after it is filled to minimize the possibility of contamination.

7. Secure the cap to the bottle with tape.

8. Log in the total number of samples prepared, the date prepared, and the name of the analyst or technician.

9. Place samples in storage at 4°C by lot and ID number to await shipment.

10. Discard any water remaining in Tygon tubing. Do not drain residual lake water into the stock barrel.

2.0 Preparation of Synthetic Audit Samples

To prepare the field synthetic audit samples of the desired concentrations, Radian technicians diluted the lot stock concentrates with ASTM Type I reagent-grade water. Each diluted 2-L synthetic audit samples were prepared for shipment to the field laboratory as follows:

1. Fill a 2-L volumetric flask with 1.5 L deionized water.

2. Add a predetermined volume of each of the four stock concentrates (see Table C-1) to the flask.

3. Fill the flask to volume and mix the solution thoroughly.

4. When the dilution is complete, transfer the 2-L sample to a carboy. (If 10 samples were prepared in one day, the carboy would eventually contain 20-L of diluted stock, prepared 2-L at a time.)

5. When these dilution and transfer steps are completed, sparge the audit sample solution in the carboy with 300 ppm CO_2 and equilibrate. (The equilibration raises the acidity of the sample, thereby counteracting the effect of adding the strong base Na_2SiO_3. It also restores any DIC lost during sample preparation steps and, by stabilizing the sample, it minimizes day-to-day sample variation caused by shipping and handling.)

Table C-1. Composition of the Field Synthetic Audit Sample Concentrates, Western Lake Survey - Phase I

Stock Concentrate	Chemical Formula	Analytes to be Measured
1	$Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$	Extractable Al, total Al, NH_4^+, SO_4^{2-}
2	$FeNH_4(SO_4)_2 \cdot 12H_2O$	Fe, NH_4^+, SO_4^{2-}
3	Na_2SiO_3	Na, SiO_2
4	$CaCl_2$	Ca, Cl^-
	$NaHCO_3$	DIC, Na
	$C_6H_4(COOH)_2$	DOC
	$MgSO_4$	Mg, SO_4^{2-}
	NaF	Total dissolved F^-, Na
	$MnSO_4 \cdot H_2O$	Mn, SO_4^{2-}
	NH_4NO_3	NH_4^+, NO_3^-
	Na_2HPO_4	Na, Total P
	$KHC_8H_4O_4$	DOC, K

Appendix D

Distribution of Data for Field, Trailer, and Calibration Blank Samples Analyzed in the Analytical Laboratories

Table D-1. Distribution of Data for Field Blank Samples Analyzed in the Analytical Laboratories

	Laboratories and Sampling Methods Pooled (n = 236)		By Laboratory				By Sampling Method			
			Lab I (n = 97)		Lab II (n = 139)		Ground (n = 112)		Helicopter (n = 124)	
Variable[a]	P_{50}	P_{95}	P_{50}	P_{95}	P_{50}	P_{95}	P_{50}	P_{95}	P_{50}	P_{95}
Al, extractable	0.001	0.004	0.000	0.003	0.001	0.004	0.001	0.004	0.001	0.004
Al, total	0.009	0.019	0.002	0.014	0.011	0.019	0.008	0.019	0.010	0.019
ANC (µeq/L)	1.3	3.9	-0.4	5.4	1.5	3.2	1.1	4.0	1.3	4.4
BNC (µeq/L)	18.7	29.8	8.3	17.5	22.5	30.3	18.0	37.1	19.8	28.3
Ca	0.014	0.072	0.042	0.077	0.007	0.037	0.018	0.075	0.012	0.071
Cl^-	0.005	0.043	0.013	0.047	0.004	0.024	0.005	0.052	0.005	0.033
Conductance (µS/cm)	0.7	1.6	1.0	2.0	0.4	1.6	0.6	1.7	0.6	1.8
DIC, air equilibrated	0.200	0.330	0.160	0.240	0.220	0.370	0.189	0.313	0.210	0.370
DIC, initial	0.180	0.430	0.110	0.340	0.210	0.440	0.200	0.490	0.170	0.390
DOC	0.14	0.30	0.22	0.35	0.10	0.23	0.15	0.31	0.13	0.32
F^-, total dissolved	0.001	0.003	0.000	0.006	0.002	0.003	0.001	0.005	0.001	0.003
Fe	0.001	0.014	0.000	0.005	0.005	0.020	0.001	0.014	0.001	0.015
K	0.001	0.012	0.003	0.014	0.000	0.008	0.001	0.014	0.001	0.012
Mg	0.001	0.006	0.002	0.007	0.001	0.005	0.001	0.004	0.001	0.008
Mn	0.000	0.014	0.000	0.001	-0.001	0.021	0.000	0.009	0.000	0.016
Na	-0.001	0.012	-0.001	0.012	-0.001	0.014	-0.001	0.008	-0.001	0.014
NH_4^+	-0.003	0.010	-0.007	0.012	0.002	0.009	-0.003	0.008	-0.003	0.012

(continued)

Table D-1. Continued

Variable[a]	Laboratories and Sampling Methods Pooled (n = 236)		By Laboratory				By Sampling Method			
			Lab I (n = 97)		Lab II (n = 139)		Ground (n = 112)		Helicopter (n = 124)	
	P_{50}	P_{95}	P_{50}	P_{95}	P_{50}	P_{95}	P_{50}	P_{95}	P_{50}	P_{95}
NO_3^-	0.008	0.071	0.010	0.045	0.006	0.078	0.009	0.061	0.006	0.072
P, total	0.001	0.006	0.000	0.017	0.001	0.005	0.001	0.008	0.001	0.006
pH, acidity (pH units)	5.66	5.78	5.70	5.79	5.64	5.73	5.65	5.78	5.66	5.78
pH, alkalinity (pH units)	5.64	5.74	5.67	5.77	5.63	5.71	5.64	5.75	5.65	5.74
pH, air equilibrated (pH units)	5.70	5.83	5.68	5.75	5.71	5.88	5.69	5.80	5.70	5.86
SiO_2	0.047	0.179	0.046	0.271	0.047	0.116	0.040	0.150	0.052	0.248
SO_4^{2-}	0.012	0.065	0.028	0.123	0.006	0.021	0.013	0.129	0.011	0.047

[a] units in mg/L unless otherwise noted; units shown at the number of significant figures reported by the analytical laboratories.
P_{50} = 50th percentile.
P_{95} = 95th percentile.

Table D-2. Distribution of Data for Trailer Blank Samples Analyzed in the Analytical Laboratories

Variable[a]	Trailer Blank Samples (n = 22) P_{50}	P_{95}
Al, extractable	0.001	0.003
Al, total	0.008	0.013
ANC (μeq/L)	0.9	2.0
BNC (μeq/L)	16.9	30.4
Ca	0.001	0.029
Cl^-	0.007	0.050
Conductance (μS/cm)	0.6	1.3
DIC, air equilibrated	0.195	0.300
DIC, initial	0.122	0.243
DOC	0.09	0.27
F^-, total dissolved	0.001	0.002
Fe	0.001	0.009
K	-0.001	0.002
Mg	0.000	0.003
Mn	0.000	0.014
Na	-0.003	0.002
NH_4^+	-0.004	0.004
NO_3^-	0.007	0.074
P, total	0.001	0.012
pH, acidity (pH units)	5.67	5.96
pH, alkalinity (pH units)	5.64	5.90
pH, air equilibrated (pH units)	5.69	5.81
SiO_2	0.057	0.152
SO_4^{2-}	0.013	0.057

[a] units in mg/L unless otherwise noted; units shown at the number of significant figures reported by the analytical laboratories.
P_{50} = 50th percentile.
P_{95} = 95th percentile.

Table D-3. Distribution of Data for Analytical Laboratory Calibration and Reagent Blank Samples

Variable[c]	Required Detection Limit	Instrument Detection Limit[a]			Calibration Blank[b] Concentrations					
					Labs Pooled (n = 149)		Lab I (n = 58)		Lab II (n = 91)	
		Labs Pooled	Lab I	Lab II	P_{50}	P_{95}	P_{50}	P_{95}	P_{50}	P_{95}
Al, extractable	0.005	0.002	0.001	0.002	0.001	0.004	0.000	0.005	0.001	0.002
Al, total[d]	0.005	0.001	0.001	0.001	0.005	0.008	0.000	0.009	0.005	0.008
ANC (µeq/L)	10.0	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
BNC (µeq/L)	10.0	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ca	0.01	0.007	0.007	0.007	N/A	N/A	0.004	0.009	N/A	N/A
Cl^-	0.01	0.004	0.010	0.003	0.003	0.013	0.004	0.016	0.003	0.007
Conductance (µS/cm)	0.9	0.2	0.3	0.2	0.0	0.6	0.5	0.7	0.0	0.1
DIC, air equilibrated	0.05	N/A	N/A	N/A	0.001	0.046	0.020	0.090	-0.010	0.007
DIC, initial	0.05	0.020	0.030	0.020	0.002	0.060	0.020	0.090	-0.010	0.007
DOC	0.1	0.08	0.09	0.07	0.10	0.17	0.12	0.19	0.04	0.11
F^-, total dissolved	0.005	0.001	0.002	0.001	0.000	0.002	0.000	0.000	0.001	0.003
Fe	0.01	0.007	0.006	0.009	N/A	N/A	0.003	0.008	N/A	N/A
K	0.01	0.004	0.007	0.004	N/A	N/A	-0.007	0.008	N/A	N/A
Mg	0.01	0.002	0.001	0.002	N/A	N/A	0.001	0.004	N/A	N/A
Mn	0.010	0.005	0.002	0.009	N/A	N/A	0.000	0.005	N/A	N/A
Na	0.01	0.003	0.005	0.003	N/A	N/A	-0.008	0.000	N/A	N/A
NH_4^+	0.01	0.005	0.007	0.004	-0.002	0.006	-0.001	0.010	-0.002	0.002
NO_3^-	0.005	0.004	0.005	0.004	0.005	0.013	0.008	0.018	0.004	0.009
P, total	0.002	0.001	0.001	0.001	0.000	0.002	0.000	0.001	0.000	0.002
pH, acidity (pH units)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
pH, alkalinity (pH units)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
pH, air equilibrated (pH units)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
SiO_2[d]	0.05	0.021	0.038	0.016	0.008	0.065	0.024	0.093	0.008	0.024
SO_4^{2-}	0.05	0.012	0.016	0.011	0.005	0.033	0.022	0.039	0.003	0.010

[a] Calculated at three times the standard deviation of 10 nonconsecutively analyzed calibration blanks; required to be performed weekly.
[b] Calibration blanks analyzed as part of daily instrument calibration.
[c] Units in mg/L unless otherwise noted; units shown at the number of significant figures reported by the analytical laboratories.
[d] Reagent blanks used in instrument calibration.
N/A = not applicable P_{50} = 50th percentile P_{95} = 95th percentile

Appendix E

Field Laboratory Precision Data for Audit Sample Measurements of Dissolved Inorganic Carbon, pH, Turbidity, and True Color

Table E-1. Comparison of Field Laboratory and Analytical Laboratory Measurements for Dissolved Inorganic Carbon, Western Lake Survey - Phase I

Audit Sample		Field Base (Subregion) Measurement for Closed-System DIC						Analytical Laboratory Measurement for Open-System DIC		
		California (4A)	Pacific NW (4B)	No. Rockies (4C)	Cent. Rockies (4D)	So. Rockies (4E)	Subregions Pooled	Lab I	Lab II	Labs I and II Pooled
FN3 (Lake Superior)	n	5	5	10	9	9	38	19	19	38
	$\bar{X}$	10.34	10.35	10.28	10.23	10.31	10.29	10.34	9.39	9.86
	%RSD	2.6	1.1	4.7	1.8	1.40	2.7	12.8	3.0	10.7
FN4 (Big Moose Lake)	n	4	4	4	4	4	20	9	11	20
	$\bar{X}$	0.62	0.64	0.63	0.57	0.65	0.62	0.49	0.53	0.51
	%RSD	3.6	11.5	8.3	9.8	2.0	8.5	14.4	38.7	30.4
FN5 (Bagley Lake)	n	19	12	15	12	10	68	24	44	68
	$\bar{X}$	2.16	2.12	2.21	2.14	2.18	2.16	2.04	1.83	1.91
	%RSD	4.1	3.9	4.4	3.5	3.4	4.1	17.9	6.1	13.3
FN6 (Bagley Lake)	n	22	11	--	--	4	37	8	29	37
	$\bar{X}$	1.65	1.63	--	--	1.67	1.65	1.63	1.42	1.47
	%RSD	3.9	3.3	--	--	1.9	3.6	5.1	3.6	7.0
FL11 (Synthetic)	n	2	2	6	5	6	21	11	10	21
	$\bar{X}$	1.64	1.70	1.57	1.56	1.52	1.57	1.49	1.97	1.72
	%RSD	1.0	0.1	11.6	13.5	6.5	9.5	26.4	2.7	21.9
FL12 (Synthetic)	n	8	8	4	2	4	26	6	20	26
	$\bar{X}$	1.41	1.36	1.43	1.46	1.43	1.41	1.31	1.41	1.39
	%RSD	5.3	4.7	4.2	0.5	6.7	5.2	5.8	9.9	9.7
FL11 and FL12 (Pooled Synthetics)	n	10	10	10	7	10	47	17	30	47
	$\bar{X}$	1.45	1.43	1.52	1.53	1.48	1.48	1.42	1.60	1.54
	%RSD	8.1	10.6	10.3	11.7	6.9	9.5	22.8	18.3	20.4

$\bar{X}$ = mean in mg/L.

Table E-2. Comparison of Mean pH Values for Field Audit Samples, Western Lake Survey - Phase I

Audit Sample		Field Base (Subregion) Measurement for Closed-System pH						Analytical Laboratory[a] Measurement for Open-System pH		
		California (4A)	Pacific NW (4B)	No. Rockies (4C)	Cent. Rockies (4D)	So. Rockies (4E)	Subregions Pooled	Lab I	Lab II	Labs I and II Pooled
FN3 (Lake Superior)	n	5	5	10	9	8	37	19	19	38
	$\bar{X}$	7.76	7.66	7.81	7.86	7.83	7.80	7.88	7.84	7.86
	SD	0.07	0.17	0.06	0.04	0.05	0.10	0.05	0.09	0.08
FN4 (Big Moose Lake)	n	4	4	4	4	4	20	9	11	20
	$\bar{X}$	4.72	4.75	4.86	4.79	4.79	4.78	4.68	4.68	4.68
	SD	0.02	0.04	0.06	0.03	0.06	0.06	0.03	0.02	0.03
FN5 (Bagley Lake)	n	19	12	15	12	10	68	24	44	68
	$\bar{X}$	6.98	7.01	6.95	7.04	7.05	7.00	7.08	6.97	7.01
	SD	0.04	0.05	0.06	0.06	0.07	0.07	0.08	0.07	0.09
FN6 (Bagley Lake)	n	21	11	--	--	4	36	8	29	37
	$\bar{X}$	7.14	7.08	--	--	7.18	7.13	7.11	7.07	7.08
	SD	0.05	0.09	--	--	0.07	0.07	0.06	0.07	0.07
FL11 (Synthetic)	n	2	2	6	5	6	21	11	10	21
	$\bar{X}$	6.87	6.86	6.97	7.01	6.91	6.94	6.97	6.92	6.94
	SD	0.01	0.06	0.06	0.02	0.11	0.08	0.15	0.12	0.14
FL12 (Synthetic)	n	8	8	4	2	4	26	6	20	26
	$\bar{X}$	7.00	7.06	7.04	7.12	7.06	7.04	6.99	6.93	6.95
	SD	0.07	0.07	0.10	0.02	0.02	0.07	0.07	0.11	0.10
FL11 and FL12 (Pooled Synthetics)	n	10	10	10	7	10	47	17	30	47
	$\bar{X}$	6.98	7.02	7.00	7.04	6.97	7.00	6.98	6.93	6.95
	SD	0.08	0.11	0.08	0.06	0.12	0.09	0.13	0.11	0.12

[a] All analytical laboratory pH precision estimates are calculated from the pooled pH (acidity and alkalinity) determinations.
$\bar{X}$ = mean in pH units.

Table E-3. Comparison of Mean Turbidity Values for Field Audit Samples, Western Lake Survey - Phase I

Audit Sample		Field Base (Subregion) California (4A)	Pacific NW (4B)	No. Rockies (4C)	Cent. Rockies (4D)	So. Rockies (4E)	Sub-regions Pooled
FN3 (Lake Superior)	n	4	5	9	9	6	33
	$\bar{X}$	0.1	0.1	0.1	0.2	0.2	0.1
	%RSD	66.7	36.2	50.0	101.7	192.2	123.0
FN4 (Big Moose Lake)	n	3	4	4	4	1	16
	$\bar{X}$	0.2	0.3	0.7	0.3	0.1	0.4
	%RSD	50.0	12.4	73.7	62.1	--	90.4
FN5 (Bagley Lake)	n	7	9	15	12	5	48
	$\bar{X}$	0.3	0.2	0.1	0.3	0.1	0.2
	%RSD	51.3	37.1	83.5	63.1	104.6	74.6
FN6 (Bagley Lake)	n	20	11	--	--	4	35
	$\bar{X}$	0.1	0.1	--	--	0	0.1
	%RSD	110.0	27.6	--	--	0.0	90.0
FL11 (Synthetic)	n	1	2	6	3	4	16
	$\bar{X}$	0.2	0.3	0.2	0.1	0.4	0.2
	%RSD	--	0.0	31.6	43.3	82.6	70.2
FL12 (Synthetic)	n	6	7	4	2	4	23
	$\bar{X}$	0.1	0.1	0.1	0.3	0.3	0.1
	%RSD	122.5	38.0	66.7	84.8	148.0	125.8
FL11 and FL12 (Pooled Synthetics)	n	7	9	10	5	8	39
	$\bar{X}$	0.1	0.2	0.2	0.2	0.3	0.2
	%RSD	105.0	52.0	56.7	72.4	103.2	98.3

Note: Audit samples were filtered before shipment to field laboratories. Field natural audit samples were filtered in the audit preparation laboratory (see Appendix C); the synthetic audits were deionized water with added analytes spiked into them. Routine samples and audit samples were prepared differently; therefore, for turbidity no inferences should be drawn from the precision estimates calculated for audit samples. The data are presented here for illustrative purposes. To estimate precision for the turbidity measurement with confidence, the data user should employ field duplicate pairs.

$\bar{X}$ = mean in NTU.

Table E-4. Comparison of Mean True Color Values for Field Audit Samples, Western Lake Survey - Phase I

Audit Sample		Field Base (Subregion) California (4A)	Pacific NW (4B)	No. Rockies (4C)	Cent. Rockies (4D)	So. Rockies (4E)	Sub-regions Pooled
FN3 (Lake Superior)	n	3	5	9	9	3	29
	$\bar{X}$	1.7	6	3.9	3.9	5	4.1
	%RSD	173.2	69.7	56.7	107.1	100.0	86.0
FN4 (Big Moose Lake)	n	3	4	4	4	1	16
	$\bar{X}$	21.7	13.8	17.5	28.8	25	20.6
	%RSD	13.3	86.0	16.5	8.7	--	39.5
FN5 (Bagley Lake)	n	7	9	15	12	2	45
	$\bar{X}$	0.7	1.7	4.7	2.5	2.5	2.8
	%RSD	264.6	150.0	63.6	104.4	141.4	105.5
FN6 (Bagley Lake)	n	17	11	--	--	4	32
	$\bar{X}$	0.3	1.8	--	--	3.8	1.3
	%RSD	412.3	139.0	--	--	66.7	176.0
FL11 (Synthetic)	n	2	2	5	4	1	14
	$\bar{X}$	0	2.5	6	2.5	5	3.6
	%RSD	--	141.4	37.3	115.5	--	85.6
FL12 (Synthetic)	n	6	7	4	2	3	22
	$\bar{X}$	0.8	2.9	3.8	7.5	1.7	2.7
	%RSD	244.9	93.5	66.7	47.1	173.2	109.2
FL11 and FL12 (Pooled Synthetics)	n	8	9	9	6	4	36
	$\bar{X}$	0.7	2.8	5	4.2	2.5	3.1
	%RSD	282.8	93.0	50.0	90.3	115.5	98.0

$\bar{X}$ = mean in PCU.

Appendix F
Estimated Precision for Audit Sample by Lot

The following tables, figures, and discussions are useful for the data user who is interested in components of variability in each audit sample.

FN3 (Lake Superior) - Table F-1, Figures J-1 through J-26. Of the 38 samples, 19 were analyzed by each laboratory. The %RSDs for SiO_2 (18.3%), total dissolved F^- (21.5%), and DOC (20.6%) are higher than is desirable for pooled values or for single-laboratory values. (The mean concentration for DOC, however, is only 1.4 mg/L and for total dissolved F^- is 0.035 mg/L). This factor indicates that for FN3 the ability to make consistent DOC and SiO_2 measurements was difficult, regardless of laboratory. Much of the imprecision appears to result from one unusually low measurement in Laboratory II and one unusually high measurement in Laboratory I. The precision estimates for Cl^- were higher for Laboratory I (9.6%) than for Laboratory II (2.1%). There were not sufficient levels of extractable Al, total Al, BNC, Fe, Mn, NH_4^+, or total P in this Lake Superior sample to determine confidence in precision. Precision estimates for all other analytes are considered reasonable relative to the DQOs.

FN4 (Big Moose Lake) - Table F-2, Figures J-1 through J-26. Laboratory II analyzed 11 samples and Laboratory I analyzed 9 samples. Of all six audit lots, only FN4 contained levels of total Al and extractable Al high enough to allow meaningful precision estimates to be determined. Both laboratories had difficulty with extractable Al precision; however, only one routine sample had a concentration above 0.100 mg/L. That sample was collected from a hot spring that had a pH of about 5.70. Only Laboratory II had difficulty with total Al precision (probably as the result of two unusually low measurements). Laboratory I had much better precision than did Laboratory II for Mn (1.3% as compared to 13.6%); however, the pooled %RSD was 9.9 percent. The mean concentrations for Mn are the same, which indicates that the concentrations are variable about the same mean for the two laboratories. Mn, like extractable Al, generally was found in extremely low concentrations in WLS-I lakes; consequently, it may be of little concern. The same trend was observed for total dissolved F^- as for Mn. Laboratory I's %RSD for SiO_2 (16.2%) is higher than desired for FN4, but Laboratory II had a low %RSD (3.4%). Precision estimates for DIC (initial and air equilibrated), NH_4^+, and total P could not be determined confidently because of their low concentrations. All other analytes for this field audit were close to the DQO for precision.

FN5 (Bagley Lake, sampled in January 1985) - Table F-3, Figures J-1 through J-26. Because Laboratory II analyzed almost twice as many samples (44) as Laboratory I (24), Laboratory II's results have a greater effect on overall precision. That is, overall precision estimates are weighted toward Laboratory II's results. Cl^- was measured with a %RSD of 17.1 percent by Laboratory I, whereas Laboratory II's %RSD for Cl^- was 6.2 percent; the pooled estimate was 11.8 percent. For conductance, Laboratory II had a %RSD of 6.9 percent; Laboratory I's %RSD for conductance was below 4.8 percent; the pooled %RSD was 6.4 percent. Laboratory I's %RSDs were above 17 percent for air-equilibrated and initial DIC; Laboratory II's %RSDs were near 6 percent. Each laboratory's mean values, however, were identical in concentration, which indicates greater variability among Laboratory I's measurements. The %RSDs for NO_3^- were much higher for FN5 than for any other field audit sample that contained NO_3^- levels high enough to permit relevant precision estimates to be calculated (FN3, FN4, FL11, and FL12). The pooled %RSD of 23.1 percent represents Laboratory II's variability of 26.5 percent and Laboratory I's variability of 11.7 percent and shows the effect of the weighting factor. Air-equilibrated pH for both laboratories is about 0.13 pH unit. Although the pooled value (8.6%) for SiO_2 in this field audit was only slightly higher than the DQO, Laboratory I's %RSD of 12.3 percent is twice that of Laboratory II's %RSD of 5.9 percent. Analytes with concentrations below which reliable precision estimates are questionable include extractable Al, total Al, BNC, DOC, total dissolved F^-, Fe, Mn, NH_4^+, and total P.

FN6 (Bagley Lake, sampled in September 1986) - Table F-4, Figures J-1 through J-26. Of the 37 samples analyzed, 29 were analyzed by Laboratory II and 8 were analyzed by Laboratory I; consequently, the pooled precision is weighted toward Laboratory II. Although the means and the %RSDs for BNC are very different for Laboratory II (mean = 31.3, %RSD = 6.1) and Laboratory I (mean = 18.5, %RSD =

Table F-1. Precision Estimated from Audit Samples Analyzed Among Batches (Field Natural Audit Lot 3 [FN3, Lake Superior]), Western Lake Survey - Phase I

	Laboratories Pooled (n = 38)		Laboratory I (n = 19)		Laboratory II (n = 19)	
Variable[a]	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD
Al, extractable	0.002	116.1	0.001	233.0	0.003	59.6
Al, total	0.012	51.8	0.008	66.8	0.017	20.1
ANC(μeq/L)	846.1	5.0	867.3	4.3	824.9	4.5
BNC(μeq/L)	21.9	59.5	16.9	63.6	27.0	49.8
Ca	13.84	4.8	14.40	1.8	13.28	3.2
Cl^-	1.43	6.9	1.43	9.6	1.43	2.1
Conductance (μS/cm)	95.5	1.9	95.2	1.7	95.9	2.0
DIC, air equilibrated	9.90	9.7	10.36	11.5	9.45	2.1
DIC, initial	9.86	10.7	10.34	12.8	9.39	3.0
DOC	1.4	20.6	1.5	15.1	1.3	23.2
F^-, total dissolved	0.035	21.5	0.037	16.6	0.033	25.3
Fe	0.005	155.8	0.001	649.7	0.009	87.8
K	0.52	4.4	0.51	4.4	0.53	3.9
Mg	2.90	2.6	2.95	2.6	2.86	1.5
Mn	-0.002	439.2[b]	0.000	668.6	-0.004	259.9[b]
Na	1.36	2.5	1.35	2.8	1.37	2.0
NH_4^+	-0.010	221.2[b]	-0.019	154.6[b]	-0.001	358.6[b]
NO_3^-	1.418	4.7	1.393	5.3	1.443	3.3
P, total	0.001	296.7	-0.000	1011.2[b]	0.002	81.6
pH, acidity (pH units)	7.86	0.08[c]	7.89	0.05[c]	7.83	0.10[c]
pH, alkalinity (pH units)	7.85	0.07[c]	7.86	0.06[c]	7.84	0.08[c]
pH, air equilibrated (pH units)	8.13	0.09[c]	8.11	0.04[c]	8.15	0.12[c]
SiO_2	2.51	18.3	2.47	21.1	2.55	15.5
SO_4^{2-}	3.24	6.4	3.13	7.2	3.35	3.6

[a] All variables are measured in mg/L unless otherwise noted.
[b] The absolute value of the %RSD.
[c] Standard deviation values were calculated for pH measurements.

18.1), these values are close enough to zero that they should not be of great concern to the data user. The overall precision for pH (air equilibrated) for Laboratory II is 0.16 pH unit, which is slightly higher than Laboratory I's 0.10 pH unit. For SiO_2, the differences in the mean concentration between laboratories (9.65 mg/L for Laboratory II and 8.33 mg/L for Laboratory I) may be of practical significance. Extractable Al, total Al, BNC, DOC, total dissolved F^-, Fe, Mn, NH_4^+, NO_3^- and total P all had mean concentrations that were too low to allow precision to be estimated confidently for FN6. Of added note is the NH_4^+ precision estimate of 20,069.1 percent for Laboratory II where, of the 29 values, 28 were near or at 0.000 mg/L and 1 was 0.034 mg/L. This shows how variable the %RSD can be at extremely low concentrations.

There are differences between FN5 and FN6, the two Bagley Lake samples that were collected during different seasons of the same year. Of the 24 variables measured, 13 showed a significant change between FN5 and FN6, 8 were near the detection limit for both field audits, and 3 had no significant change. All the measurable anions and cations decreased from FN5 to FN6 (most notably NO_3^-, the mean concentrations for which decreased from 0.147 mg/L to 0.016 mg/L). Air-equilibrated and initial DIC, conductance, ANC, BNC, and SiO_2 mean concentration also decreased. Only the initial and air-equilibrated pH values showed no significant difference between the two field audits. Although there may be many factors that contribute to these decreases in analyte concentrations over time, seasonal effects are likely to be the primary factor.

Table F-2. Precision Estimated from Audit Samples Analyzed Among Batches (Field Natural Audit Lot 4 [FN4, Big Moose Lake]). Western Lake Survey - Phase I

	Laboratories Pooled (n = 20)		Laboratory I (n = 9)		Laboratory II (n = 11)	
Variable[a]	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD
Al, extractable	0.195	31.1	0.236	18.4	0.162	32.4
Al, total	0.352	13.2	0.368	5.5	0.339	17.2
ANC(μeq/L)	-24.1	10.2[b]	-22.9	12.7[b]	-25.0	6.2[b]
BNC(μeq/L)	119.8	10.9	107.1	6.9	130.2	2.9
Ca	2.10	3.6	2.16	1.8	2.06	3.4
Cl^-	0.54	6.1	0.56	8.0	0.53	2.5
Conductance (μS/cm)	32.2	3.6	32.0	2.4	32.4	4.4
DIC, air equilibrated	0.32	80.9	0.15	20.2	0.47	60.3
DIC, initial	0.51	30.4	0.49	14.4	0.53	38.7
DOC	8.1	2.1	8.0	1.8	8.2	1.0
F^-, total dissolved	0.074	11.7	0.079	7.5	0.069	10.8
Fe	0.07	10.2	0.07	5.3	0.08	9.3
K	0.68	2.7	0.67	2.3	0.69	2.4
Mg	0.36	1.3	0.36	1.1	0.36	1.3
Mn	0.078	9.9	0.078	1.3	0.078	13.6
Na	0.74	3.7	0.74	5.1	0.74	2.3
NH_4^+	-0.001	1770.4[b]	-0.007	215.3[b]	0.004	182.8
NO_3^-	2.351	4.8	2.330	6.0	2.368	3.8
P, total	0.002	141.4	0.001	345.1	0.003	87.4
pH, acidity (pH units)	4.68	0.03[c]	4.68	0.05[c]	4.68	0.02[c]
pH, alkalinity (pH units)	4.68	0.02[c]	4.68	0.02[c]	4.68	0.02[c]
pH, air equilibrated (pH units)	4.70	0.03[c]	4.69	0.02[c]	4.71	0.04[c]
SiO_2	4.45	11.0	4.29	16.2	4.58	3.4
SO_4^{2-}	6.68	5.5	6.81	7.3	6.58	2.5

[a] All variables are measured in mg/L unless otherwise noted.
[b] The absolute value of the %RSD.
[c] Standard deviation values were used for pH measurements.

FL11 (Field Low Synthetic, Lot 11) - Table F-5, Figures J-1 through J-26. Of the 21 samples analyzed, Laboratory II analyzed 10 and Laboratory I analyzed 11. For Ca, the mean concentrations for the two laboratories differ; this difference, coupled with Laboratory I's precision estimate at almost three times that of Laboratory II's precision estimate, results in a %RSD of 17.3 percent for the laboratories pooled. This is consistent with the field natural audit precision results. Both DIC determinations (laboratories pooled and by laboratory) show a %RSD that is higher than desired (between 16% and 26%) except for the initial DIC precision for Laboratory II (2.7%). For initial DIC, however, the mean concentrations for Laboratory I (1.49 mg/L) and Laboratory II (1.97 mg/L) are far enough apart that the precision for the laboratories pooled results in a %RSD of 21.9 percent. For DOC, there are laboratory (mean concentration) differences and there is variability for the laboratories pooled and separated, but the concentration (0.9 mg/L) may be too low to be of concern. Precision for Na was much better for Laboratory II (5.3%) than for Laboratory I (17.0%), with a precision of 12.7 percent for the laboratories pooled. In fact, there is one sample concentration that makes the estimate so high; it was identified as a dilution error at Laboratory I. When the dilution error is corrected, the precision for Na is 4.8 percent. Similarly, the precision estimates for K were much better for Laboratory II (6.3%) than for Laboratory I (11.6%). The NH_4^+ means and %RSDs were almost identical, with a %RSD of 18.8 percent at a mean concentration of 0.13 mg/L for the laboratories pooled. Concentrations for extractable Al, total Al, BNC, and Fe were too low for confident statistical comparisons to be obtained.

FL12 (Field Low Synthetic, Lot 12) - Table F-6, Figures J-1 through J-26. Of the 26 samples

Table F-3. Precision Estimated from Audit Samples Analyzed Among Batches (Field Natural Audit Lot 5 [FN5, Bagley Lake, First Sampling]), Western Lake Survey - Phase I

	Laboratories Pooled (n = 68)		Laboratory I (n = 24)		Laboratory II (n = 44)	
Variable[a]	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD
Al, extractable	0.002	120.4	0.001	193.5	0.002	89.4
Al, total	0.010	43.1	0.007	37.4	0.012	34.8
ANC(μeq/L)	146.7	3.5	149.4	5.0	145.3	1.6
BNC(μeq/L)	37.1	16.1	34.7	16.1	38.3	15.2
Ca	1.99	3.2	2.05	2.3	1.95	2.2
Cl^-	0.24	11.8	0.25	17.1	0.23	6.2
Conductance (μS/cm)	17.8	6.4	17.5	4.8	18.0	6.9
DIC, air equilibrated	1.83	11.3	1.83	17.6	1.83	5.9
DIC, initial	1.91	13.3	2.04	17.9	1.83	6.1
DOC	0.4	79.2	0.5	25.6	0.4	102.7
F^-, total dissolved	0.025	8.0	0.025	11.0	0.025	5.3
Fe	0.004	177.8	0.001	744.4	0.006	131.7
K	0.36	5.5	0.36	4.9	0.36	5.7
Mg	0.24	2.0	0.24	2.1	0.24	1.9
Mn	0.003	351.7	0.001	359.8	0.004	299.0
Na	1.06	5.2	1.08	7.1	1.04	3.2
NH_4^+	0.011	106.1	0.007	160.8	0.013	86.7
NO_3^-	0.147	23.1	0.139	11.7	0.151	26.5
P, total	0.004	197.2	0.003	140.9	0.004	202.7
pH, acidity (pH units)	7.00	0.10[b]	7.10	0.07[b]	6.95	0.07[b]
pH, alkalinity (pH units)	7.02	0.09[b]	7.07	0.09[b]	7.00	0.07[b]
pH, air equilibrated (pH units)	7.29	0.13[b]	7.29	0.13[b]	7.29	0.13[b]
SiO_2	11.37	8.6	11.17	12.3	11.47	5.9
SO_4^{2-}	0.97	7.6	0.93	9.2	0.98	5.8

[a] All variables are measured in mg/L unless otherwise noted.
[b] Standard deviation values were used for pH measurements.

analyzed, Laboratory II analyzed 20 and Laboratory I analyzed 6. For FL11, the Ca mean concentrations differ considerably between laboratories. Laboratory I's %RSD of 16.0 percent for Ca contributes significantly to the %RSD of 12.2 percent for the laboratories pooled. For the laboratories pooled, the conductance precision (4.5%) was affected most by the performance indicated from Laboratory II, which had a %RSD of 5.0 percent for conductance. As with FL11, the %RSDs for air-equilibrated DIC are less than desirable for each laboratory and for the laboratories pooled (about 15%). The initial %RSD for DIC, however, was reasonable for all subsets. The fact that Laboratory I analyzed only 6 FL12 samples may help to account for the high variability for total dissolved F^- (11.5%) as compared to Laboratory II (4.9%). Although the laboratories had very similar mean concentrations for SiO_2 (1.19 mg/L and 1.14 mg/L), Laboratory I's %RSD was 16.3 percent as compared to Laboratory II's %RSD of 7.2 percent. The %RSD of 9.9 percent for the laboratories pooled also was acceptable. Precision for total P showed a large degree of variability for Laboratory II and for the laboratories pooled; all %RSDs were 19 percent or greater. Laboratory II's imprecision for all pH precision greatly contributed to the estimates for the laboratories pooled. Extractable Al, total Al, BNC, and Fe all had levels too low to allow consideration of their precision estimates.

Table F-4. Precision Estimated from Audit Samples Analyzed Among Batches (Field Natural Audit Lot 6 [FN6, Bagley Lake, Second Sampling]), Western Lake Survey - Phase I

	Laboratories Pooled (n = 37)		Laboratory I (n = 8)		Laboratory II (n = 29)	
Variable[a]	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD
Al, extractable	0.006	39.1	0.008	25.3	0.006	40.7
Al, total	0.015	18.6	0.012	21.3	0.016	14.4
ANC(μeq/L)	121.3	1.6	122.4	3.3	120.9	0.4
BNC(μeq/L)	28.5	20.3	18.5	18.1	31.3	6.1
Ca	1.59	2.6	1.64	1.2	1.57	2.0
Cl^-	0.16	5.7	0.17	8.7	0.16	4.1
Conductance (μS/cm)	14.2	3.5	14.0	3.5	14.3	3.4
DIC, air equilibrated	1.48	5.9	1.52	3.2	1.47	6.3
DIC, initial	1.47	7.0	1.63	5.1	1.42	3.6
DOC	0.2	50.4	0.4	19.3	0.2	44.1
F^-, total dissolved	0.021	9.9	0.022	18.9	0.021	5.3
Fe	0.01	75.6	0.002	81.0	0.01	58.0
K	0.29	2.9	0.29	3.7	0.29	2.6
Mg	0.17	2.0	0.18	2.7	0.17	1.6
Mn	0.003	261.0	0.001	282.8	0.004	231.4
Na	0.81	2.1	1.81	2.2	0.81	2.1
NH_4^+	-0.001	629.6[b]	-0.007	209.3[b]	0.000	20069.1[c]
NO_3^-	0.016	234.2	0.050	148.9	0.007	78.4
P, total	0.002	191.6	0.001	89.9	0.002	208.5
pH, acidity (pH units)	7.07	0.08[d]	7.14	0.05[d]	7.05	0.07[d]
pH, alkalinity (pH units)	7.09	0.07[d]	7.09	0.07[d]	7.09	0.07[d]
pH, air equilibrated (pH units)	7.25	0.15[d]	7.22	0.10[d]	7.26	0.16[d]
SiO_2	9.36	7.2	8.33	5.3	9.65	4.0
SO_4^{2-}	0.63	4.5	0.62	5.5	0.64	3.9

[a] All variables are measured in mg/L unless otherwise noted.
[b] The absolute value of the %RSD.
[c] Of the 29 values for this estimate, 28 were at or near 0.000 mg/L and 1 was 0.034 mg/L.
[d] Standard deviation values were used for pH measurements.

Table F-5. Precision Estimated from Audit Samples Analyzed Among Batches (Field Low Synthetic Audit Lot 11 [FL11]), Western Lake Survey - Phase I

	Laboratories Pooled (n = 21)		Laboratory I (n = 11)		Laboratory II (n = 10)	
Variable[a]	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD
Al, extractable	0.004	39.0	0.005	35.5	0.003	35.3
Al, total	0.027	37.5	0.019	28.1	0.035	20.3
ANC(μeq/L)	114.2	7.4	112.6	6.4	116.0	8.5
BNC(μeq/L)	28.1	31.2	22.6	19.6	34.1	24.7
Ca	0.23	17.3	0.26	15.0	0.20	5.7
Cl^-	0.37	5.3	0.37	6.6	0.38	3.4
Conductance (μS/cm)	19.6	4.4	19.5	4.0	19.6	5.1
DIC, air equilibrated	1.35	19.7	1.22	18.9	1.48	15.9
DIC, initial	1.72	21.9	1.49	26.4	1.97	2.7
DOC	0.9	38.9	1.1	28.0	0.8	45.9
F^-, total dissolved	0.044	5.6	0.044	5.8	0.044	5.6
Fe	0.005	153.7	0.003	222.6	0.008	115.9
K	0.22	9.9	0.22	11.6	0.21	6.3
Mg	0.46	4.1	0.46	3.5	0.46	4.8
Mn	0.087	12.9	0.097	3.2	0.077	9.5
Na	2.79	12.5	2.75	17.0	2.83	5.3
NH_4^+	0.13	18.8	0.13	19.8	0.13	18.9
NO_3^-	0.490	5.3	0.474	5.2	0.507	2.9
P, total	0.024	10.2	0.024	10.8	0.025	9.5
pH, acidity (pH units)	6.95	0.16[b]	6.98	0.16[b]	6.93	0.16[b]
pH, alkalinity (pH units)	6.93	0.12[b]	6.95	0.15[b]	6.91	0.08[b]
pH, air equilibrated (pH units)	7.29	0.12[b]	7.21	0.08[b]	7.37	0.11[b]
SiO_2	1.04	8.0	1.00	7.9	1.07	6.6
SO_4^{2-}	2.35	6.2	2.27	5.2	2.44	5.0

[a] All variables are measured in mg/L unless otherwise noted.
[b] Standard deviation values were used for pH measurements.

Table F-6. Precision Estimated from Audit Samples Analyzed Among Batches (Field Synthetic Audit Lot 12 [FL12]), Western Lake Survey - Phase I

	Laboratories Pooled (n = 26)		Laboratory I (n = 6)		Laboratory II (n = 20)	
Variable[a]	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD	Mean Concentration	Estimated Precision as %RSD
Al, extractable	0.005	50.9	0.007	19.2	0.005	58.8
Al, total	0.028	21.8	0.022	24.2	0.030	17.4
ANC(μeq/L)	108.4	3.0	106.8	5.4	108.9	1.9
BNC(μeq/L)	31.6	28.0	19.0	7.5	35.4	17.2
Ca	0.20	12.2	0.24	16.0	0.19	3.3
Cl^-	0.35	4.1	0.34	6.4	0.35	2.8
Conductance (μS/cm)	19.7	4.5	19.6	1.6	19.8	5.0
DIC, air equilibrated	1.51	16.1	1.33	15.6	1.56	14.7
DIC, initial	1.39	9.7	1.31	5.8	1.41	9.9
DOC	1.1	8.8	1.18	2.2	1.1	9.5
F^-, total dissolved	0.042	7.6	0.044	11.5	0.041	4.9
Fe	0.006	154.2	-0.001	248.6[b]	0.009	113.2
K	0.21	7.1	0.22	5.0	0.20	6.9
Mg	0.44	1.8	0.45	2.0	0.44	1.4
Mn	0.105	9.4	0.092	1.1	0.109	7.3
Na	2.76	2.5	2.84	2.4	2.74	1.9
NH_4^+	0.17	5.2	0.18	4.7	0.17	2.1
NO_3^-	0.478	7.4	0.456	6.3	0.485	7.1
P, total	0.025	28.0	0.029	19.6	0.024	29.4
pH, acidity (pH units)	6.93	0.11[c]	7.02	0.05[c]	6.91	0.10[c]
pH, alkalinity (pH units)	6.96	0.10[c]	6.97	0.08[c]	6.96	0.11[c]
pH, air equilibrated (pH units)	7.20	0.14[c]	7.15	0.06[c]	7.22	0.15[c]
SiO_2	1.15	9.9	1.19	16.3	1.14	7.2
SO_4^{2-}	2.26	3.8	2.16	2.6	2.29	2.9

[a] All variables are measured in mg/L unless otherwise noted.
[b] The absolute value of the %RSD.
[c] Standard deviation values were used for pH measurements.

Appendix G

Estimated Analytical Accuracy for Field Synthetic Audit Samples by Lot

Table G-1 presents accuracy calculations for FL11 only, with the laboratories pooled and separate. Ca was biased high as a result of Laboratory I's inaccuracy of +32.6 percent. Accuracy for total Al was poor solely due to Laboratory II's value of +73.0 percent. Mn was biased marginally low at -10.8% also as a result of Laboratory II's values; total P was biased high as a result of Laboratory I's values. The only specific trend is for NH_4^+, where both laboratories were biased low. When NH_4^+ concentration is plotted over time (over a 3-week period), the concentration tends to drop, producing high inaccuracy (-13.1% in week 1 and -33.0% in week 3). DOC also was biased low only for Laboratory II.

Table G-2 presents accuracy calculations for FL12 (laboratories pooled and separate). Two analytes showed high inaccuracy: total Al reflects the high value for Laboratory II (+46.5%) and DOC reflects the high value for Laboratory I (+18.0%). Laboratory II showed slight inaccuracy for Mn (+11.2%) and total P (-12.2%), but these values are not high enough to affect overall accuracy. Laboratory II's values for Ca (+21.6%) and SiO_2 (+11.2%) also were not high enough to affect overall accuracy.

Table G-1. Estimated Analytical Accuracy for Field Synthetic Audit Lot 11 (FL11), Western Lake Survey - Phase I

		Laboratories Pooled		Laboratory I		Laboratory II	
Variable[a]	Theoretical Concentration	Mean Concentration (n = 21)	Accuracy[b] (%)	Mean Concentration (n = 11)	Accuracy[b] (%)	Mean Concentration (n = 10)	Accuracy[b] (%)
Al, extractable	0.020	0.0041	-79.5	0.0047	-76.5	0.0034	-83.0
Al, total	0.020	0.0265	+32.5	0.0192	-4.0	0.0346	+73.0
ANC(μeq/L)	----	114.2	----	112.6	----	116.1	----
BNC(μeq/L)	----	28.1	----	22.6	----	34.12	----
Ca	0.194	0.231	+19.1	0.257	+32.6	0.202	+4.2
Cl^-	0.343	0.371	+8.2	0.366	+6.7	0.375	+9.4
Conductance (μS/cm)	----	19.6	----	19.5	----	19.6	----
DIC, air equilibrated	----	1.35	----	1.22	----	1.48	----
DIC, initial	0.959	1.720	+79.4	1.49	+55.4	1.97	+105.4
DOC	1.0	0.942	-5.8	1.10	+10.0	0.80	-20.0
F^-, total dissolved	0.042	0.0441	+4.8	0.0443	+5.5	0.0438	+4.3
Fe	0.059	0.0053	-91.0	0.0026	-95.6	0.0082	-86.1
K	0.203	0.216	+6.4	0.222	+9.4	0.209	+3.0
Mg	0.447	0.460	+2.8	0.459	+2.7	0.461	+3.1
Mn	0.098	0.087	-11.2	0.097	-1.0	0.077	-21.4
Na	2.74	2.791	+1.9	2.751	+0.4	2.828	+3.2
NH_4^+	0.168	0.134	-20.2	0.134	-20.2	0.134	-20.2
NO_3^-	0.464	0.490	+5.6	0.474	+2.2	0.507	+9.3
P, total	0.027	0.0241	-10.7	0.0235	-13.0	0.0247	-8.5
pH, acidity (pH units)	----	6.95	----	6.98	----	6.93	----
pH, alkalinity (pH units)	----	6.93	----	6.95	----	6.91	----
pH, air equilibrated (pH units)	----	7.29	----	7.21	----	7.37	----
SiO_2	1.07	1.04	-2.9	1.00	+7.0	1.07	+0.3
SO_4^{2-}	2.28	2.35	+3.1	2.27	-0.4	2.44	+7.0

[a] All variables are measured in mg/L unless otherwise noted. Mean concentrations are presented at the number of significant figures useful in estimating accuracy.

[b] A plus sign (+) indicates that the mean concentration was higher than the theoretical concentration; a minus sign (-) indicates that the mean concentration was lower than the theoretical concentration.

Table G-2. Estimated Analytical Accuracy for Field Synthetic Audit Lot 12 (FL12), Western Lake Survey - Phase I

		Laboratories Pooled		Laboratory I		Laboratory II	
Variable[a]	Theoretical Concentration	Mean Concentration (n = 26)	Accuracy[b] (%)	Mean Concentration (n = 6)	Accuracy[b] (%)	Mean Concentration (n = 20)	Accuracy[b] (%)
Al, extractable	0.020	0.0050	-75.0	0.0066	-67.0	0.0046	-77.0
Al, total	0.020	0.0275	+37.5	0.0216	+8.0	0.0293	+46.5
ANC(μeq/L)	----	108.4	----	106.8	----	108.9	----
BNC(μeq/L)	----	31.6	----	19.0	----	35.4	----
Ca	0.194	0.204	+5.2	0.236	+21.6	0.195	+0.5
Cl^-	0.343	0.348	+1.5	0.338	-1.4	0.351	+2.3
Conductance (μS/cm)	----	19.7	----	19.6	----	19.8	----
DIC, air equilibrated	----	1.51	----	1.33	----	1.56	----
DIC, initial	0.959	1.39	+44.9	1.31	+36.6	1.41	+47.0
DOC	1.0	1.12	+12.0	1.18	+18.0	1.10	+10.0
F^-, total dissolved	0.042	0.0419	-0.2	0.0443	+5.5	0.0412	-1.9
Fe	0.059	0.0063	-89.3	-0.001	-101.7	0.009	-84.7
K	0.203	0.207	+2.0	0.219	+7.9	0.204	+0.5
Mg	0.447	0.440	-1.6	0.448	+0.2	0.438	-2.0
Mn	0.098	0.105	+7.1	0.092	-6.1	0.109	+11.2
Na	2.74	2.76	+0.7	2.84	+3.6	2.74	0.0
NH_4^+	0.168	0.170	+1.2	0.184	+9.5	0.166	-1.2
NO_3^-	0.464	0.478	+3.0	0.456	-1.8	0.485	+4.5
P, total	0.027	0.0249	-7.8	0.0290	+7.4	0.0237	-12.2
pH, acidity (pH units)	----	6.93	----	7.02	----	6.91	----
pH, alkalinity (pH units)	----	6.96	----	6.97	----	6.96	----
pH, air equilibrated (pH units)	----	7.20	----	7.15	----	7.22	----
SiO_2	1.07	1.15	+7.5	1.19	+11.2	1.14	+6.5
SO_4^{2-}	2.28	2.26	-0.9	2.16	-5.2	2.29	+0.4

a All variables are measured in mg/L unless otherwise noted. Mean concentrations are presented at the number of significant figures useful in estimating accuracy.

b A plus sign (+) indicates that the mean concentration was higher than the theoretical concentration; a minus sign (-) indicates that the mean concentration was lower than the theoretical concentration.

Appendix H

Field Audit Sample Control Limits and Summary of Field Audit Samples Outside Control Limits

Final audit sample control limits were generated after all analytical laboratory data (149 batches) had been entered into the raw data set. Values that were outside the control limits were considered suspect and were the basis for requesting confirmation of the values reported by the analytical laboratories.

Table H-1. Field Audit Sample Control Limits, Western Lake Survey - Phase I

Variable[a]	FN3 (Lake Superior; n = 38) Control Limits Lower Limit	FN3 Control Limits Upper Limit	FN3 Number of Samples Outside Control Limits Below	FN3 Number of Samples Outside Control Limits Above	FN4 (Big Moose Lake; n = 20) Control Limits Lower Limit	FN4 Control Limits Upper Limit	FN4 Number of Samples Outside Control Limits Below	FN4 Number of Samples Outside Control Limits Above
Al, extractable	-0.0029	0.0071	2	-	0.0655	0.3244	-	-
Al, total	-0.001	0.0250	-	-	0.2488	0.4517	1	1
ANC (μeq/L)	807.36	882.89	1	5	-29.32	-18.81	-	-
BNC (μeq/L)	-4.81	48.64	1	1	91.96	147.59	-	1
Ca	12.48	15.21	-	-	1.941	2.263	-	-
Cl^-	1.354	1.510	4	2	0.491	0.588	1	-
Conductance (μS/cm)	93.67	97.78	2	2	30.18	33.89	-	1
DIC, air equilibrated	9.034	10.138	-	5	-0.235	0.881	-	2
DIC, initial	7.696	12.033	-	4	0.338	0.624	-	1
DOC	1.13	1.58	2	3	7.74	8.46	-	-
F^-, total dissolved	0.0307	0.0405	3	3	0.0552	0.0920	1	1
Fe	-0.010	0.019	-	2	0.058	0.088	-	1
K	0.472	0.567	2	1	0.638	0.716	-	1
Mg	2.748	3.058	-	1	0.351	0.371	-	-
Mn	-0.0120	0.0075	1	3	0.063	0.094	-	2
Na	1.300	1.423	1	1	0.679	0.796	1	1
NH_4^+	-0.015	0.010	5	1	-0.027	0.026	1	-
NO_3^-	1.283	1.554	-	1	2.116	2.614	-	-
P, total	-0.0030	0.0041	-	2	-0.0056	0.0107	-	-
pH, acidity (pH units)	7.700	8.028	2	-	4.607	4.756	1	-
pH, alkalinity (pH units)	7.724	7.988	2	1	4.636	4.717	-	1
pH, air-equlibrated (pH units)	8.018	8.224	1	2	4.654	4.759	1	1
SiO_2	2.196	3.002	4	2	3.561	5.134	1	1
SO_4^{2-}	2.814	3.668	1	2	6.089	7.085	-	3

(continued)

[a] mg/L unless otherwise indicated.

Table H-1. (continued)

Variable[a]	FN5 (Bagley Lake; n = 68) Control Limits Lower Limit	Control Limits Upper Limit	Number of Samples Outside Control Limits Below	Number of Samples Outside Control Limits Above	FN6 (Bagley Lake; n = 37) Control Limits Lower Limit	Control Limits Upper Limit	Number of Samples Outside Control Limits Below	Number of Samples Outside Control Limits Above
Al, extractable	-0.0024	0.0059	2	2	0.0012	0.0115	-	1
Al, total	-0.0032	0.0161	-	3	0.0095	0.0212	1	1
ANC (μeq/L)	137.86	154.87	1	6	119.82	122.01	1	5
BNC (μeq/L)	27.61	45.53	2	4	166.67	40.41	2	-
Ca	1.860	2.116	1	3	1.505	1.673	-	-
Cl^-	0.213	0.248	-	9	0.147	0.178	1	1
Conductance (μS/cm)	15.68	19.89	2	4	13.21	15.24	1	-
DIC, air equilibrated	1.409	2.257	3	3	1.305	1.662	2	-
DIC, initial	1.397	2.407	-	7	1.285	1.632	-	3
DOC	0.09	0.66	1	4	-0.01	0.49	-	1
F^-, total dissolved	0.0214	0.0284	2	2	0.0169	0.0255	2	1
Fe	-0.008	0.016	1	4	-0.006	0.029	-	2
K	0.325	0.394	1	4	0.274	0.309	1	-
Mg	0.228	0.246	1	1	0.167	0.180	1	2
Mn	-0.013	0.019	3	4	-0.015	0.021	-	-
Na	0.980	1.124	1	2	0.779	0.850	-	-
NH_4^+	-0.013	0.035	2	1	-0.017	0.013	3	2
NO_3^-	0.116	0.160	-	7	-0.005	0.021	-	5
P, total	-0.0021	0.0057	-	8	-0.0017	0.0036	-	3
pH, acidity (pH units)	6.800	7.208	2	1	6.909	7.223	1	-
pH, alkalinity (pH units)	6.852	7.195	2	1	6.952	7.237	2	-
pH, air-equlibrated (pH units)	7.096	7.510	6	1	7.051	7.503	3	-
SiO_2	9.157	13.725	1	3	8.182	10.654	2	-
SO_4^{2-}	0.827	1.095	-	3	0.576	0.692	-	2

(continued)

[a]mg/L unless otherwise indicated.

Table H-1. (continued)

Variable[a]	FL11 (Synthetic, Lot 11; n = 21) Control Limits Lower Limit	Control Limits Upper Limit	Number of Samples Outside Control Limits Below	Above	FL12 (Synthetic, Lot 12; n = 26) Control Limits Lower Limit	Control Limits Upper Limit	Number of Samples Outside Control Limits Below	Above
Al, extractable	0.0007	0.0075	-	-	-0.0003	0.0104	-	-
Al, total	0.0054	0.0477	-	-	0.0149	0.0401	1	1
ANC (μeq/L)	99.14	126.87	-	1	102.46	113.68	2	1
BNC (μeq/L)	9.45	46.73	-	-	13.08	50.14	-	-
Ca	0.158	0.293	-	1	0.181	0.208	-	4
Cl^-	0.337	0.399	-	1	0.318	0.378	1	-
Conductance (μS/cm))	17.72	21.40	-	-	18.09	21.19	-	2
DIC, air equilibrated	0.628	2.223	-	-	0.999	2.016	-	-
DIC, initial	0.902	2.377	-	-	1.108	1.673	-	-
DOC	0.16	1.83	-	-	0.909	1.321	-	-
F^-, total dissolved	0.0388	0.0494	-	-	0.0370	0.0454	-	2
Fe	-0.012	0.023	-	1	-0.014	0.027	-	2
K	0.170	0.262	-	-	0.176	0.237	-	1
Mg	0.420	0.500	-	-	0.423	0.457	-	1
Mn	0.064	0.111	-	-	0.084	0.125	-	-
Na	2.565	3.149	1	-	2.616	2.905	-	2
NH_4^+	0.078	0.184	-	-	0.154	0.184	-	2
NO_3^-	0.440	0.544	1	-	0.447	0.521	2	1
P, total	0.0188	0.0293	-	-	0.0202	0.0290	2	2
pH, acidity (pH units)	6.619	7.295	-	1	6.714	7.156	1	-
pH, alkalinity (pH units)	6.673	7.189	-	-	6.749	7.173	1	-
pH, air-equlibrated (pH units)	7.026	7.547	-	1	6.912	7.496	-	2
SiO_2	0.860	1.211	-	-	1.053	1.238	1	1
SO_4^{2-}	2.039	2.663	-	-	2.081	2.440	1	1

[a] mg/L unless otherwise indicated.

Table H-2. Cumulative Number of Field Audit Samples Outside Control Limits, Western Lake Survey - Phase I

Variable	No. of Samples Below Limit	No. of Samples Above Limit	Total (n = 210)[a]
Al, extractable	4	1	5
Al, total	3	6	9
ANC	5	18	23
BNC	5	6	11
Ca	1	8	9
CL^-	7	13	20
Conductance	5	9	14
DIC, air equilibrated	5	10	15
DIC, initial	-	15	15
DOC	3	8	11
F^-, total dissolved	8	9	17
Fe	1	12	13
K	4	7	11
Mg	2	5	7
Mn	4	9	13
Na	4	6	10
NH_4^+	11	6	17
NO_3^-	3	14	17
P, total	2	15	17
pH, acidity	6	3	9
pH, alkalinity	7	3	10
pH, air equilibrated	11	7	18
SiO_2	9	7	16
SO_4^{2-}	2	11	13
			Total 320

[a] n = the number of audit samples. There are 24 variables per n; therefore, 5,040 analyses were performed.

Appendix I

Relative Interlaboratory Bias in the Western Lake Survey - Phase I

Prepared by

Thomas Permutt, Mithra Moezzi and Stella C. Grosser
Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903

Introduction

In the Western Lake Survey, water from approximately 700 lakes in the western United States was sampled to study its chemical composition. After preservative treatment at field laboratories, the samples were shipped to one of two contract laboratories for analysis. Water from each lake was thus analyzed by one laboratory. Futhermore, water from all lakes in an area was analyzed by the same laboratory.

Some water was analyzed by both laboratories. For example, 50 wilderness lakes were visited both by helicopter and ground access, and duplicate samples from these lakes were sent to both laboratories. This report focuses on audit samples, another example of water analyzed by both laboratories.

Two types of audit samples were included. Natural audits were made of water collected one time in large quantities from Lake Superior and Big Moose Lake and two times from Bagley Lake. Small samples of this water were shipped to the field laboratories, treated as usual, and reshipped to the contract laboratories. Synthetic audits were made up from stock solutions according to a recipe designed to give concentrations close to the limits of quantitation for most analytes. These were shipped to the field laboratories also, and treated and reshipped for analysis along with routine samples.

Since they are repeated measurements of the same water, the audit determinations provide information about the precision of the measurement process. Also, for the synthetic audits, the measurements can be compared with the theoretically known composition to provide information about absolute bias. The subject of this work, however, is relative interlaboratory bias. That is, how do measurements of the same water by the two contract laboratories differ on average?

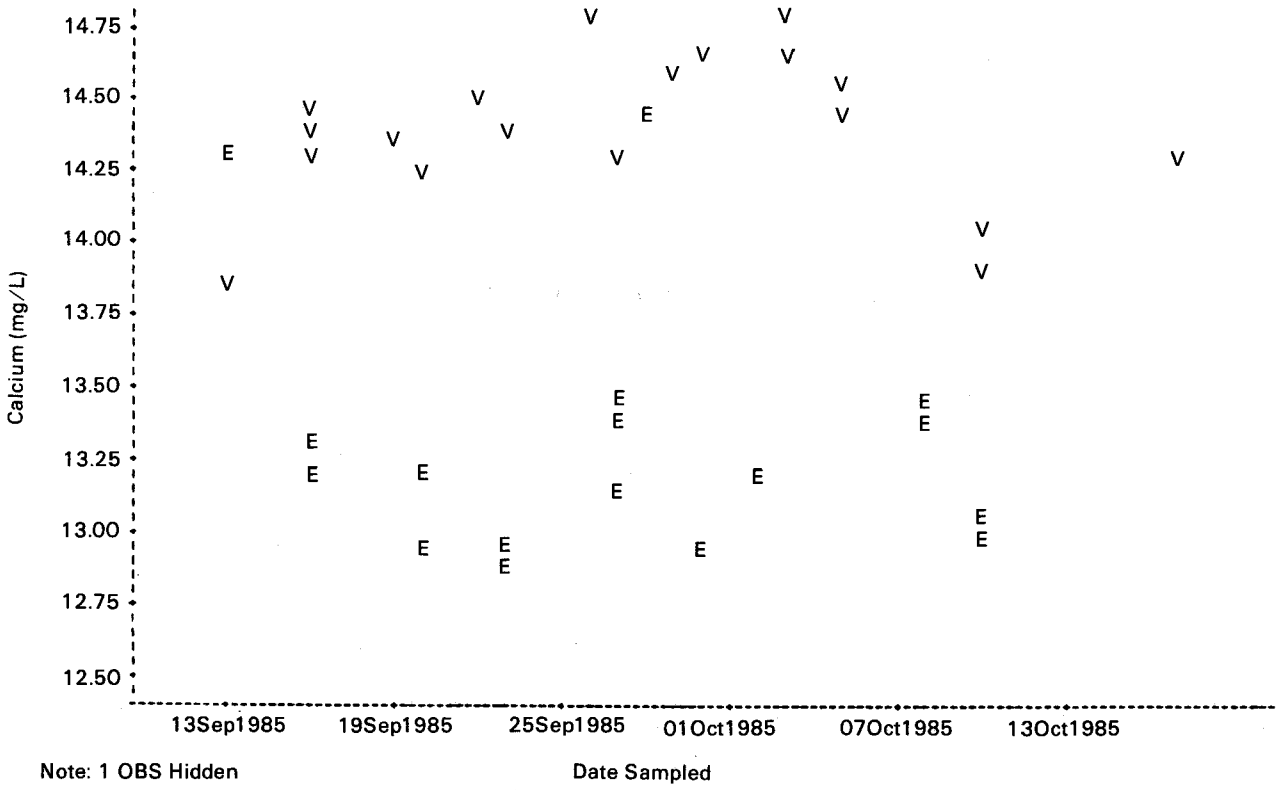
The question is especially important in view of the design of the Western Lake Survey. Because samples from different regions went to different laboratories, what is really a difference between laboratories could appear as a difference between regions or vice versa. The audit samples, however, should allow any differences that are only due to laboratories to be distinguished.

Preliminary Analysis

We will illustrate the analysis of relative bias by looking at one parameter, calcium, in detail. Figure I-1 shows the concentrations of calcium measured by the two contract laboratories in audit samples of water from Lake Superior (sample code FN3). The measurements by Versar (V) are consistently somewhat higher than those by EMSI (E). The difference in means is 1.11 mg/L, or about 8 percent of the concentration. The standard deviations are only 0.43 and 0.26 mg/L, so the measurements by the two laboratories overlap very little. The standard errors are 0.10 and 0.06 mg/L, so the standard error of the difference is 0.12 mg/L. That is, we can be 95 percent certain that if there were a very large number of audit samples from Lake Superior, the difference in means would be within 0.24 mg/L of 1.11 mg/L. Whatever the practical significance of a relative bias of this magnitude, there is clearly no doubt as to its statistical significance.

Figure I-2 shows the measurements of calcium in audit samples from Bagley Lake (sample code FN5). The pattern is similar, on a different scale. The

Figure I-1. Measurements of calcium in Lake Superior audit samples (FN3). (V = VERSAR, E = EMSI).



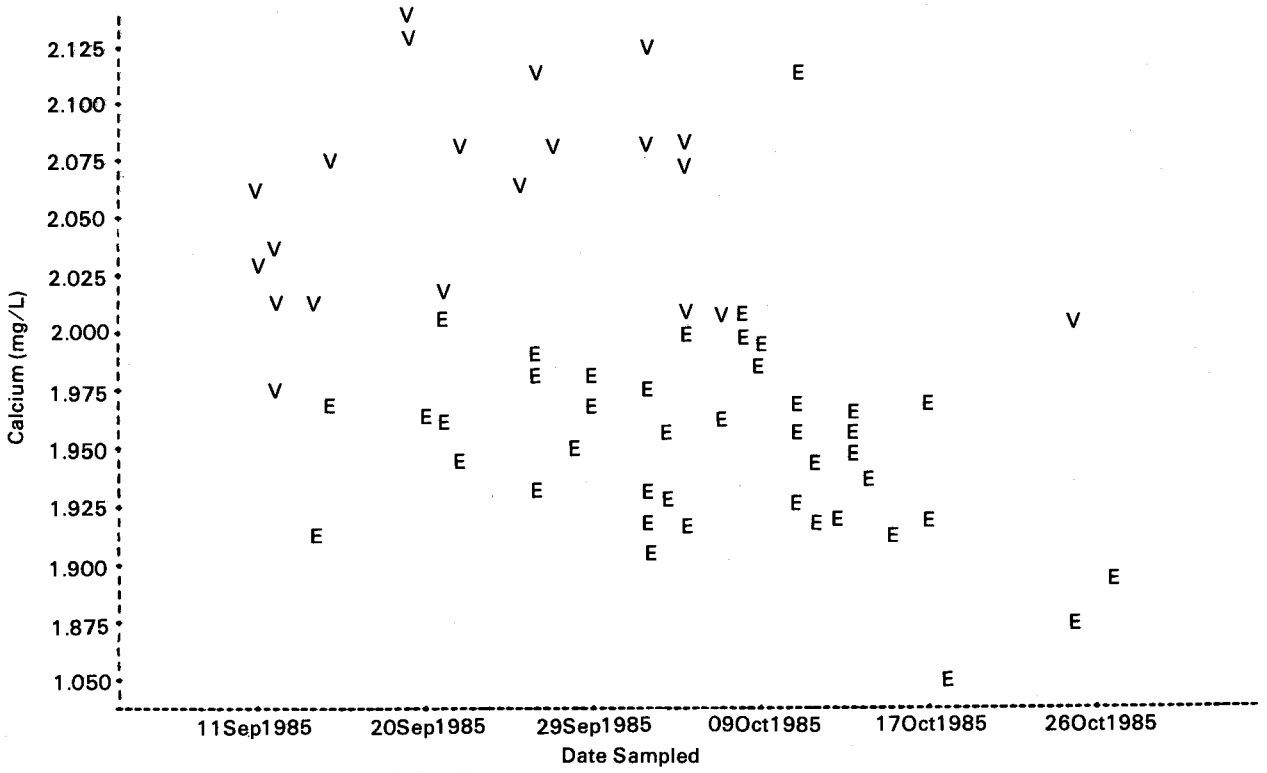
difference in means is 0.10 mg/L, or about 5 percent of the concentration. Apparently neither the amount of the bias (in mg/L) nor the bias as a percentage of the concentration stays the same from lake to lake.

This variation complicates the application of audit data to routinely sampled lakes. If, for example, the estimated bias for all the lots of audit samples were 0.10 mg/L, we might reasonably suppose that a similar bias applied to routine samples as well. If, instead, the bias appeared to be 8 percent of the concentration in each lot of audit samples, we might suppose the bias in routine samples to be 8 percent. With different biases in different lots, however, it is difficult to say what bias should be expected in a given routine sample.

Perhaps bias in the audit samples can be explained as a slightly more complex function of concentration, and this function can be assumed to apply to routine samples. A plausible model is that bias is a linear function of concentration with nonzero slope and intercept. To examine its applicability, we have summarized the data from Figures I-1 and I-2 along with the four other lots of natural and synthetic audits in Figure I-3. Because Lake Superior is so different from the rest, we have drawn the same figure on two different scales, one including and one excluding Lake Superior. Each of the six stars represents the two mean measurements of calcium in one of the six lots of audit samples. Error bars show the standard deviations, and ellipses show 95 percent confidence regions for the means. Thus most of the spread of the individual measurements is within the error bars; and we can be confident that the means of a large number of measurements would fall inside the ellipse. The line of identity is shown; if there were no bias the stars would lie close (within an ellipse or so) to this line. We also show the straight line that fits best, in a sense that we will make precise later.

The intercept of the line is 0.02 mg/L, and the slope is 1.04. The points on this line therefore represent a relative bias of 0.02 mg/L plus 4 percent of the concentration. At low concentrations the intercept dominates, so the line indicates a bias of about 0.02 mg/L, whereas at high concentrations the slope dominates, so the line indicates a bias of about 4 percent of the concentration. The estimated bias at a concentration of 14 mg/L (Lake Superior) would be 0.02 + (.04) (14) = 0.58 mg/L. This is only about

Figure I-2. Measurements of calcium in Bagley Lake audit samples (FN5). (V = VERSAR, E = EMSI).



Note: 2 OBS had missing values 3 OBS Hidden

half the observed difference in laboratory means for Lake Superior.

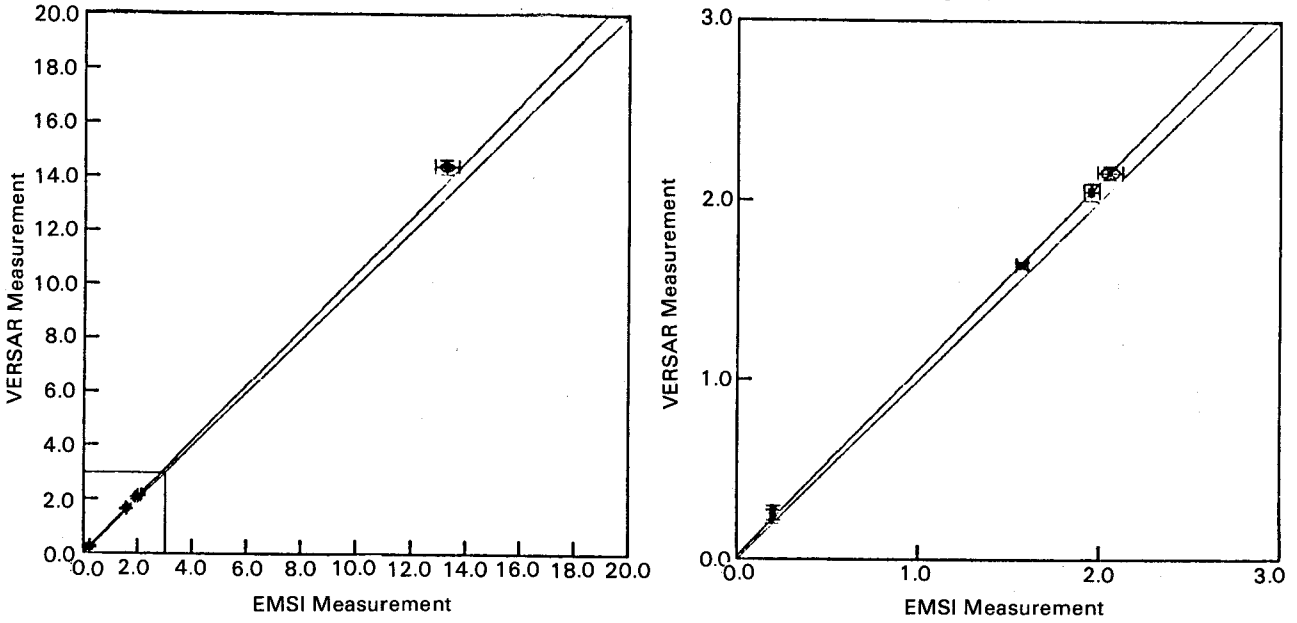
Thus, the fit is not very good. The scale on which deviations of the stars from the line should be regarded is indicated by the ellipses.These show the amount of uncertainty in the position of the stars due to random errors in measurement. It is impossible to draw a line through all the ellipses. Thus, relative bias cannot be described simply as a linear function of concentration.

Several explanations of the variation in bias can be posited. For example, the deviation of the extreme upper-right star (Lake Superior) could be supposed to result from a nonlinear effect. That is, the line could be bent between this star and the next one. Obviously there is little information about the shape of the curve between these two stars, so that the bias at concentrations between about 2 and 13 mg/L would be hard to estimate.

Even below 2 mg/L, the fit of the line is not as good as might be expected if bias were really a linear function of concentration. Lots FL11 and FL12, for example, have about the same concentration of calcium, but the differences in laboratory means are 0.055 mg/L for lot FL11 and 0.041 mg/L for lot FL12. The difference here is not statistically significant, but the pattern persists for some other parameters, especially total aluminum and dissolved inorganic carbon. Different lots have different biases, even at the same concentration; therefore, the bias for a given lot may also depend on properties other than the concentration of the analyte in question. For calcium for the synthetic audits FL11 and FL12, the important other property (if there is one) may be time. Lot FL12 was analyzed later, and the bias may have changed a little. It seems likely that the bias for a given analyte for a given lot depends not only on the concentration of the analyte but also on the concentrations of other species.

Unfortunately, the data do not allow statistical evaluation of the many possible explanations for variation in bias. After all, there are only six lots of audit samples; they come from only three lakes; and the three lakes were not chosen randomly. The replication of measurements within lots permits fairly precise estimation of the bias for each lot as well as the testing of hypotheses concerning linear relationships. The limited number of lots, however,

Figure I-3. Means by laboratory of natural and synthetic audit measurements for CA11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and elipses (95% confidence region).



prevents authoritative statistical treatment of the variation from lot to lot.

The audit data appear to be sufficient for the intended purpose of assuring that interlaboratory biases are within quality assurance guidelines. A precise knowledge of the bias that would apply to replicated measurements from any given lake, such as would be required to correct individual observations for bias, appears to be out of reach for calcium and some other parameters because of the variability of the bias. In these cases, the best estimate of the bias for a given lake would depend on a judgment as to which of the audit lots the lake is most like. This judgment may be based on factors other than concentration and cannot be considered a purely statistical problem.

Statistical Methods

In this section we propose five alternative statistical models of the relative bias and random variation in the measurements by the two laboratories on the six lots of natural and synthetic audit samples. We describe a method of estimating the parameters of these models. We also discuss statistical hypothesis tests that can be used to choose an appropriate model for each parameter.

When we speak of relative bias, we mean the difference between the long-run means of measurements by Versar and EMSI. We would like to be able to conclude that there is no relative bias at all. Failing this, it would be good to be able to identify a simple relationship among the biases for the six lots. For example, if the bias were the same for each of the six lots, it would lend credence to the argument that the bias is also the same for routine lake samples. If this bias could be estimated with satisfactory precision, it could then be used to adjust the routine measurements for relative bias. Similarly, if the bias were the same fraction of the measured concentration for each lot, this relationship might apply to routine samples. Alternatively, the relative bias might be a linear function of concentration with both slope and intercept nonzero.

Obviously many other, more complicated relationships could exist between bias and concentration. Indeed, there is certain to be some fairly simple function whose graph passes through all six stars, as with any six points. Given the wide choice of functions, however, it would be impossible to obtain statistical confirmation that the chosen function was the correct one, and difficult to argue its applicability to routine samples.

We therefore confine our attention to four simple, useful models of bias; for the purpose of hypothesis testing we also include a completely general model. The four simple models are no bias, constant bias, constant fraction bias, and bias as a linear function of concentration. The general model is that the bias is different for each lot; that is, six parameters are required to describe the bias in six lots rather than the one or two parameters of the linear model.

The general model has much in common with random-effects models. Besides the within-lot variability, there is assumed to be an additional source of variation that affects different lots differently but is consistent within lots. Formal random-effects models are not appropriate to this problem, however. In the first place, the lots are not a random sample from any population of lots, and no *a priori* assumption about the distribution of lot effects seems reasonable. Second, with only six lots no empirical model of the lot-to-lot variation could be adequately tested.

With respect to Figure I-1, the five models can be summarized as follows:

1. The true, long-run positions of the stars are on a line through the origin with slope 1. Deviations of the actual locations from the line result from random error.
2. The true positions are on a line with slope 1, but not through the origin.
3. The line goes through the origin, but the slope is not 1.
4. The true positions of the stars are on a line not through the origin and with slope different from 1.
5. The true positions of the stars are not on a line. The observed deviations are too large to have resulted from random error.

More formally, we may write

$$E_{ij} = \mu_i + \delta_{ij}$$

and one of the following:

$$(1)\ V_{ij} = \mu_i + \varepsilon_{ij}$$

$$(2)\ V_{ij} = \mu_i + \alpha + \varepsilon_{ij}$$

$$(3)\ V_{ij} = \mu_i + \beta\mu_i + \varepsilon_{ij}$$

$$(4)\ V_{ij} = \mu_i + \alpha + \beta\mu_i + \varepsilon_{ij}$$

$$(5)\ V_{ij} = \mu_i + \gamma_i + \varepsilon_{ij};$$

with

$$\delta_{ij} \sim N(0, \sigma_i^2), \quad \varepsilon_{ij} \sim N(0, \tau_i^2),$$

where E_{ij} is the jth measurement by EMSI on the ith lot and V_{ij} is the same by Versar. The terms δ and ε are independent, normally distributed errors; their variances, σ_i^2 and τ_i^2, may vary from lot to lot as well as from laboratory to laboratory. The term μ_i is the long-run mean concentration that would be measured by EMSI; the terms in α, β, or γ_i, depending on the model, represent the interlaboratory bias (Versar relative to EMSI). Of course, there is no implication that it is Versar's measurements that are biased; the model could be rewritten, switching the roles of the two laboratories, without affecting the results.

The problem is conceptually similar to what has been called structural or orthogonal regression. In ordinary.regression a line is chosen to minimize the sum of squared vertical distances from points to the line. This imposes an asymmetry on the problem in that vertical and horizontal; variables, which we have assigned arbitrarily to Versar and EMSI, are treated differently. The effect would be to underestimate the slope of the underlying relationship, and to overestimate the intercept. Thus a slope significantly less than 1 and an intercept significantly different from zero might be expected to result from random error alone even if there were no interlaboratory bias.

In structural regression the two variables are treated symmetrically. In the common situation of paired observations the structural problem is difficult. Not all the parameters can be estimated, and it is therefore necessary to make assumptions about relationships among them. The present problem is different because of the multiple observations on each lot. All the parameters α, β, γ_i, μ_i, σ_i^2, and τ_i^2 can be estimated by the method of maxium likelihood.

The computations can be done by iteratively reweighted least squares using a nonlinear least-squares program like SAS PROC NLIN or BMDP3R. Given estimates of the σ_i^2 and τ_i^2 can be estimated from the deviations of the data from the fitted values. The weighted least-squares estimates and the weights are alternately recalculated until convergence is achieved.

The method of maximum likelihood also provides statistical tests of various relevant hypotheses. If the statistic $\lambda = -2 \log L$ is calculated for each model, where L is the maximum value of the likelihood function, differences in λ from model to model can be referred to the chi-square distribution. For example, the difference between the no-bias model and the two-parameter linear-bias model was approximately a chi-square distribution with two degrees of freedom when the hypothesis of no bias is true. Similarly, either of the one-parameter models can be tested against the two-parameter linear-bias model; and the linear-bias model can be tested against the six-parameter general model.

Results

The results of our study of interlaboratory bias in natural and synthetic audit samples are best seen in the figures collected at the end of this section. Each figure shows the following for a single parameter.

The line of identity. If there were no bias, mean measurements would fall near this line.

A star for each lot of audit samples, representing the mean measurements by EMSI and by Versar. The distance of a star from the line of identity is the apparent relative bias for that lot.

Error bars showing the spread of measurements by EMSI and Versar around the means.

A 95 percent confidence ellipse for each pair of means. It is very likely that the bar would lie somewhere in this region if there were many samples in each lot. Therefore, deviations from the line of identity or the calibration line that are larger than the ellipses cannot be supported to result from random error.

Our best estimate of the calibration line, assuming bias is a linear function of concentration. It has intercept α and slope $1 + \hat{\beta}$, where $\hat{\alpha}$ and $\hat{\beta}$ are the maximum-likelihood estimates of the slope and intercept.

Table I-1 contains likelihood-ratio statistics for testing several hypotheses. The first column is used to test the hypothesis that the bias is a linear function of concentration against the general alternative that the bias is different for each lot. The number reported is the difference between the values of $1 = -2 \log L$ for the two models, where L is the maximum value of the likelihood function. Values above 9.5 lead to rejection of the hypothesis at the 5 percent level of significance. This happens for 10 parameters, which we designate Group 1 and list in Table I-2. For these parameters bias cannot be considered to be a linear function of concentration. Table I-3 contains estimates of the bias for these (and other) parameters by lot. The mean for each laboratory is given along with the estimated relative bias, the standard error of this estimate, and the bias as a percentage of the EMSI mean.

For the other 14 cases, where the hypothesis of linear bias can be accepted, the next three columns test simpler models. The second column tests the hypothesis of no intercept against the two-parameter alternative. If the number here is less than 3.8, bias can be considered to be proportional to concentration. We have designated the six parameters for which this is so as Group 3.

Similarly, the third column tests the hypothesis that the slope of the bias is zero; i.e., that bias in absolute terms is constant across lots. We call the four parameters for which this hypothesis is accepted Group 4. Conductivity and air-equilibrated pH are in both Groups 3 and 4. The bias for these parameters is approximately constant, but the measurements are so far from zero that the fit is about equally good whether the bias is forced to have intercept zero or slope zero. Certainly, in the case of pH and perhaps in the case of conductivity, a measurement of zero has no special importance. The constant-bias model therefore seems preferable on grounds of simplicity. Statistically, however, it is not possible to discern whether the bias in conductivity or air-equilibrated pH varies with the measured value.

For two parameters, designated Group 5, the line of identity fits the data acceptably. This is indicated by a number below 4.6 in the last column. In these two cases the hypothesis that there is no bias at all can be accepted.

The four remaining parameters are called Group 2. In these cases a straight calibration line fits acceptably, but both a nonzero slope and a nonzero intercept are required.

Conclusions and Recommendations

Most of the estimated biases are well below 10 percent, which is the objective for most parameters. There are numerous exceptions at low concentrations, but this is not surprising. To take an extreme example, at zero concentration any bias at all is an infinite percentage bias. It is implicit that the data quality objective is not meant to apply at such low concentrations, but perhaps the lower limit of applicability should be an explicit part of the data quality objective.

Even though the measurements appear to meet data quality objectives in respect of interlaboratory bias, the question arises whether data quality can be improved by adjusting for the apparent bias. We do not believe this can be achieved. For almost half the parameters no acceptable model of the variation of bias with concentration was found. For the others, hypotheses that simple models apply could not be rejected, but this failure to reject should not be interpreted as strong evidence that the simple models are correct. There is evidence that interlaboratory bias varies from lake to lake. Since the sample of lakes used for audit samples is neither large nor random, not much information about the nature of this variation is available. Correcting for the estimated bias therefore seems almost as likely to do harm as good for a particular lake, and to improve overall measures of data quality very little.

We believe that most users of the data will find the relative interlaboratory bias in the Western Lake Survey to be within acceptable limits. Furthermore, the bias is unusually well documented because of the design of the quality assurance program. This documentation should provide the most sophisticated users with the means of adjusting data to suit their purposes.

Table I-1. Likelihood-Ratio Test Statistics for Testing Linear Models of Bias

Parameter*	Linear Bias? (4 d.f.)	Zero Intercept? (1 d.f.)	Zero Slope? (1 d.f.)	No Bias? (2 d.f.)
Acidity (μeq/L)	37.4			
Aluminum (extractable)	8.2	8.6	23.8	24.7
Alkalinity (μeq/L)	13.8			
Aluminum (total)	23.1			
Calcium	23.5			
Chloride	8.5	1.1	0.3	1.4
Conductivity (μS/cm)	1.3	1.0	0.5	7.1
DIC (equilibrated)	19.0			
DIC (initial)	28.1			
DOC	7.7	36.6	20.4	39.3
Iron	7.3	16.5	1.6	67.2
Fluoride (total)	7.2	1.3	3.9	10.0
Postassium	3.1	13.9	19.1	19.8
Magnesium	4.6	3.3	13.1	26.9
Manganese	61.3			
Sodium	13.9			
Ammonium	2.5	15.1	13.7	22.7
Nitrate	5.3	1.5	4.0	17.4
pH (acidity)	15.7			
pH (alkalinity)	6.3	2.4	3.5	5.3
pH (equilibrated)	8.4	0.7	2.0	7.5
Phosphorus (total)	8.2	5.7	0.4	6.4
Silica	9.6			
Sulfate	9.2	0.4	15.1	33.5
	$x_4^2, 0.95 = 9.5$	$x_1^2, 0.95 = 3.8$		$x_2^2, 0.95 = 6.0$

*All measurements are in mg/L unless otherwise noted.

Table I-2. Linear Models of Bias

GROUP 1. Bias not a linear function of concentration.

Acidity	Alkalinity	Aluminum (total)	Calcium
DIC (equilibrated)	DIC (initial)	Manganese	Sodium
pH (acidity)	Silica		

GROUP 2. Bias linear in concentration with nonzero slope and intercept.

	Intercept	Standard Error of Intercept	Slope	Standard Error of Slope
Aluminum (extractable)	-0.0019	0.0007	0.68	0.17
DOC	0.17	0.02	-0.052	0.008
Potassium	0.026	0.006	-0.075	0.015
Ammonium	-0.010	0.002	0.16	0.03

GROUP 3. Zero intercept.

Fluoride (total)	0.048	0.016
Magnesium	0.016	0.003
Nitrate	-0.041	0.009
Sulfate	-0.055	0.007
Conductivity*	-0.011	0.004
pH (equilibrated)*	-0.0048	0.0018

GROUP 4. Zero slope.

Iron	-0.0083	0.0009
Phosphorus (total)	-0.0011	0.0004
Conductivity*	-0.32	0.12
pH (equilibrated)*	-0.026	0.011

GROUP 5. No statistically significant bias.

Chloride	pH (alkalinity)

*Conductivity and pH (equilibrated) can be fit with a line of slope zero or with a different line of intercept zero, but not by a line with slope and intercept both zero.

Table I-3. Estimated Relative Bias by Lot

PARM	LOT	EMSI	VERSAR	BIAS	standard error of bias	PCBIAS*
ACCO	3	26.958	16.879	-10.079	3.9439	-37.39
ACCO	4	130.173	107.078	-23.095	2.7072	-17.74
ACCO	5	30.350	34.679	-3.671	1.4404	-9.57
ACCO	6	31.303	18.537	-12.766	1.2371	-40.78
ACCO	11	34.120	22.609	-11.511	2.9874	-33.74
ACCO	12	35.395	18.983	-16.412	1.4785	-46.37
ALEX	3	0.003	0.001	-0.002	0.0007	-63.49
ALEX	4	0.162	0.236	0.074	0.0214	45.84
ALEX	5	0.002	0.001	-0.001	0.0006	-35.03
ALEX	6	0.006	0.008	0.002	0.0009	40.85
ALEX	11	0.003	0.005	0.001	0.0006	40.80
ALEX	12	0.005	0.007	0.002	0.0008	44.74
ALKA	3	824.868	867.253	42.384	12.0174	5.14
ALKA	4	-25.036	-22.878	2.159	1.0755	.
ALKA	5	145.268	149.408	4.140	1.5718	2.85
ALKA	6	120.934	122.450	1.516	1.4437	1.25
ALKA	11	116.050	112.609	-3.441	3.7897	-2.97
ALKA	12	100.940	106.817	-2.123	2.3846	-1.95
ALTL	3	0.017	0.008	-0.009	0.0014	-54.95
ALTL	4	0.307	0.368	0.060	0.0325	19.63
ALTL	5	0.012	0.007	-0.005	0.0008	-42.02
ALTL	6	0.016	0.012	-0.004	0.0018	-23.59
ALTL	11	0.035	0.019	-0.015	0.0028	-44.51
ALTL	12	0.029	0.022	-0.008	0.0024	-26.23
CA11	3	13.285	14.402	1.117	0.1146	8.41
CA11	4	2.057	2.156	0.099	0.0245	4.82
CA11	5	1.954	2.051	0.096	0.0115	4.93
CA11	6	1.574	1.643	0.069	0.0093	4.37
CA11	11	0.202	0.257	0.055	0.0122	27.19
CA11	12	0.195	0.235	0.041	0.0154	20.99
CL11	3	1.428	1.430	0.002	0.0323	0.12
CL11	4	0.532	0.559	0.027	0.0145	5.04
CL11	5	0.234	0.248	0.014	0.0089	6.06
CL11	6	0.162	0.169	0.008	0.0054	4.70
CL11	11	0.375	0.367	-0.009	0.0083	-2.29
CL11	12	0.351	0.338	-0.013	0.0091	-3.63
COND	3	95.937	95.153	-0.784	0.5813	-0.82
COND	4	32.355	32.044	-0.310	0.5008	-0.96
COND	5	18.014	17.525	-0.489	0.2549	-2.71
COND	6	14.290	13.975	-0.315	0.1964	-2.20
COND	11	19.628	19.589	-0.111	0.3911	-0.57
COND	12	19.770	19.633	-0.137	0.2570	-0.69
DICE	3	9.447	10.351	0.904	0.2781	9.57
DICE	4	0.466	0.148	-0.318	0.0852	-68.27
DICE	5	1.835	1.829	-0.006	0.0681	-0.33
DICE	6	1.472	1.524	0.052	0.0243	3.50
DICE	11	1.651	1.220	-0.431	0.1389	-26.10
DICE	12	1.562	1.328	-0.234	0.0990	-14.98
DICI	3	9.393	10.337	0.944	0.3103	10.05
DICI	4	0.528	0.494	-0.034	0.0660	-6.46
DICI	5	1.828	2.039	0.212	0.0762	11.57
DICI	6	1.424	1.626	0.202	0.0310	14.20

Continued

Table I-3. Continued

PARM	LOT	EMSI	VERSAR	BIAS	standard error of bias	PCBIAS*
DIC1	11	1.0003	1.48527	-0.323	0.132035	-17.86
DIC1	12	1.4143	1.31083	-0.103	0.044265	-7.32
DOC1	3	1.25053	1.47947	0.229	0.084028	18.31
DOC1	4	0.21454	7.96444	-0.258	0.054223	-3.04
DOC1	5	0.38545	0.46125	0.076	0.064330	19.66
DOC1	6	0.19586	0.40750	0.212	0.032059	108.05
DOC1	11	0.901000	1.10444	0.203	0.174192	22.58
DOC1	12	1.09550	1.10000	0.005	0.025586	7.71
FE11	3	0.00863	0.00058	-0.008	0.001941	-93.29
FE11	4	0.07664	0.06211	-0.015	0.006360	-18.95
FE11	5	0.00611	0.00054	-0.006	0.001467	-91.14
FE11	6	0.01379	0.00237	-0.011	0.001635	-82.78
FE11	11	0.00820	0.00264	-0.006	0.003489	-67.85
FE11	12	0.00870	-0.00150	-0.010	0.002678	-117.24
FTL1	3	0.03316	0.03730	0.004	0.002395	12.75
FTL1	4	0.06880	0.07949	0.011	0.002996	15.54
FTL1	5	0.02461	0.02551	0.001	0.000613	3.64
FTL1	6	0.02105	0.02185	0.001	0.001477	3.79
FTL1	11	0.04381	0.04433	0.001	0.001105	1.18
FTL1	12	0.04122	0.04433	0.003	0.002132	7.55
K11	3	0.52879	0.51058	-0.018	0.006971	-3.44
K11	4	0.68618	0.66644	-0.020	0.007025	-2.88
K11	5	0.36295	0.35658	-0.006	0.004743	-1.76
K11	6	0.29086	0.29387	0.003	0.004117	1.04
K11	11	0.20880	0.22245	0.014	0.008812	6.54
K11	12	0.20355	0.21850	0.015	0.005478	7.34
MG11	3	2.85789	2.94768	0.090	0.019892	3.14
MG11	4	0.35918	0.36278	0.004	0.031983	1.00
MG11	5	0.23591	0.23892	0.003	0.001138	1.28
MG11	6	0.17324	0.17575	0.003	0.001765	1.45
MG11	11	0.46110	0.45909	-0.002	0.008530	-0.44
MG11	12	0.43765	0.44000	0.010	0.003800	2.36
MN11	3	-0.00395	0.00042	0.004	0.002441	.
MN11	4	0.07754	0.07800	0.000	0.003204	0.59
MN11	5	0.00407	0.02019	0.016	0.013635	396.36
MN11	6	0.00421	0.00025	-0.004	0.001025	-94.06
MN11	11	0.07730	0.09654	0.019	0.002500	24.90
MN11	12	0.10855	0.09233	-0.016	0.001830	-14.94
NA11	3	1.36789	1.34947	-0.018	0.016682	-1.35
NA11	4	0.73527	0.74000	0.005	0.013566	0.64
NA11	5	1.04475	1.07946	0.035	0.016528	3.32
NA11	6	0.81479	0.81237	-0.002	0.007096	-0.30
NA11	11	2.82000	2.74989	-0.079	0.148927	-2.79
NA11	12	2.73765	2.83717	0.100	0.029784	3.64
NH41	3	-0.00147	-0.01916	-0.018	0.006904	.
NH41	4	0.00427	-0.00678	-0.011	0.005404	-258.62
NH41	5	0.01341	0.00721	-0.006	0.002945	-46.25
NH41	6	0.00003	-0.00700	-0.007	0.005336	-23688.24
NH41	11	0.12120	0.10944	-0.012	0.023882	-9.70
NO31	12	0.16625	0.18367	0.017	0.003573	10.48
NO31	3	1.44347	1.39295	-0.051	0.019997	-3.50
NO31	4	2.36754	2.36109	-0.006	0.056508	-0.27

Continued

Table I-3. Continued

PARM	LOT	EMSI	VERSAR	BIAS	standard error of bias	PCBIAS*
NO31	5	0.1512	0.1395	-0.012	0.006912	-7.74
NO31	6	0.0068	0.0501	0.043	0.026413	638.07
NO31	11	0.5068	0.4706	-0.028	0.008730	-5.56
NO31	12	0.4848	0.4557	-0.029	0.014094	-6.00
PHAC	3	7.8347	7.8937	0.059	0.024382	0.75
PHAC	4	4.6845	4.6767	-0.008	0.017018	-0.17
PHAC	5	6.9523	7.1004	0.148	0.018561	2.13
PHAC	6	7.0455	7.1412	0.096	0.022500	1.36
PHAC	11	6.9300	6.9773	0.047	0.070815	0.68
PHAC	12	6.9080	7.0233	0.115	0.031018	1.67
PHAL	3	7.8432	7.8579	0.015	0.023677	0.19
PHAL	4	4.6764	4.6767	0.000	0.008542	0.01
PHAL	5	6.9980	7.0700	0.072	0.021076	1.03
PHAL	6	7.0948	7.0937	-0.001	0.029358	-0.02
PHAL	11	6.9060	6.9536	0.048	0.051914	0.69
PHAL	12	6.9575	6.9733	0.016	0.041919	0.23
PHEO	3	8.1479	8.1132	-0.035	0.029296	-0.43
PHEO	4	4.7073	4.6944	-0.013	0.013488	-0.27
PHEO	5	7.2898	7.2871	-0.003	0.032944	-0.04
PHEO	6	7.2634	7.2162	-0.047	0.047074	-0.65
PHEO	11	7.3698	7.2118	-0.157	0.042069	-2.13
PHEO	12	7.2200	7.1500	-0.070	0.041335	-0.97
PTL1	3	0.0017	-0.0002	-0.002	0.000634	-113.98
PTL1	4	0.0238	0.0008	-0.023	0.019842	-96.51
PTL1	5	0.0045	0.0028	-0.002	0.001591	-36.99
PTL1	6	0.0016	0.0014	-0.000	0.000757	-10.41
PTL1	11	0.0247	0.0235	-0.001	0.001068	-4.56
PTL1	12	0.0237	0.0290	0.005	0.002791	22.46
SIO2	3	2.5461	2.4726	-0.074	0.150276	-2.89
SIO2	4	4.5378	4.2871	-0.251	0.241476	-5.52
SIO2	5	11.6770	11.3816	-0.295	0.642900	-2.53
SIO2	6	9.6497	8.3289	-1.321	0.171586	-13.69
SIO2	11	1.0740	1.0005	-0.074	0.032665	-6.85
SIO2	12	1.1003	1.1003	0.000	0.004956	0.00
SO41	3	3.3479	3.1337	-0.214	0.058478	-6.40
SO41	4	6.5772	6.8114	0.234	0.173785	3.56
SO41	5	0.9845	0.9293	-0.055	0.019544	-5.61
SO41	6	0.6394	0.6155	-0.024	0.012842	-3.75
SO41	11	2.4430	2.2680	-0.175	0.052086	-7.16
SO41	12	2.2910	2.1565	-0.135	0.027485	-5.87

*Bias as percentage of EMSI mean.

Figure I-4. Means by laboratory of natural and synthetic audit measurements for CA11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

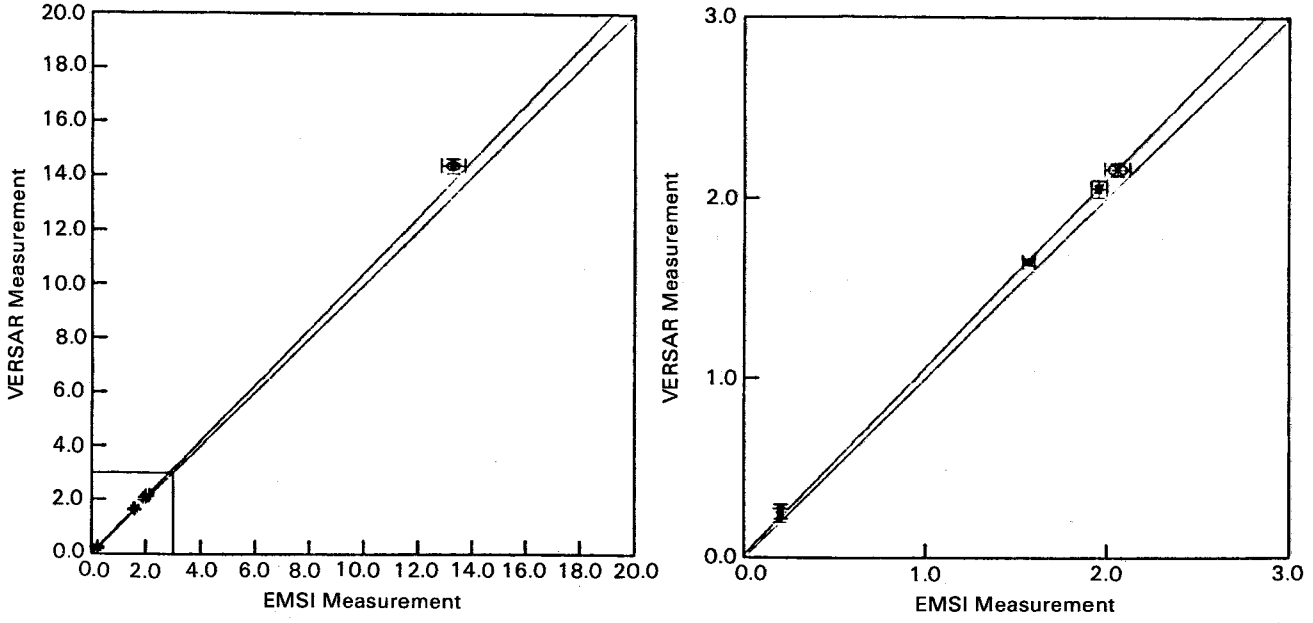


Figure I-5. Means by laboratory of natural and synthetic audit measurements for MG11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

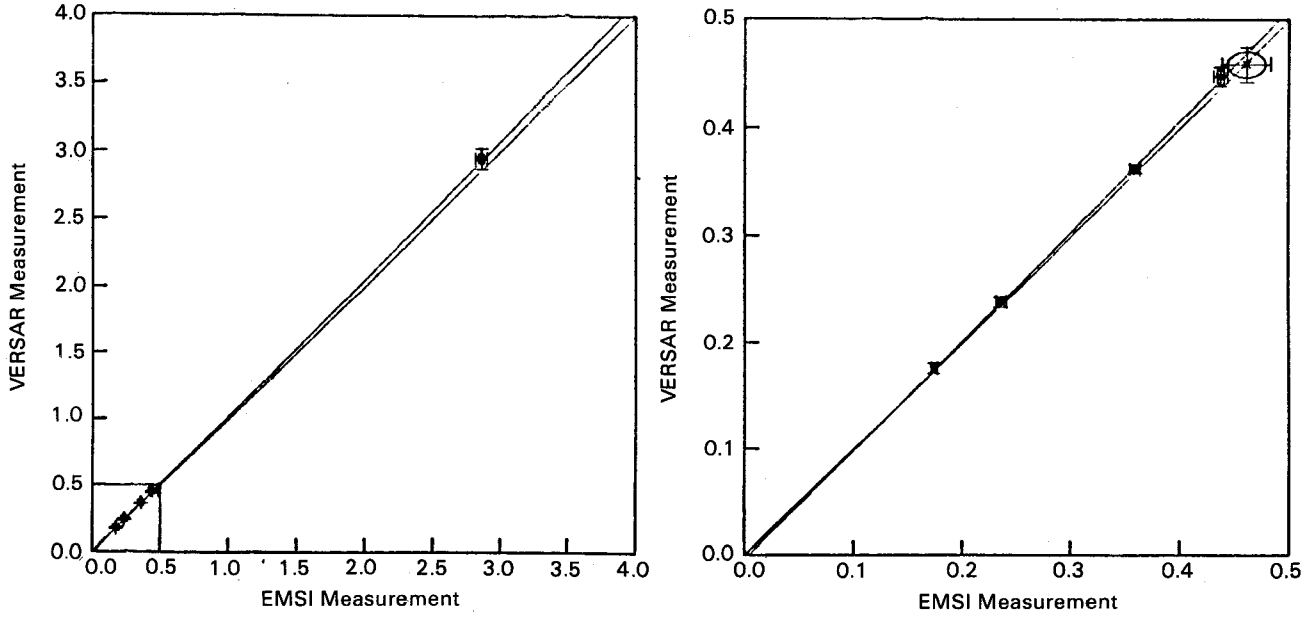


Figure I-6. Means by laboratory of natural and synthetic audit measurements for K11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

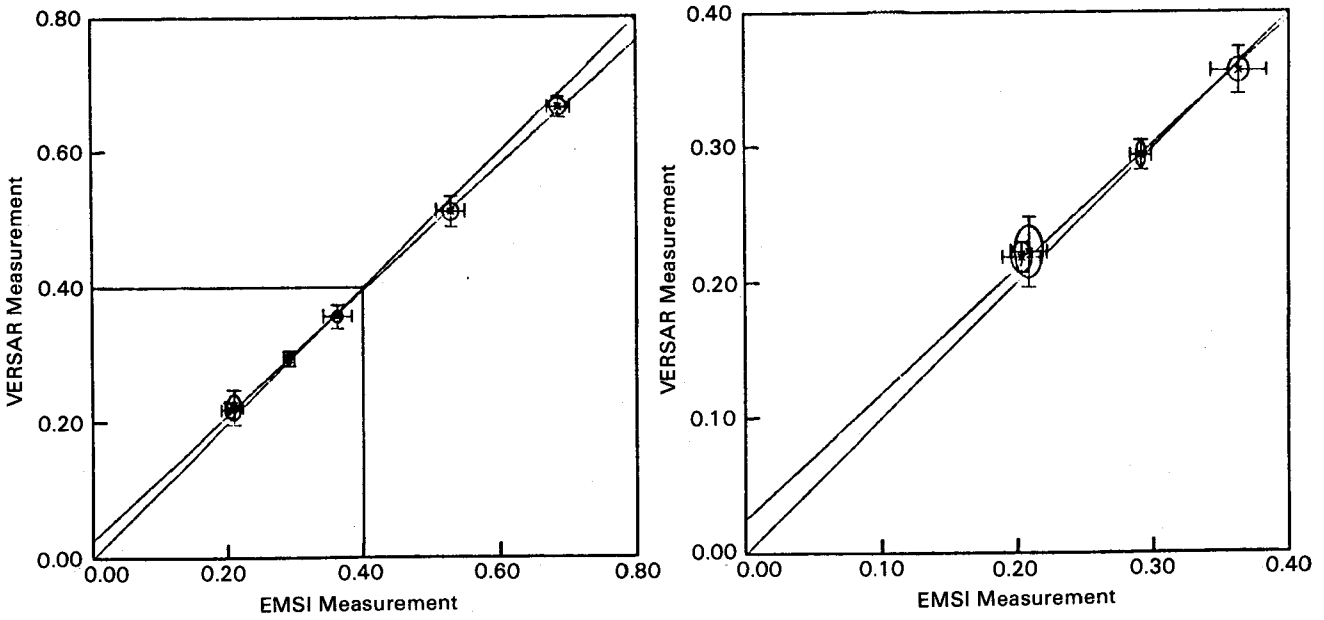


Figure I-7. Means by laboratory of natural and synthetic audit measurements for NA11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

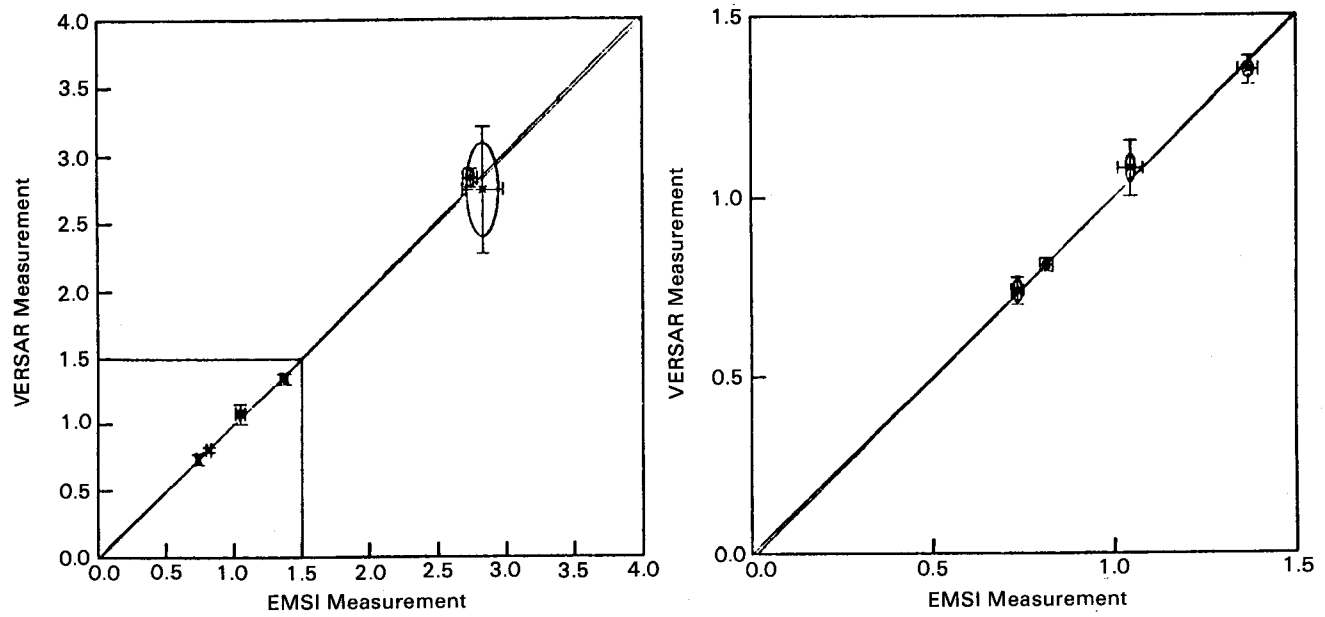


Figure I-8. Means by laboratory of natural and synthetic audit measurements for MN11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

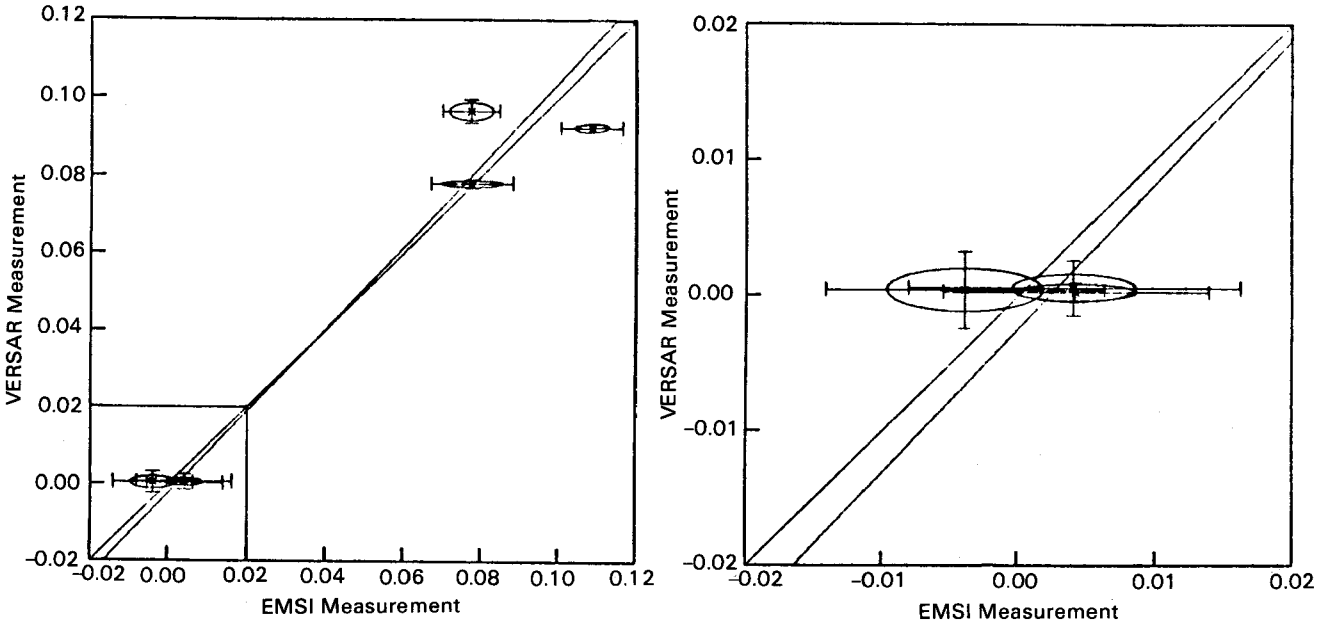


Figure I-9. Means by laboratory of natural and synthetic audit measurements for FE11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

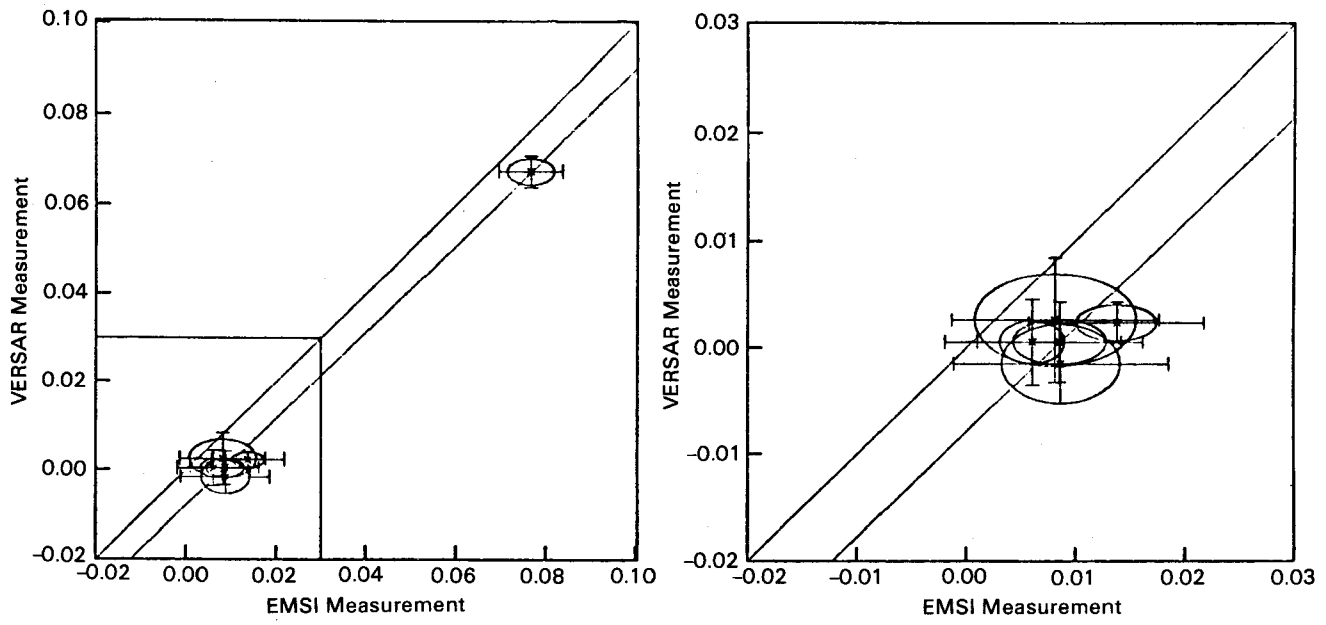


Figure I-10. Means by laboratory of natural and synthetic audit measurements for ALEX11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

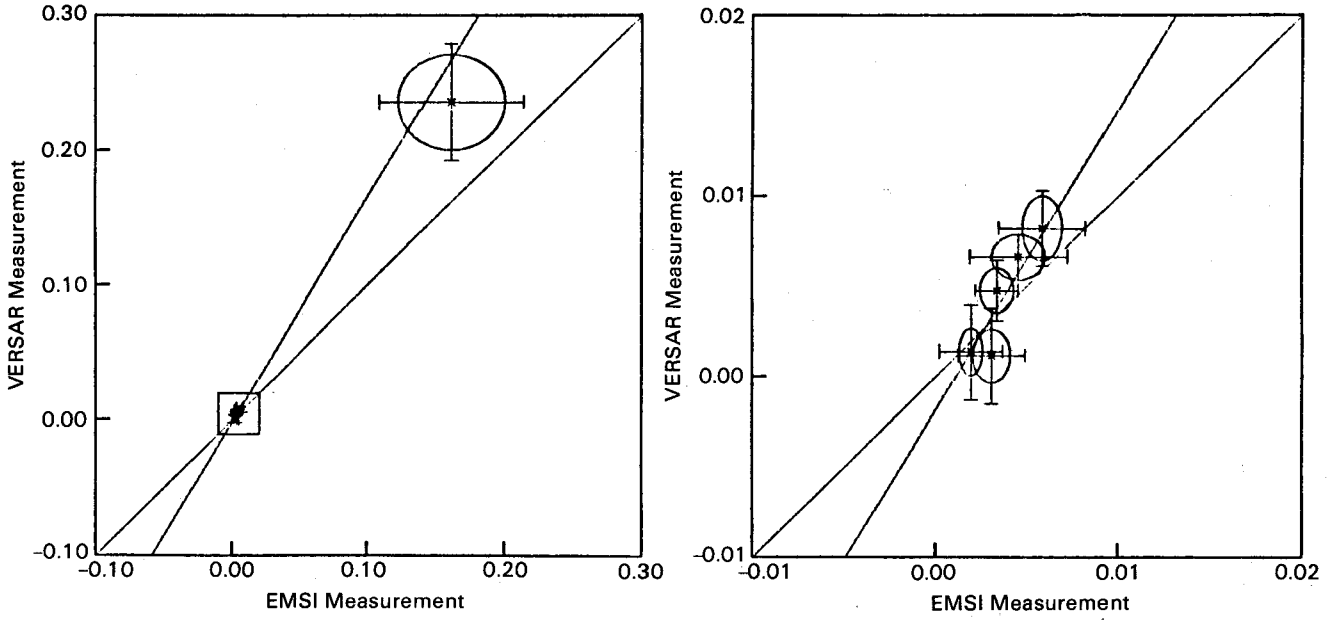


Figure I-11. Means by laboratory of natural and synthetic audit measurements for CL11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

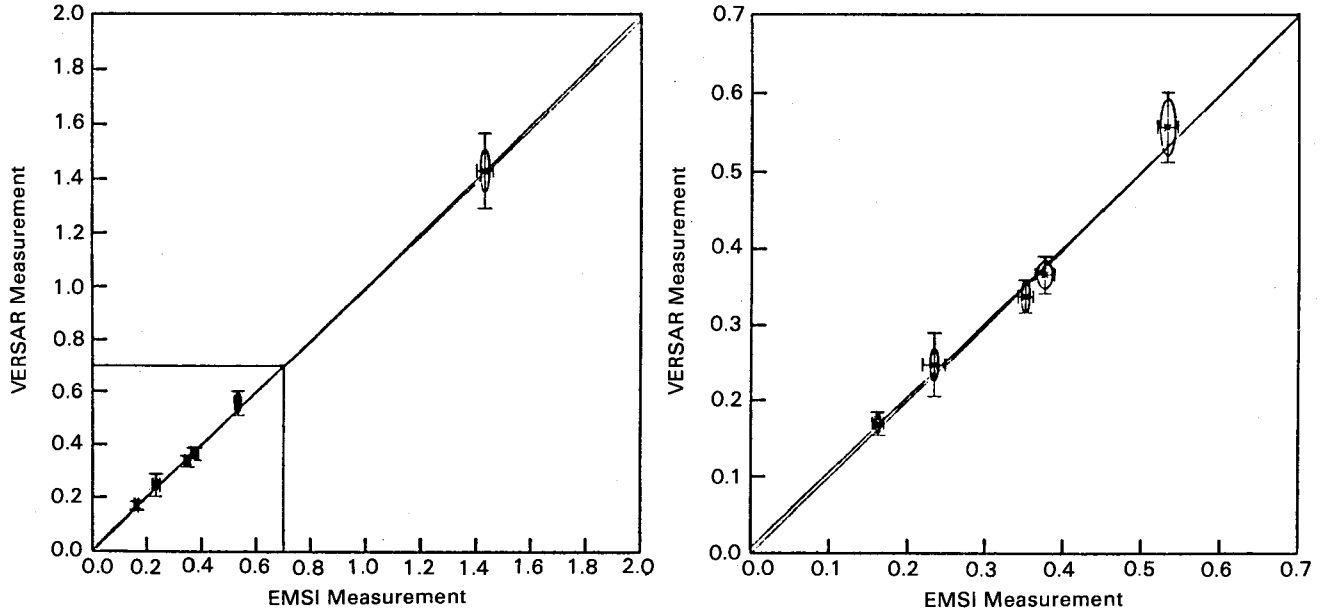


Figure I-12. Means by laboratory of natural and synthetic audit measurements for SO411. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

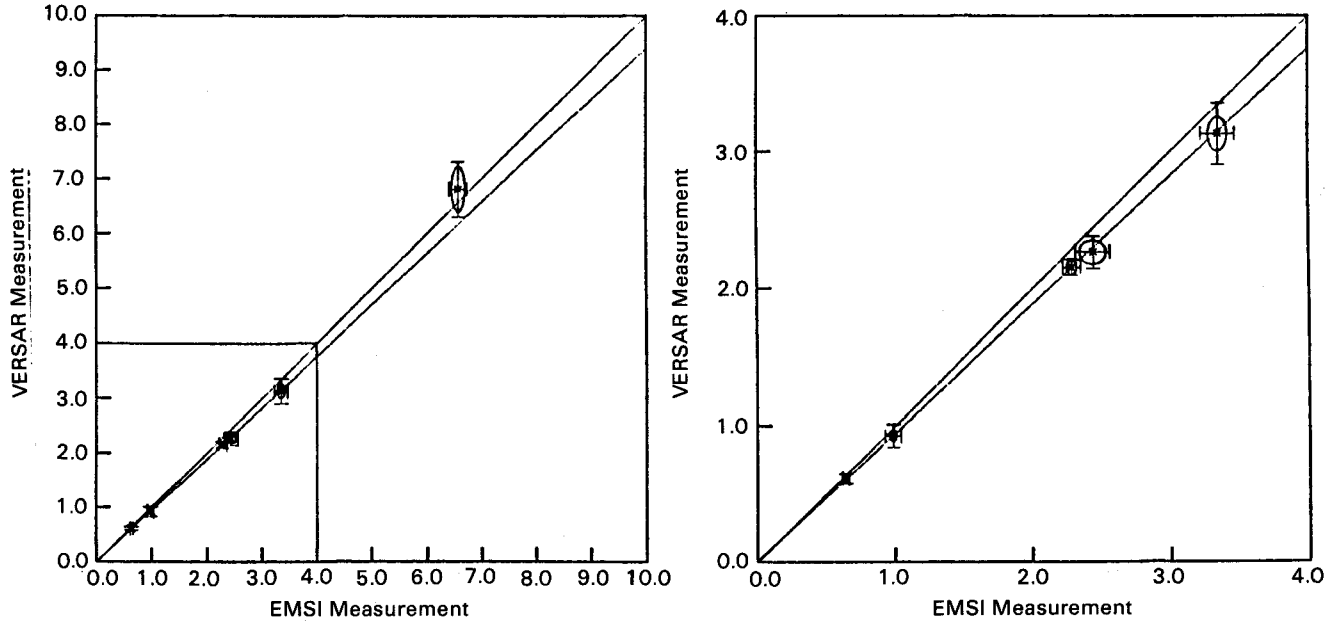


Figure I-13. Means by laboratory of natural and synthetic audit measurements for NO311. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

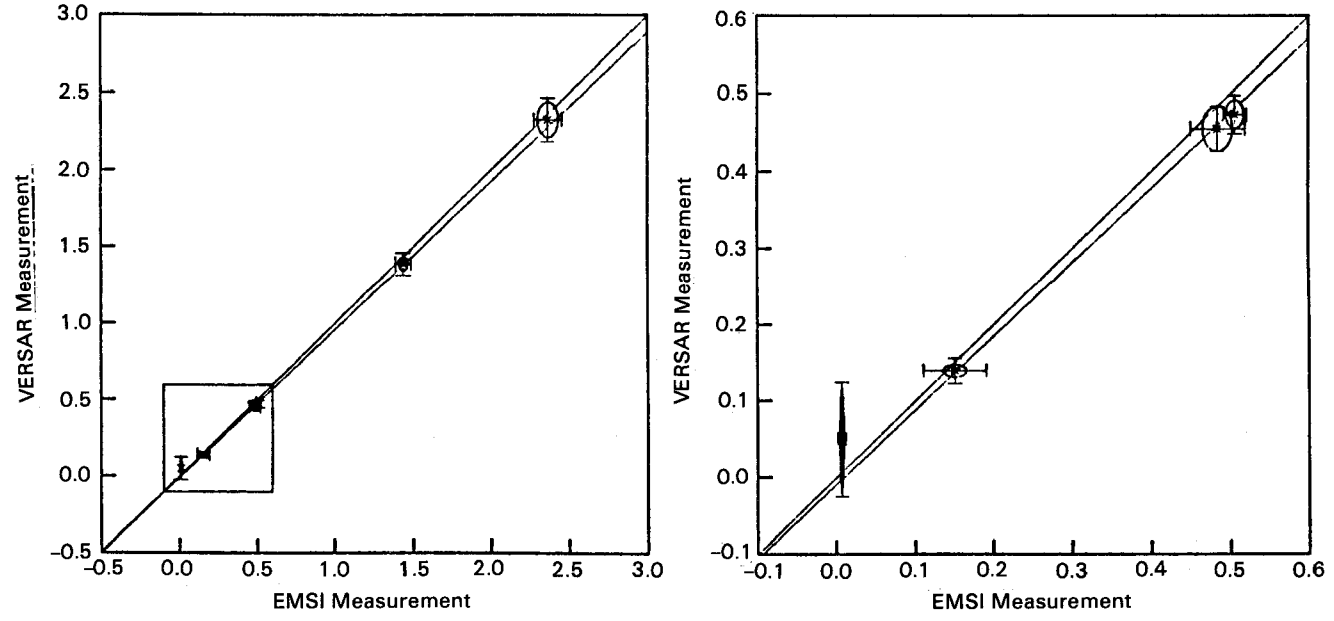


Figure I-14. Means by laboratory of natural and synthetic audit measurements for SIO211. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

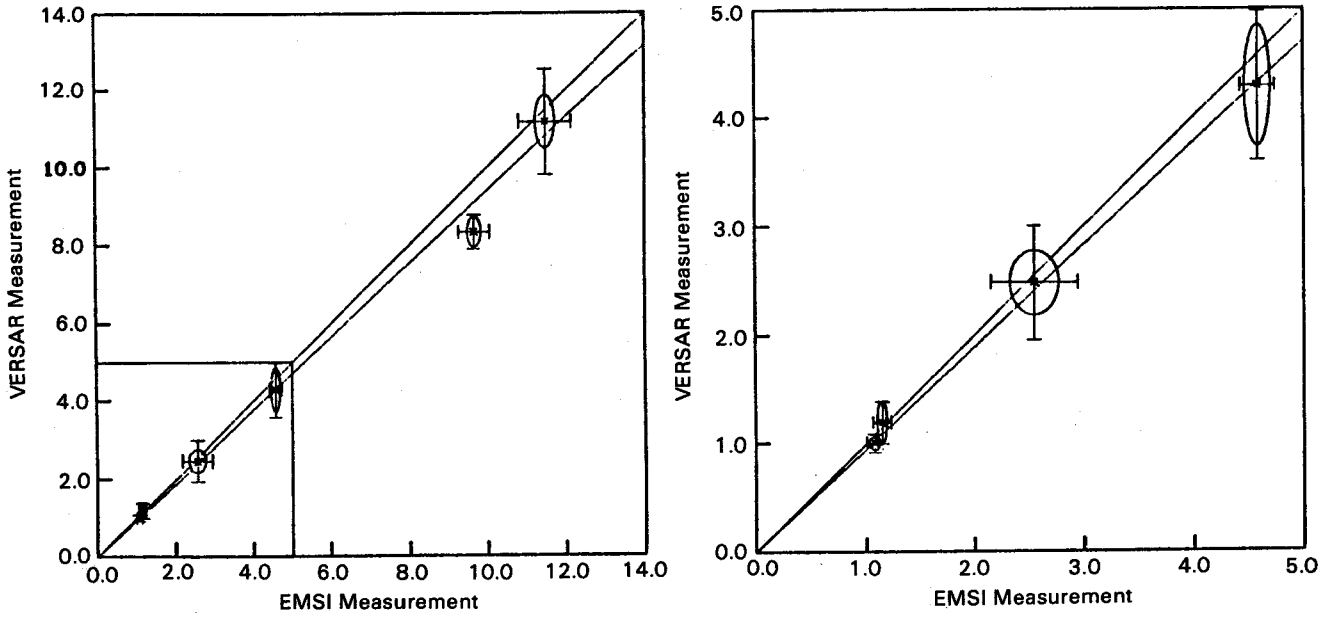


Figure I-15. Means by laboratory of natural and synthetic audit measurements for FTL11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

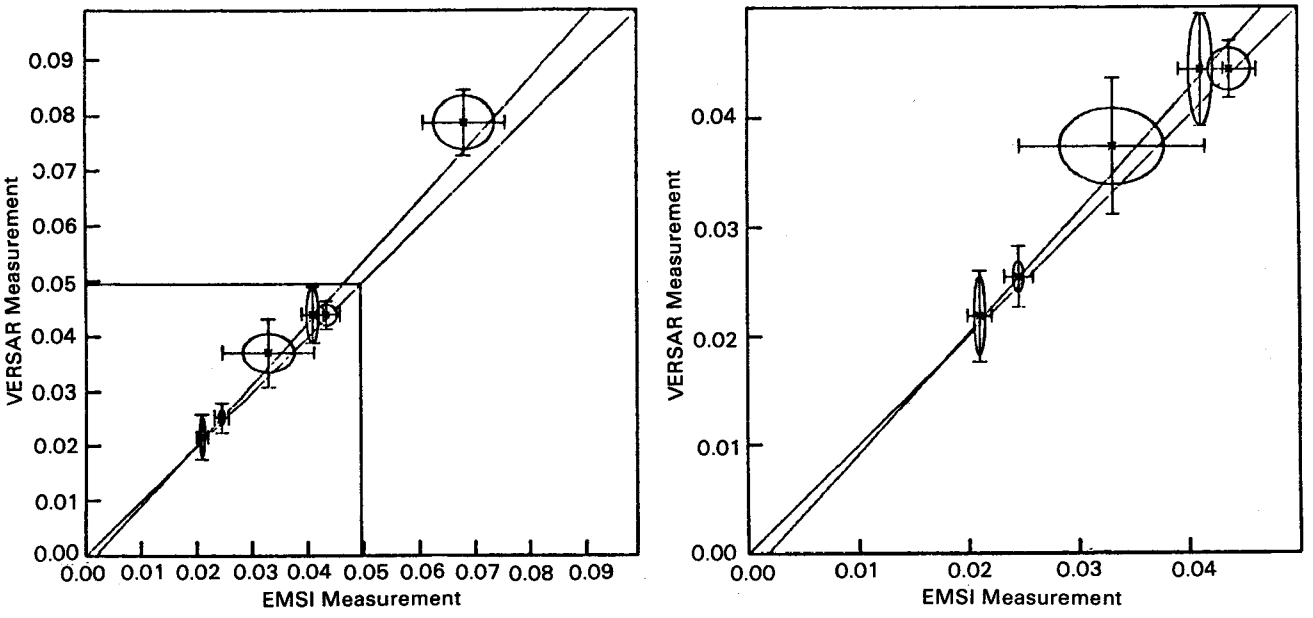


Figure I-16. Means by laboratory of natural and synthetic audit measurements for DOC11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

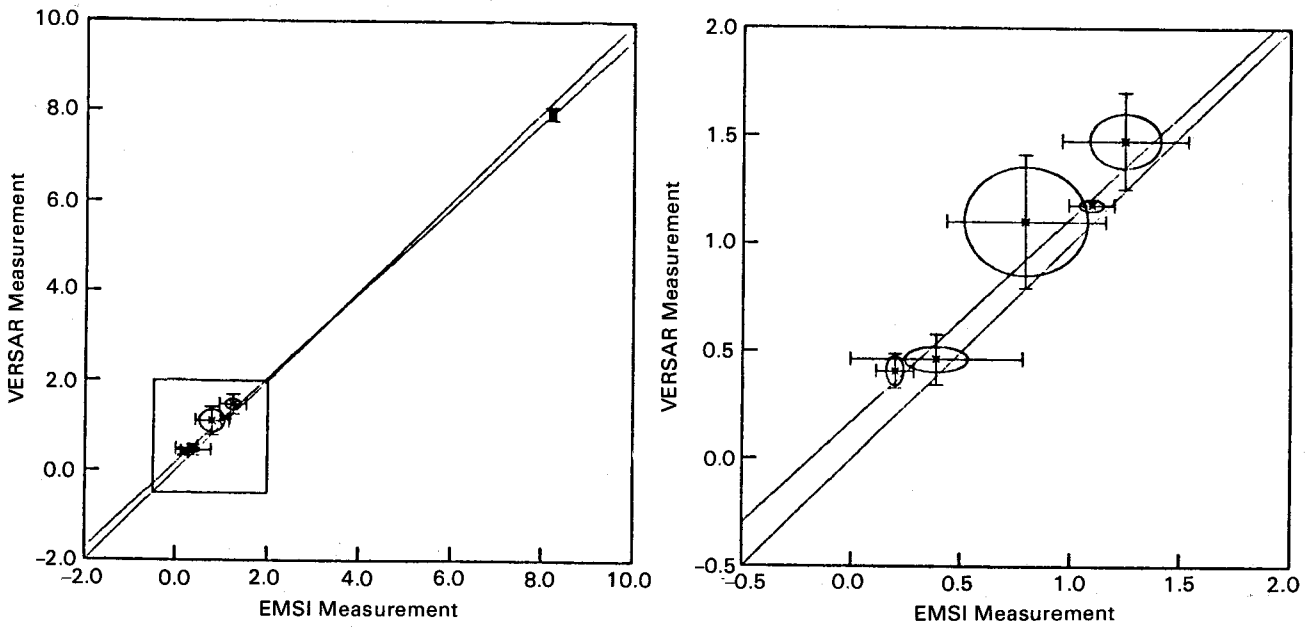


Figure I-17. Means by laboratory of natural and synthetic audit measurements for NH411. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

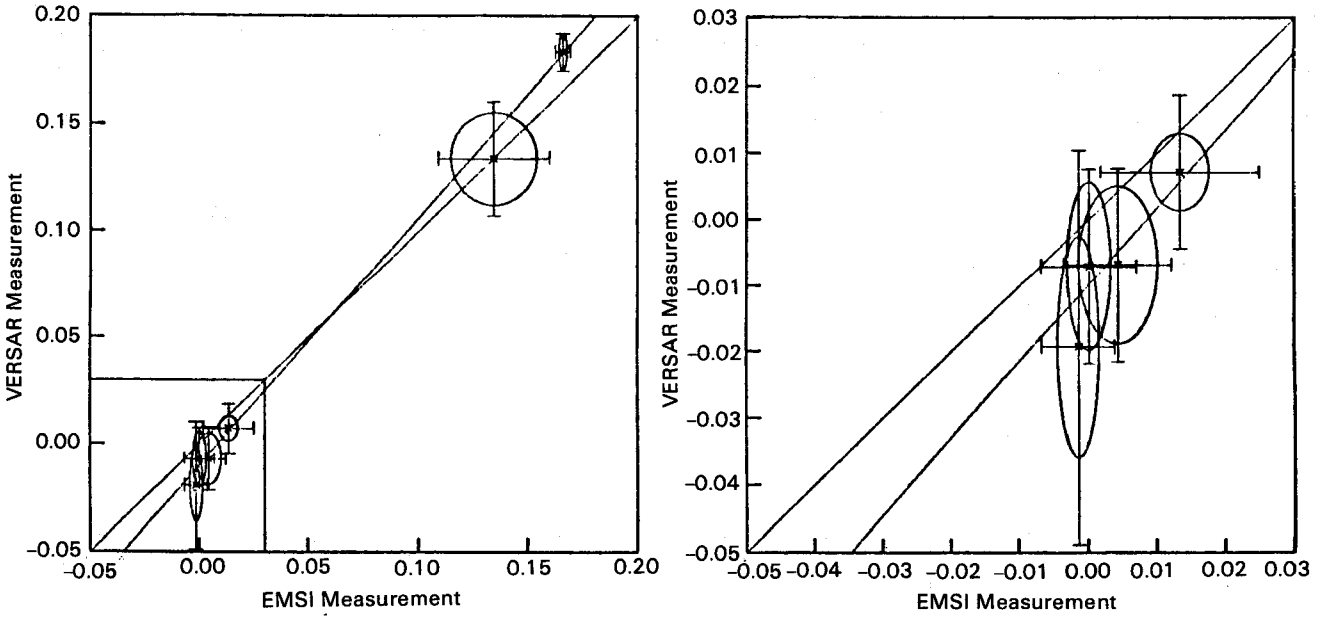


Figure I-18. Means by laboratory of natural and synthetic audit measurements for PHEQ11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

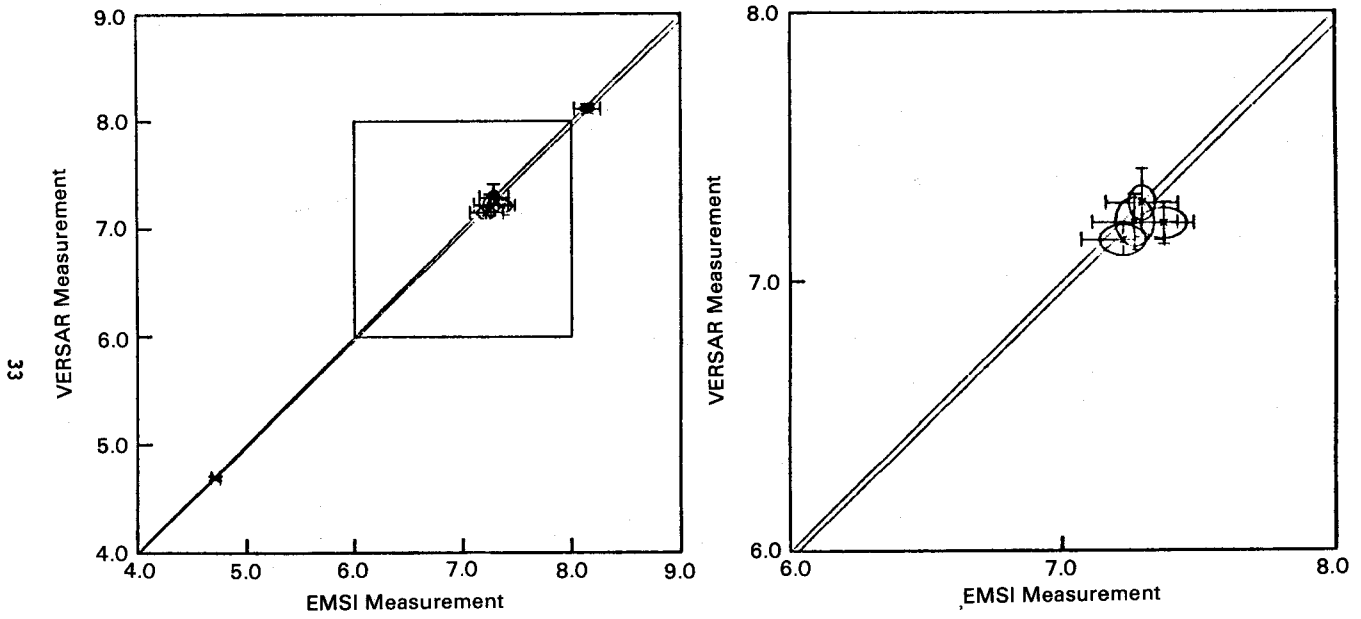


Figure I-19. Means by laboratory of natural and synthetic audit measurements for PHAL11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

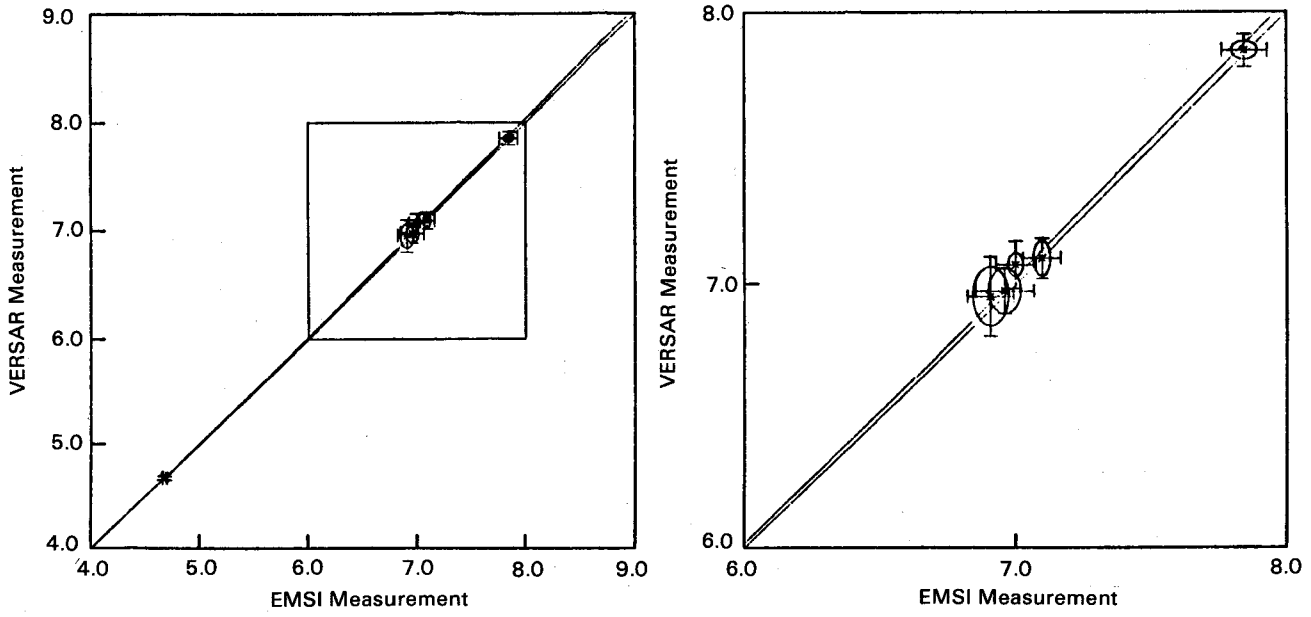


Figure I-20. Means by laboratory of natural and synthetic audit measurements for PHAC11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

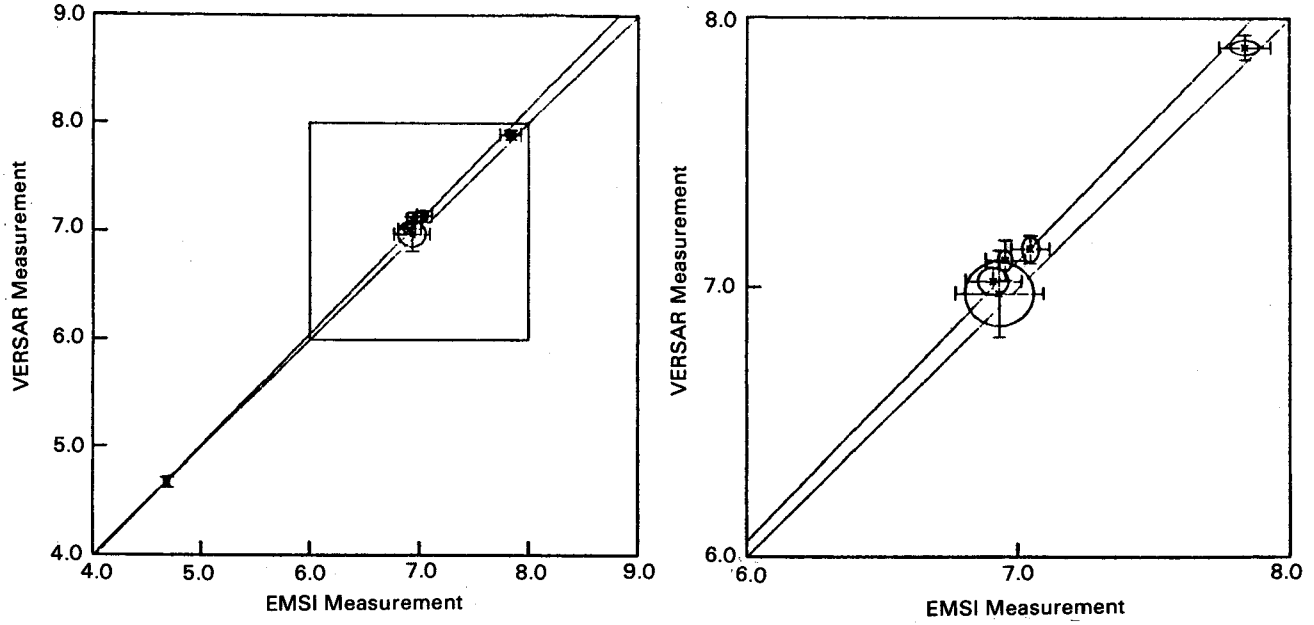


Figure I-21. Means by laboratory of natural and synthetic audit measurements for ACCO11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

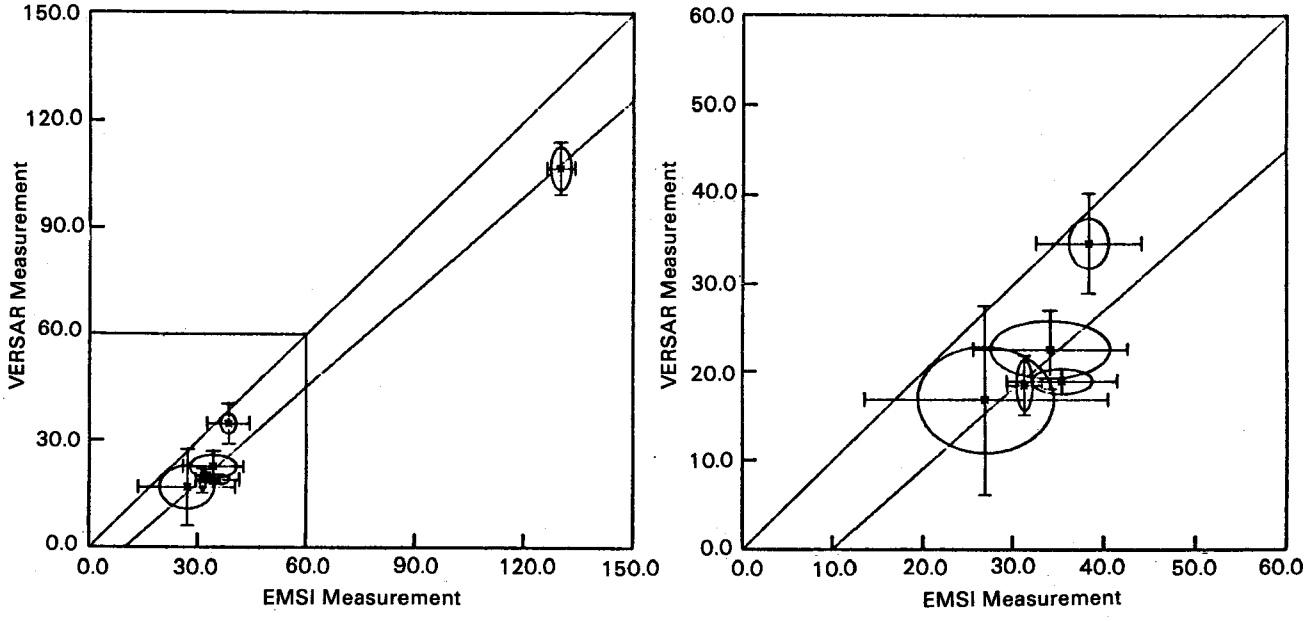


Figure I-22. Means by laboratory of natural and synthetic audit measurements for ALKA11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

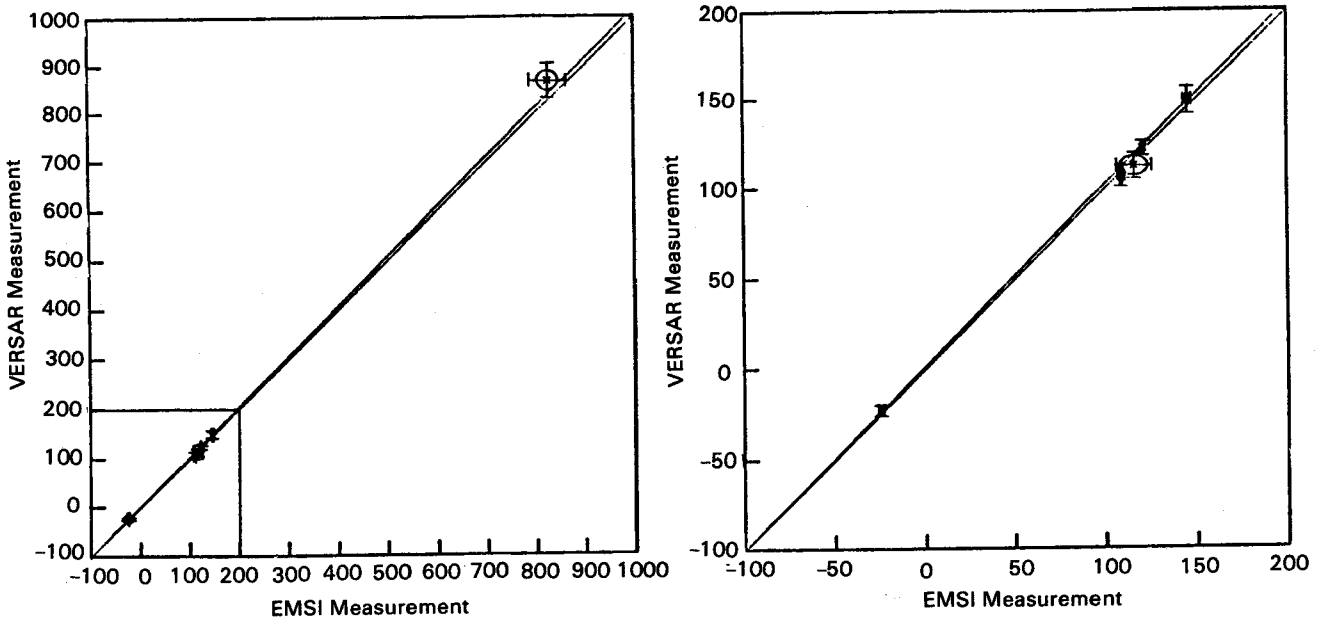


Figure I-23. Means by laboratory of natural and synthetic audit measurements for COND11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

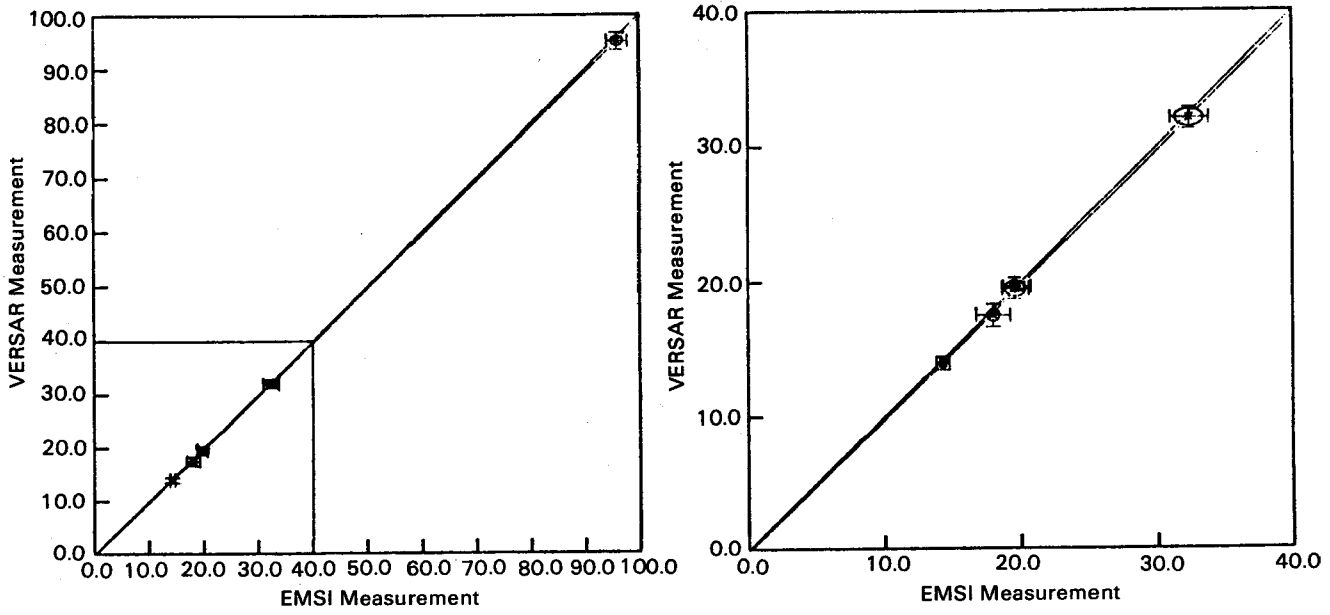


Figure I-24. Means by laboratory of natural and synthetic audit measurements for DICE11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

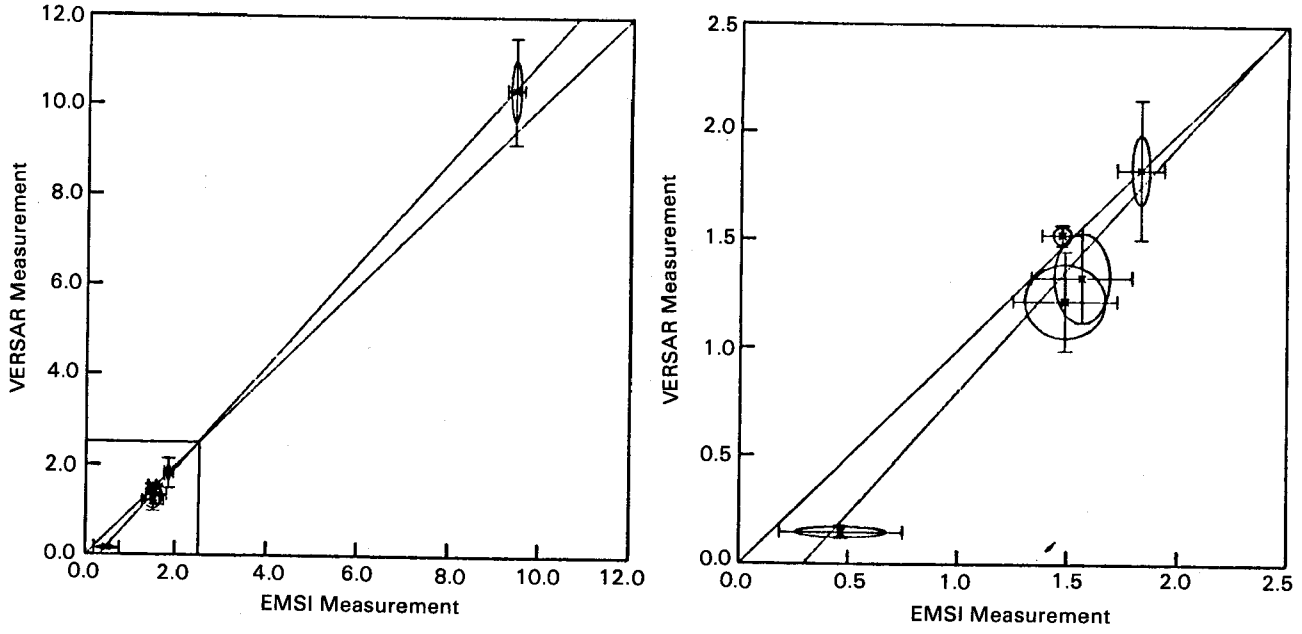


Figure I-25. Means by laboratory of natural and synthetic audit measurements for DICI11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

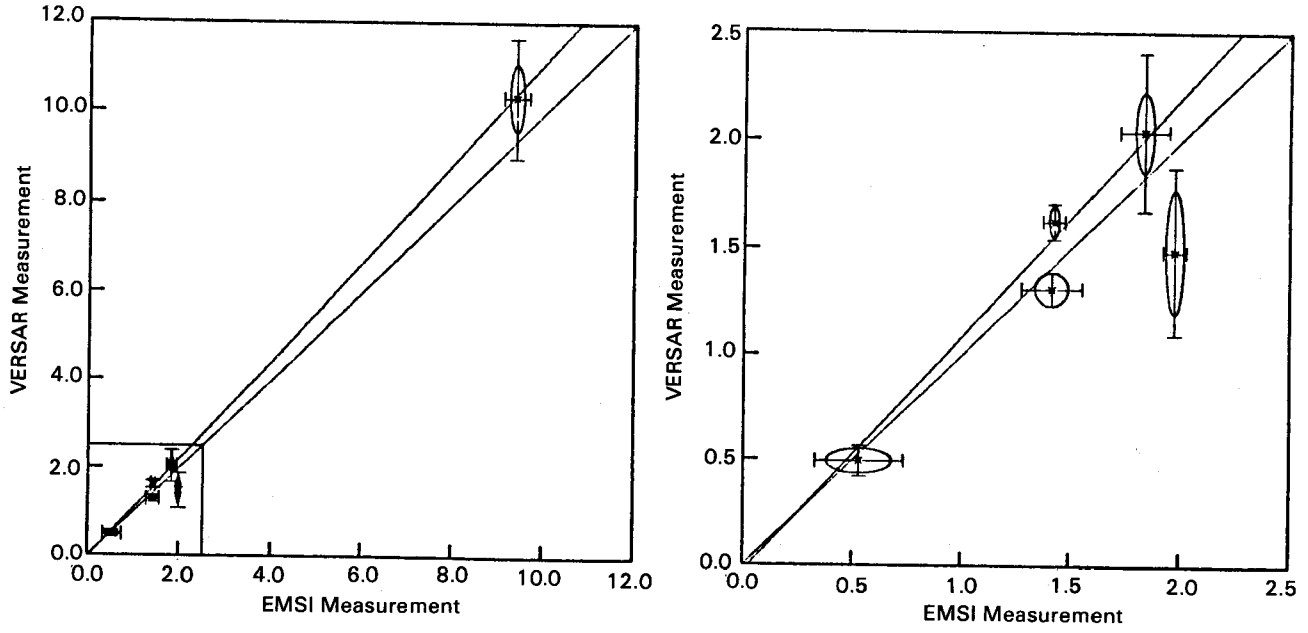


Figure I-26. Means by laboratory of natural and synthetic audit measurements for PTL11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).

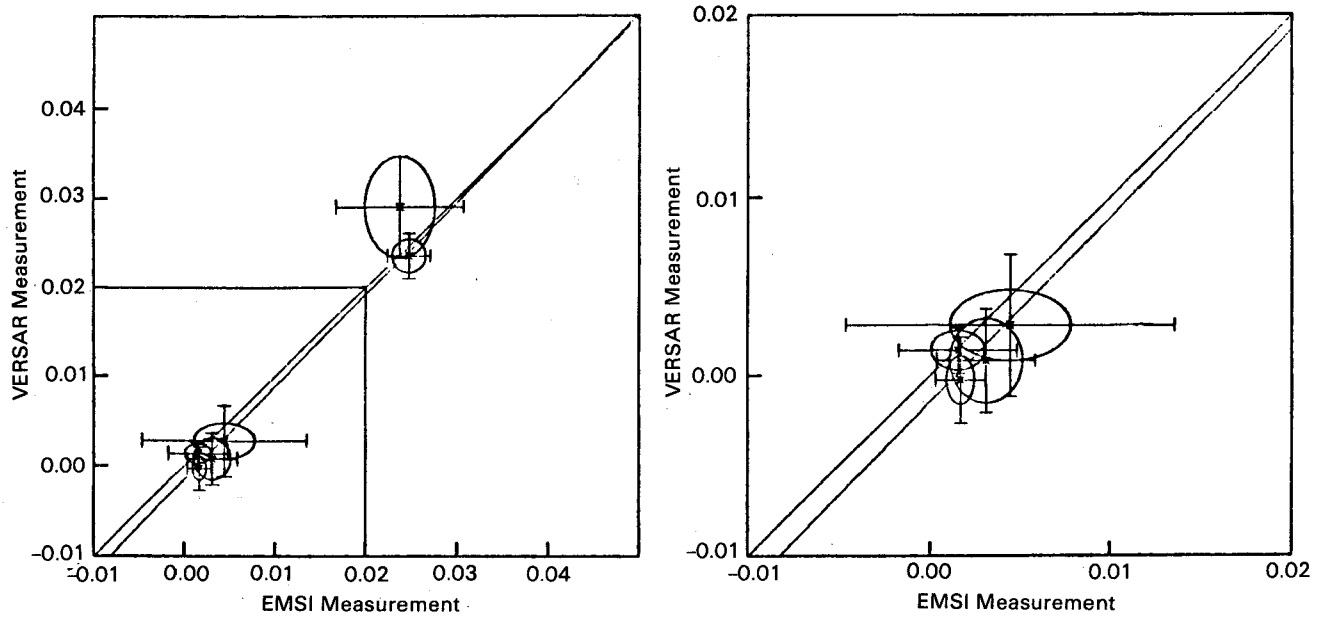
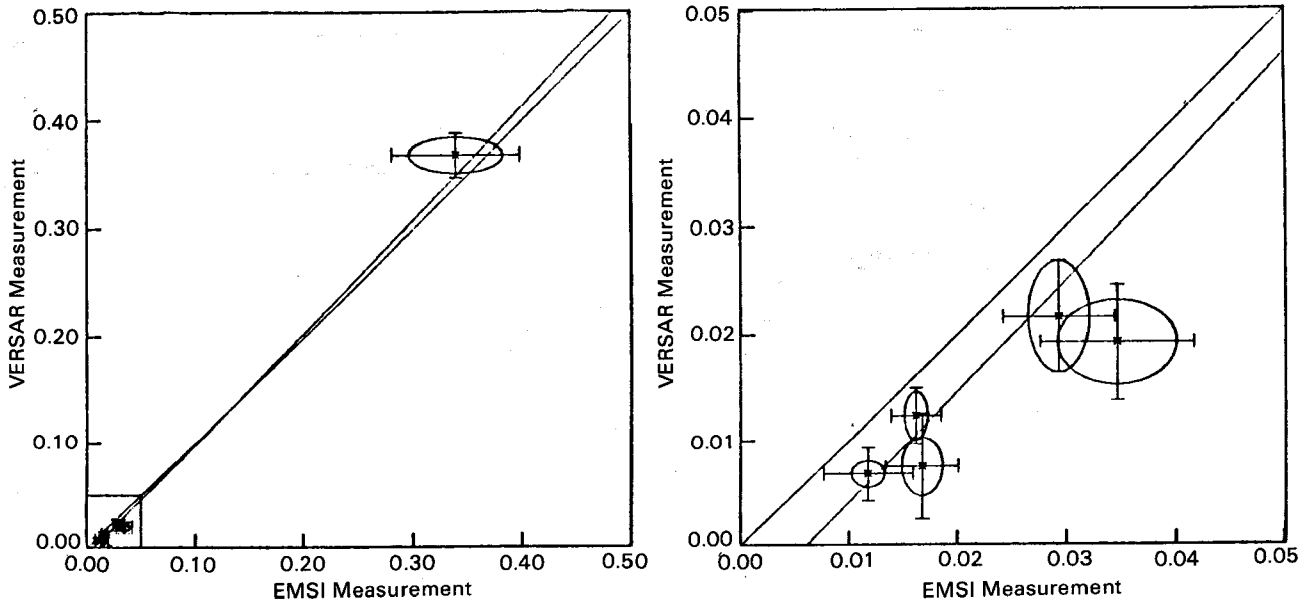


Figure I-27. Means by laboratory of natural and synthetic audit measurements for ALTL11. Each point represents one lot. Uncertainty shown by bars (standard deviation) and ellipses (95% confidence region).



Appendix J

Figures Depicting Detectability Data and the Relationship Between Precision and Mean Concentration by Analyte

The figures presented in Appendix J should be useful in assessing the quality of data in WLS-I based on QA and QC data.

- For each variable, where applicable, the calibration (or reagent) blank data are plotted as (1) the instrument detection limit and (2) the daily calibration blank (and reagent blank) distribution (P_{50}, P_{95}). These are presented and pooled by the analytical laboratory and can be compared to the required detection limits for a DQO comparison. The sample size of the calibration blanks and reagent blanks is noted in Appendix D, Table D-3.
- For each variable, where applicable, the distribution of trailer blank analyses are presented. The sample size for the trailer blanks is noted in Appendix D, Table D-2.
- For each variable, where applicable, the distribution of field blank data are presented, which is an estimation of system contamination levels. The required detection limit can be c ompared as a gauge, but should not be used as a direct comparison to assess data quality. The sample size for the field blanks is noted in Appendix D, Table D-1.
- For each variable, all of the field duplicate pair sample mean concentrations were plotted against the precision (%RSD or SD) of the pair. This shows all the field duplicate pair data above and below the quantitation limit, so precision at varying concentrations can be observed. Refer to Tables 15 and 21 in Section 6 for companion data.
- For each variable, all six of the field audit sample lot mean concentrations are plotted against the precision (%RSD, SD) and can be used in conjunction with the field duplicate pairs to observe the relationship to precision at different concentrations. Refer to Table 26 in Section 6 and Tables F-5 and F-6 in Appendix F for companion data.

Figure J-1a. ***Extractable Aluminum:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.**

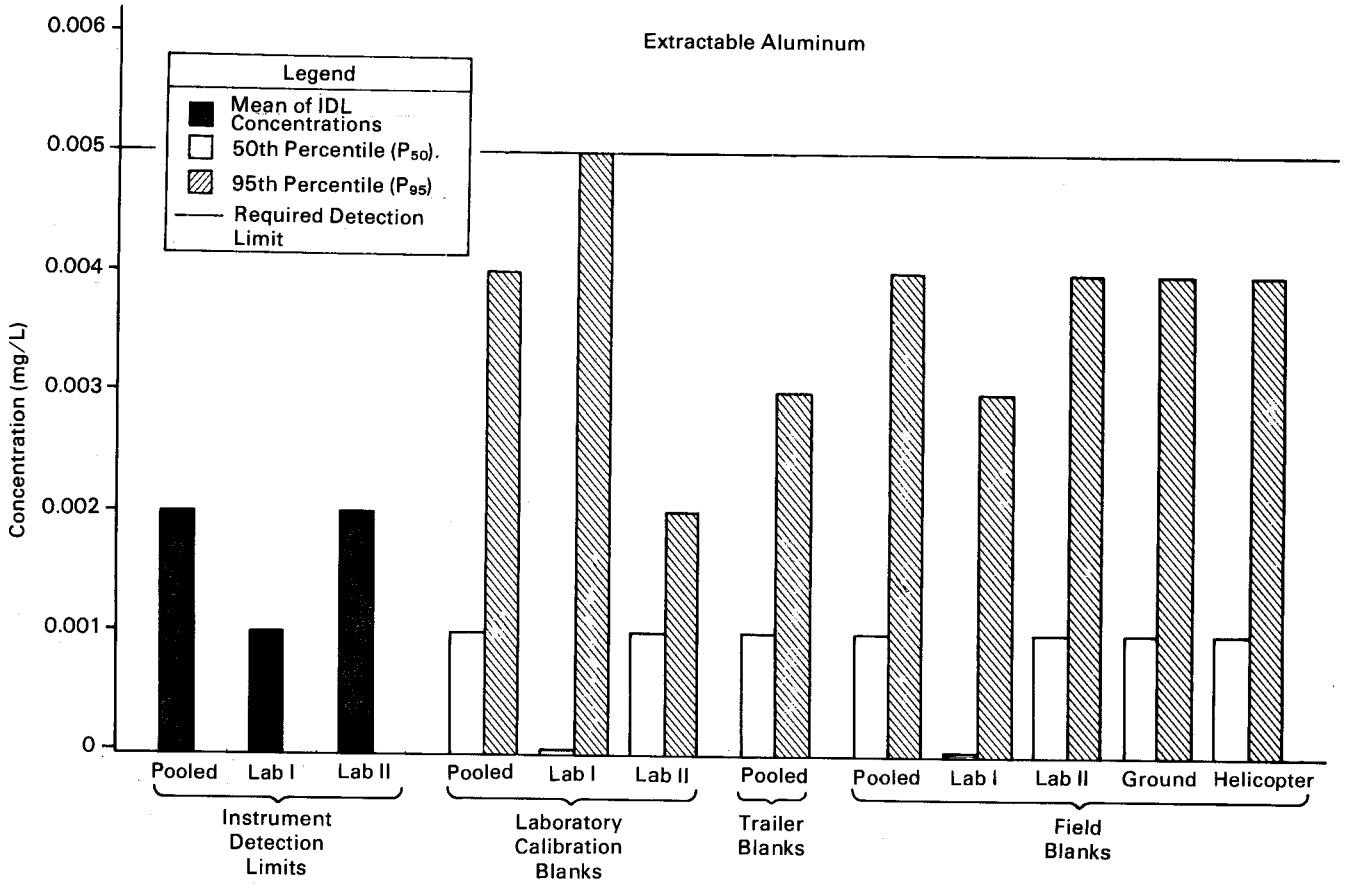


Figure J-1b. ***Extractable Aluminum:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 26 field duplicate pairs were omitted because their mean concentrations were less than or equal to 0 mg/L.**

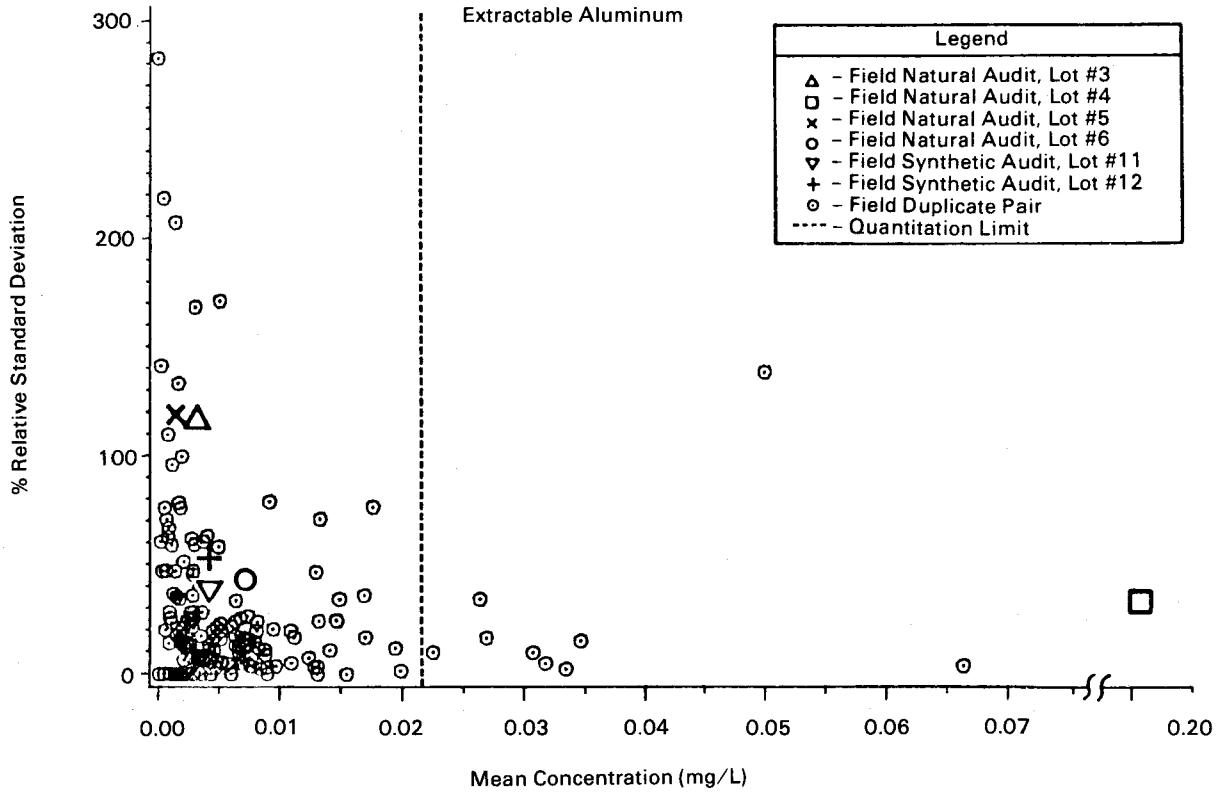


Figure J-2a. ***Total Aluminum:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.**

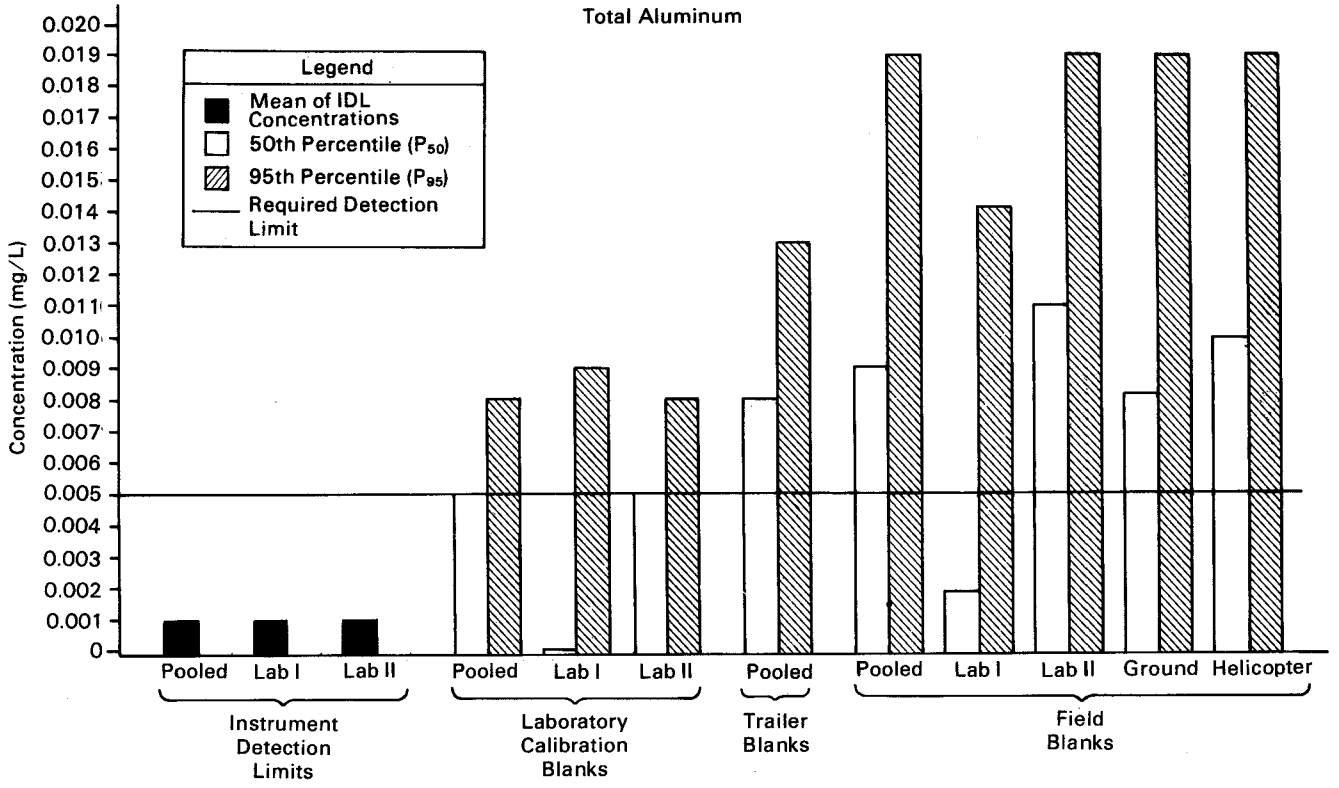


Figure J-2b. ***Total Aluminum:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 3 field duplicate pairs were omitted for purposes of resolution.**

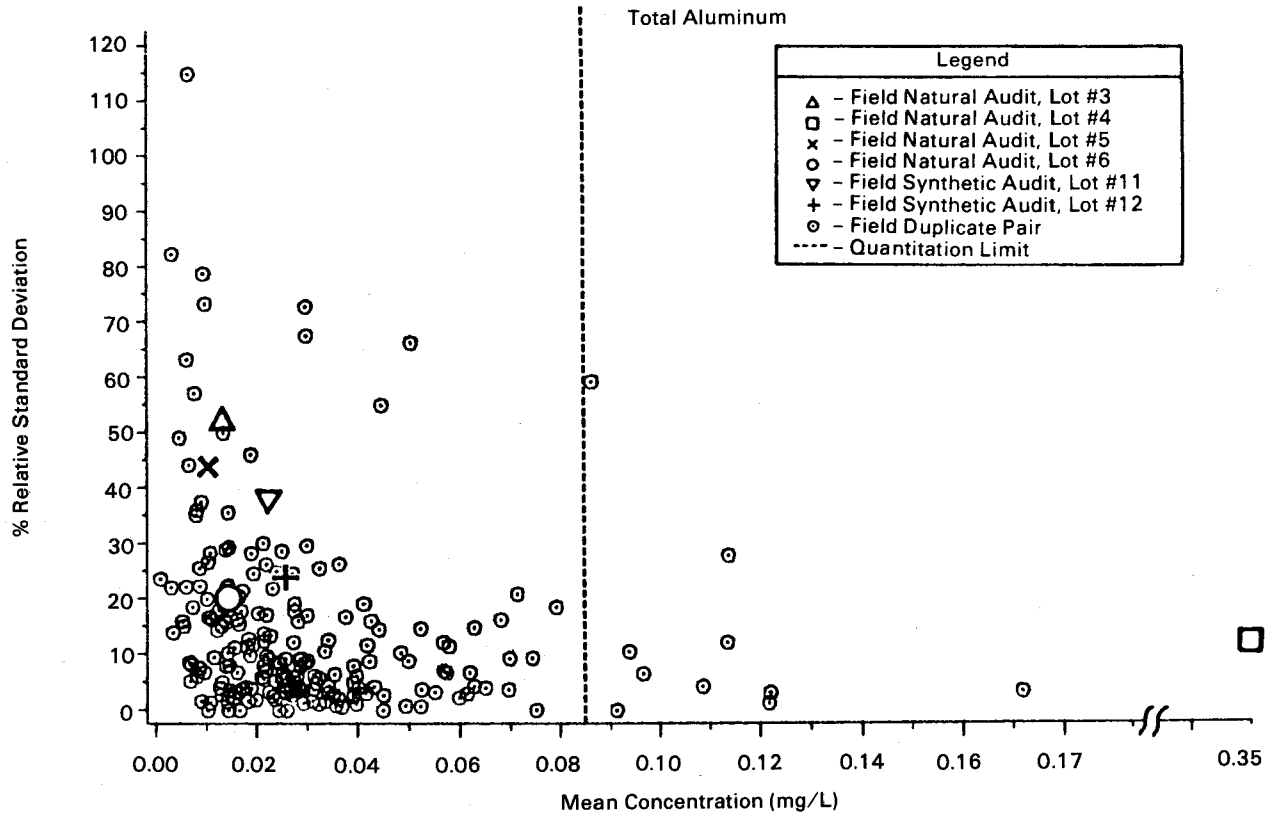


Figure J-3a. ***Acid Neutralizing Capacity:*** **Distribution (P_{50} and P_{95}) of the trailer blanks and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown. N/A denotes that blank sample data are not available for comparison.**

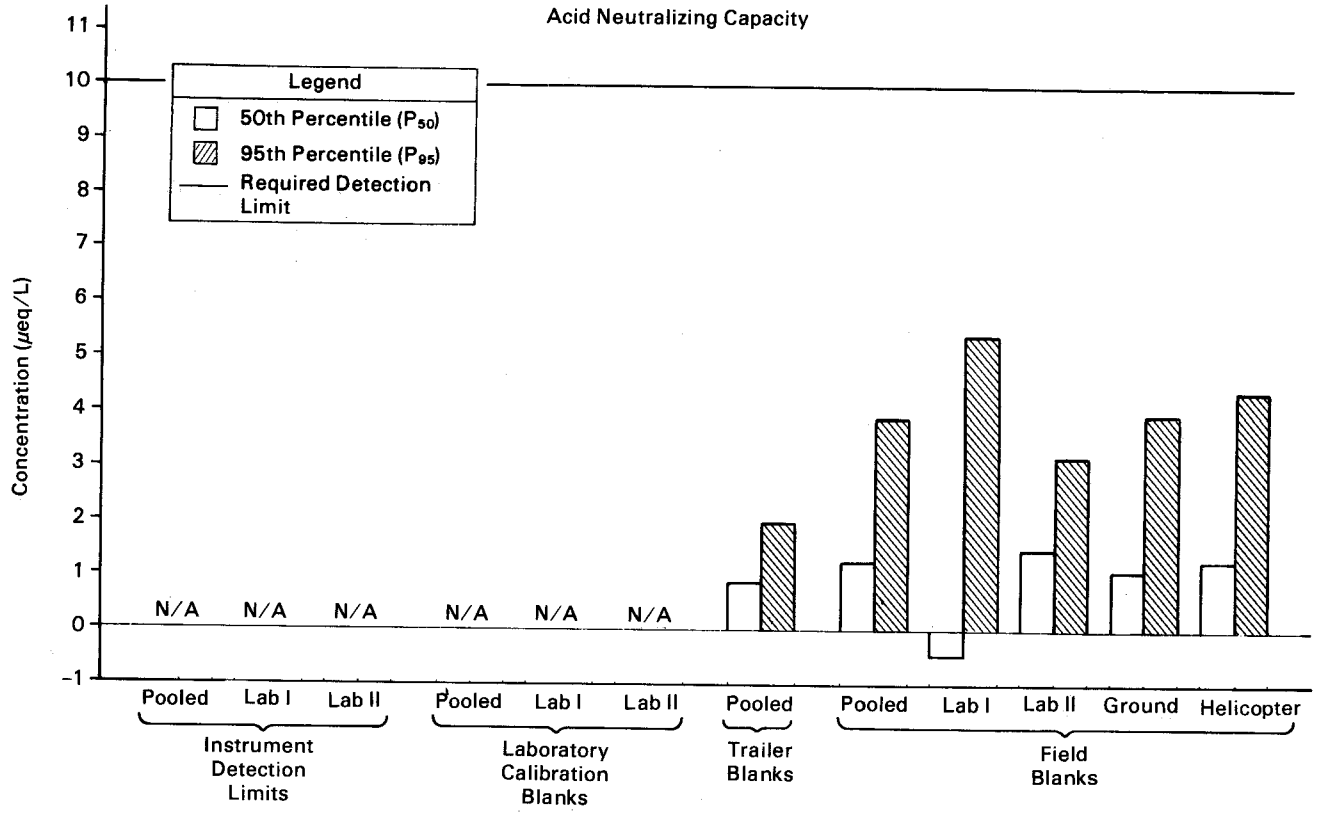


Figure J-3b. *Acid Neutralizing Capacity:* **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 17 field duplicate pairs were omitted for purposes of resolution; the field natural audit no. 4 was omitted with a mean concentration of -24.1 μeq/L.**

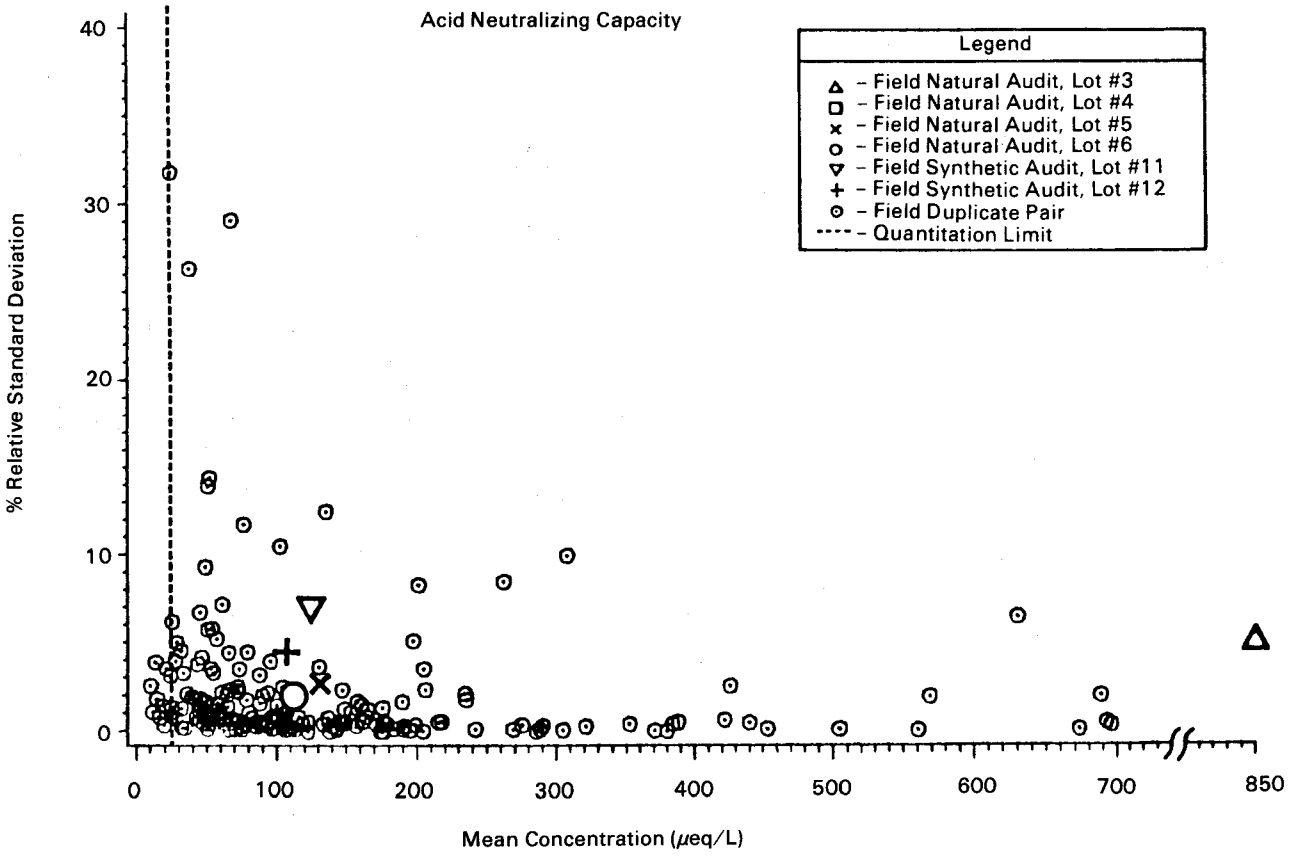


Figure J-4a. ***Base Neutralizing Capacity:*** **Distribution (P_{50} and P_{95}) of the trailer blanks and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown. N/A denotes that blank sample data are not available for comparison.**

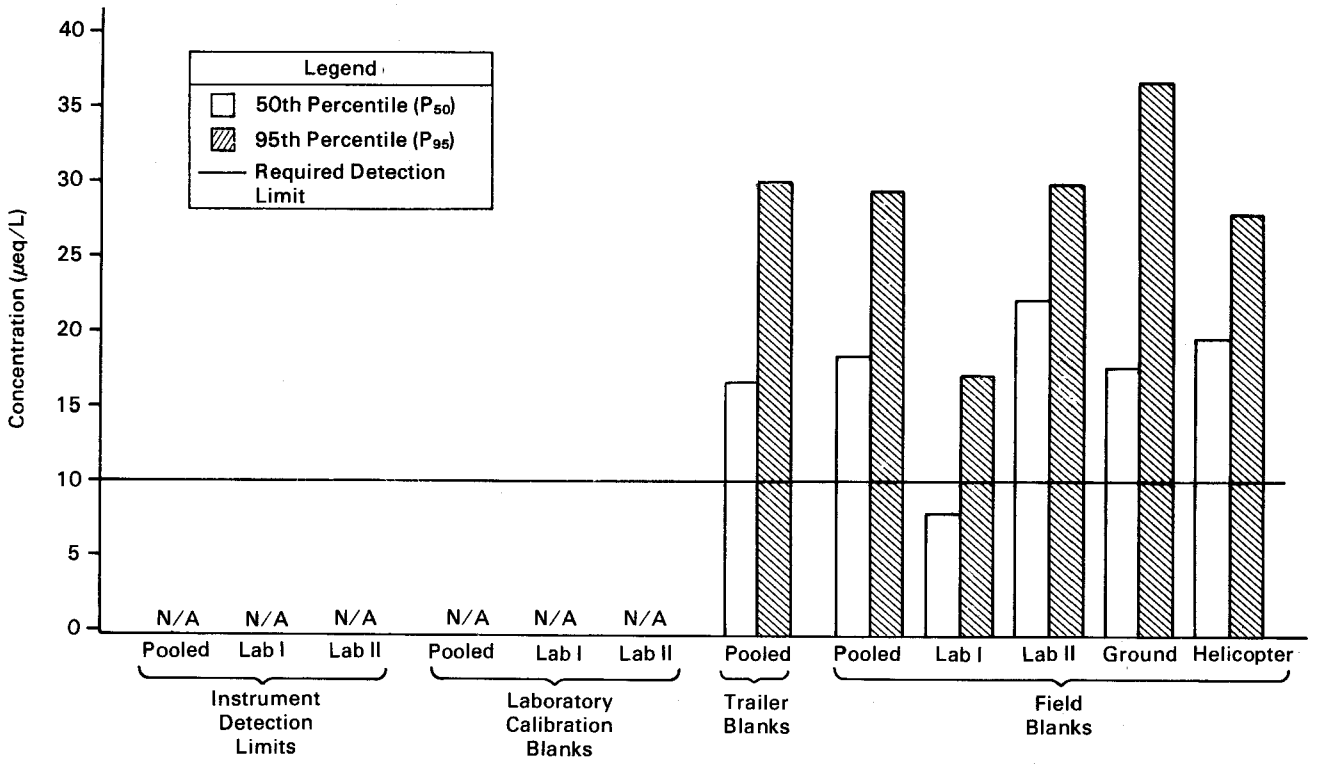


Figure J-4b. ***Base Neutralizing Capacity:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 3 field duplicate pairs were omitted for purposes of resolution; 12 field duplicate pairs were omitted with mean concentrations less than or equal to 0 μeq/L.**

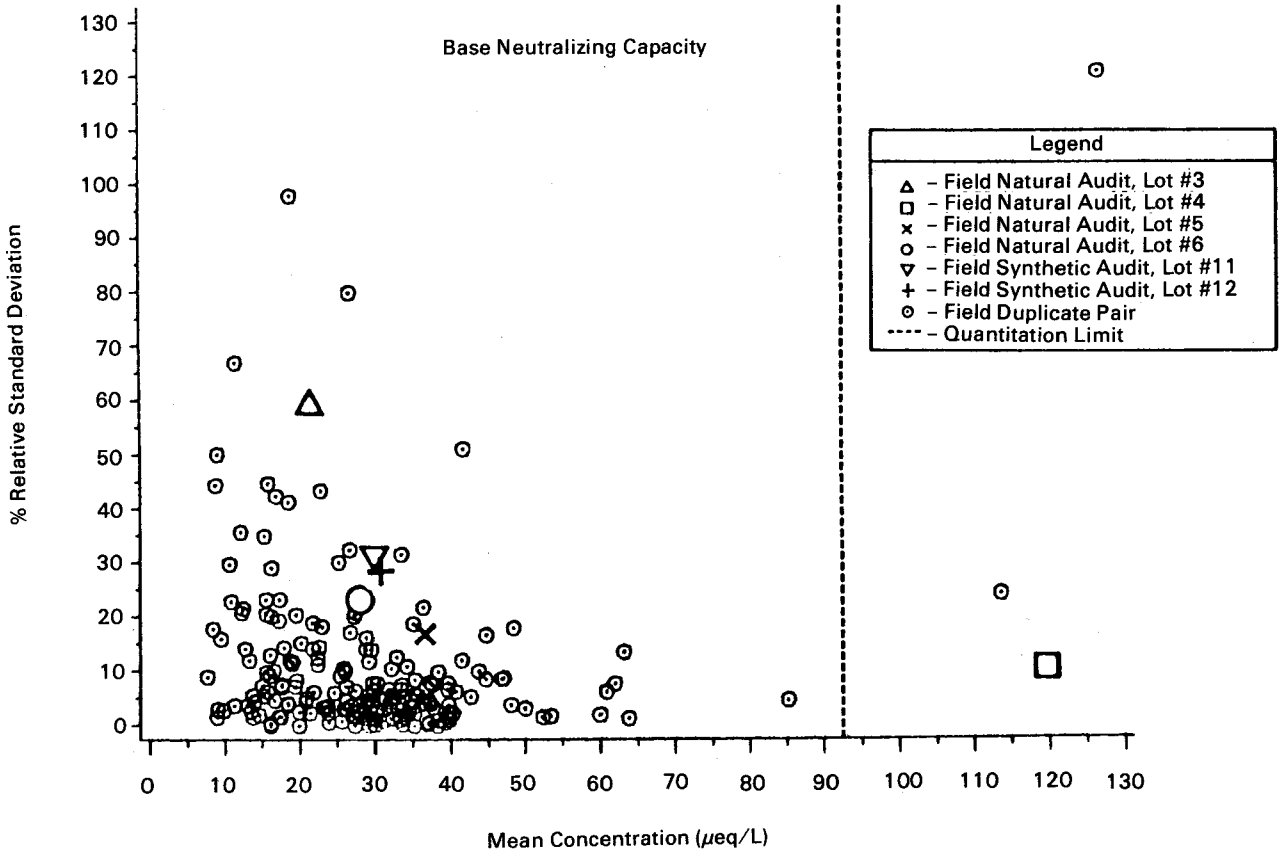


Figure J-5a. ***Calcium:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown. N/A denotes that blank sample data are not available for comparison.**

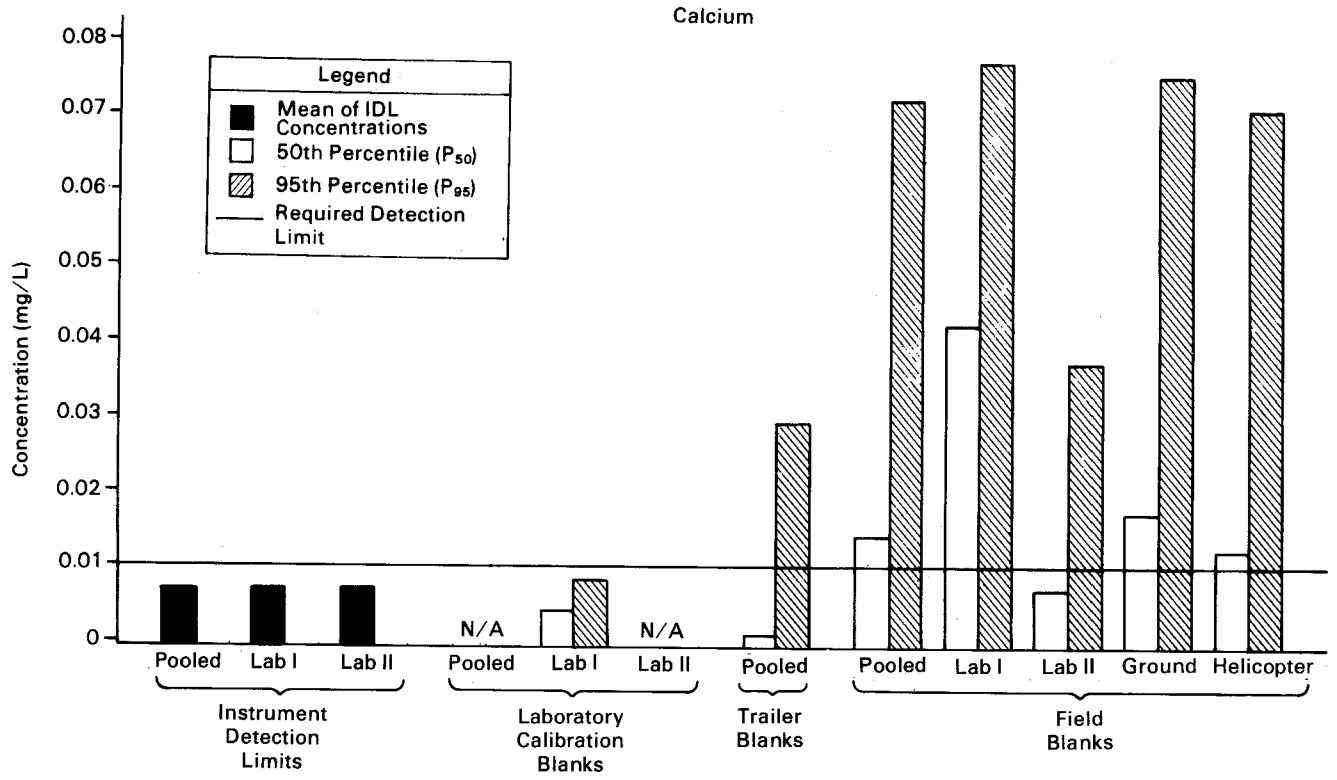


Figure J-5b. ***Calcium:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 11 field duplicate pairs were omitted for purposes of resolution.**

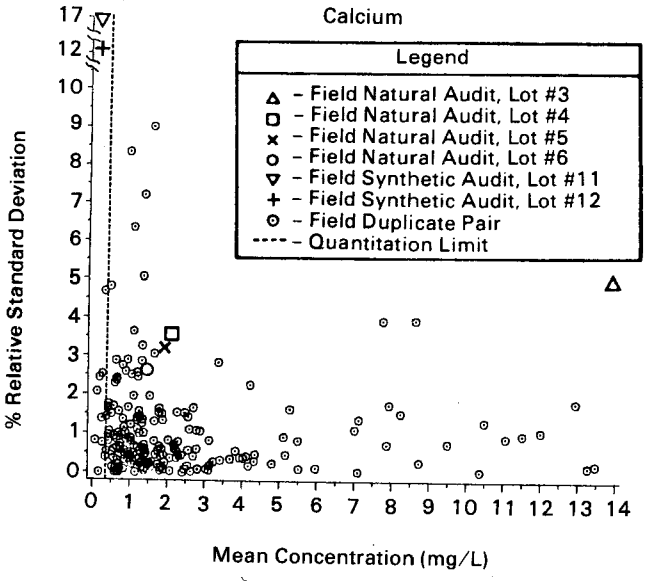


Figure J-6a. *Chloride:* Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.

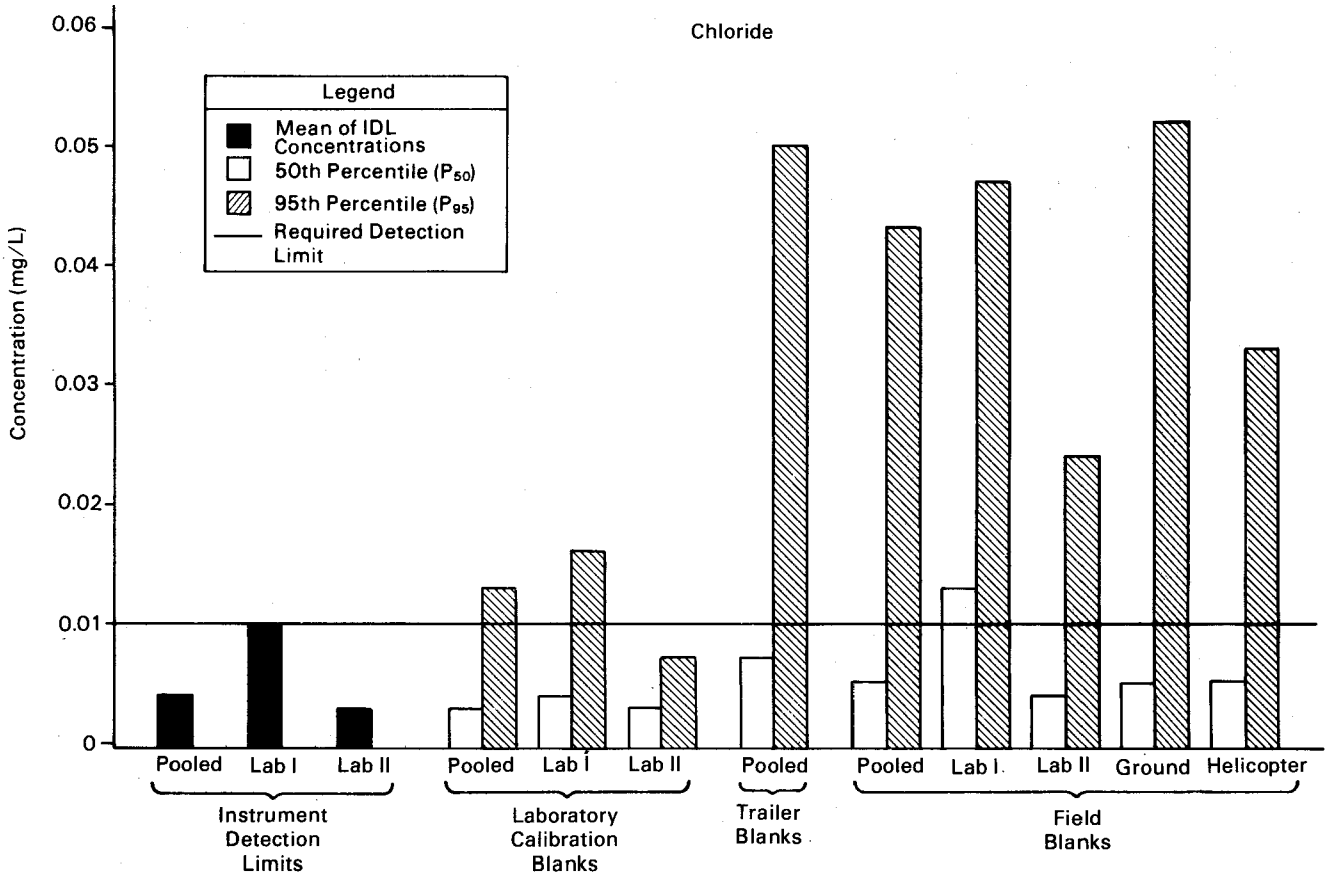


Figure J-6b. *Chloride:* **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 4 field duplicate pairs were omitted for purposes of resolution.**

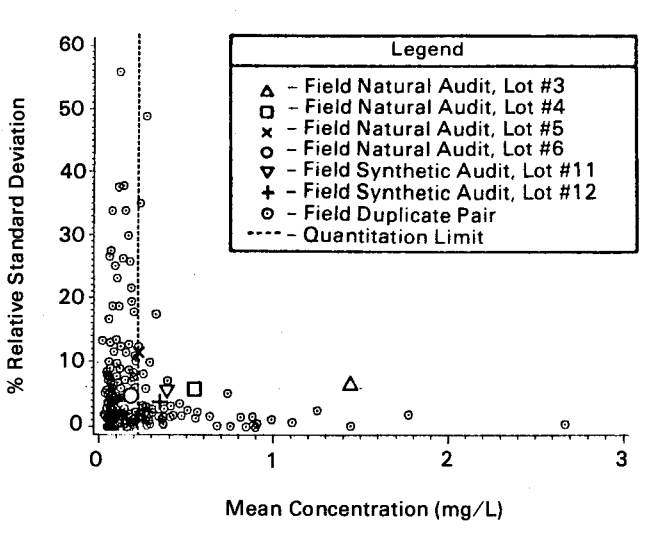


Figure J-7a. *Conductance:* Comparison of the mean instrument detection limit (IDL) of conductance to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.

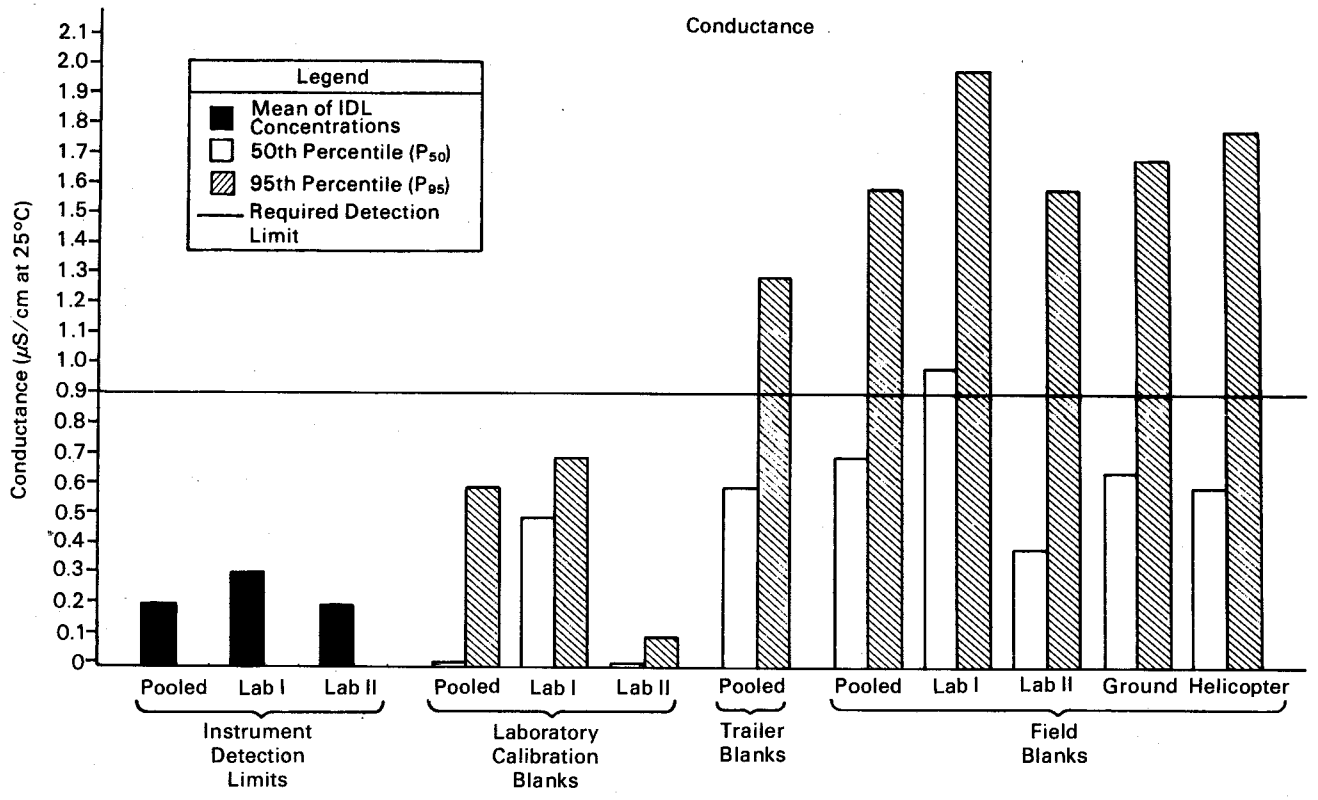


Figure J-7b. *Conductance:* Relationship between precision (percent relative standard deviation; %RSD) and mean conductance of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 7 field duplicate pairs were omitted for purposes of resolution.

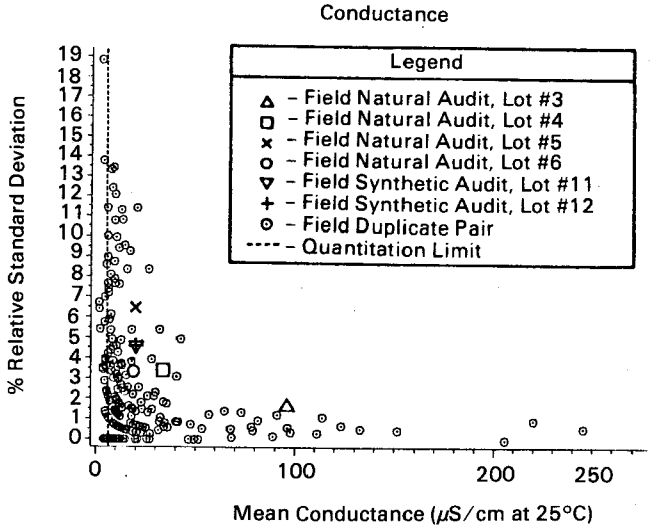


Figure J-8a. ***Dissolved Inorganic Carbon (air equilibrated):*** **Distribution (P_{50} and P_{95}) of the trailer blanks and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown. N/A denotes that blank sample data are not available for comparison.**

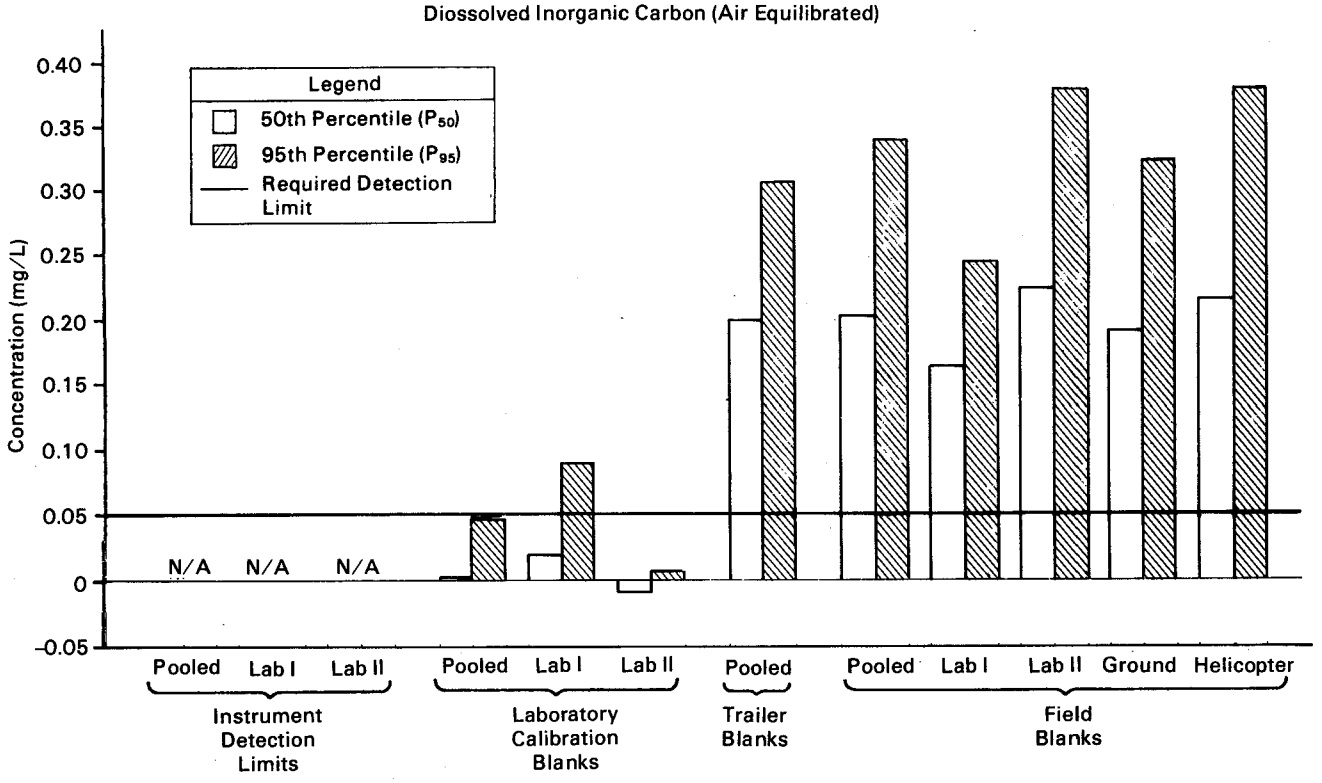


Figure J-8b. ***Dissolved Inorganic Carbon (air equilibrated):*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 6 field duplicate pairs were omitted for purposes of resolution.**

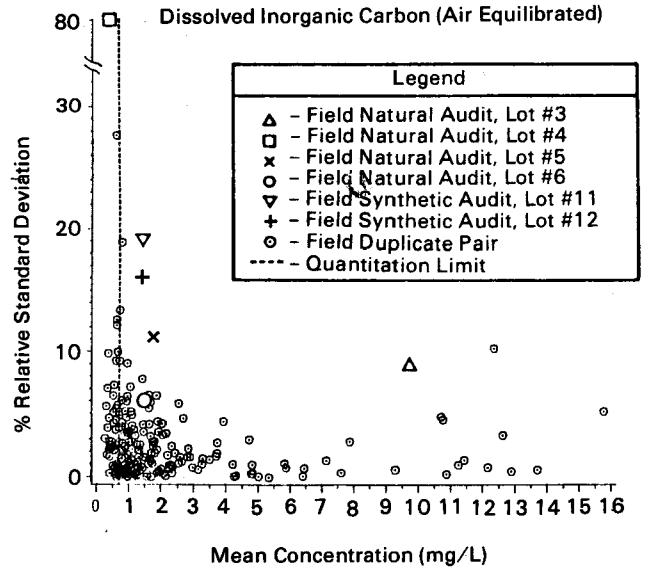


Figure J-9. ***Dissolved Inorganic Carbon (closed system):*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. One field duplicate pair was omitted for purposes of resolution.**

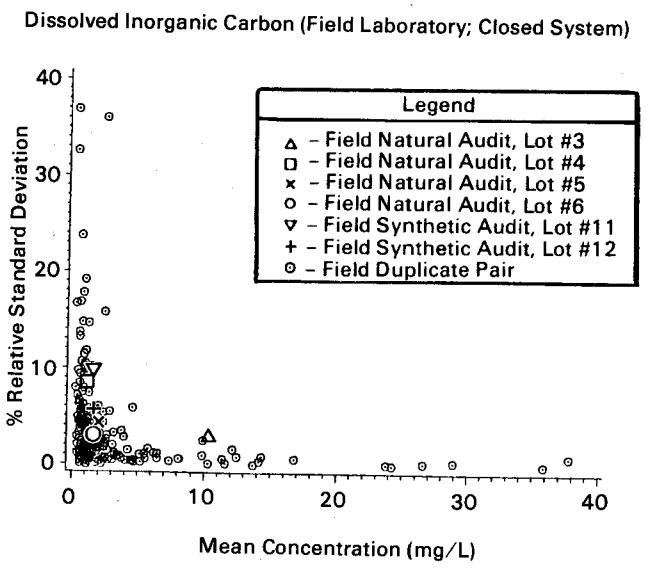


Figure J-10a. ***Dissolved Inorganic Carbon (initial; open system):*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.**

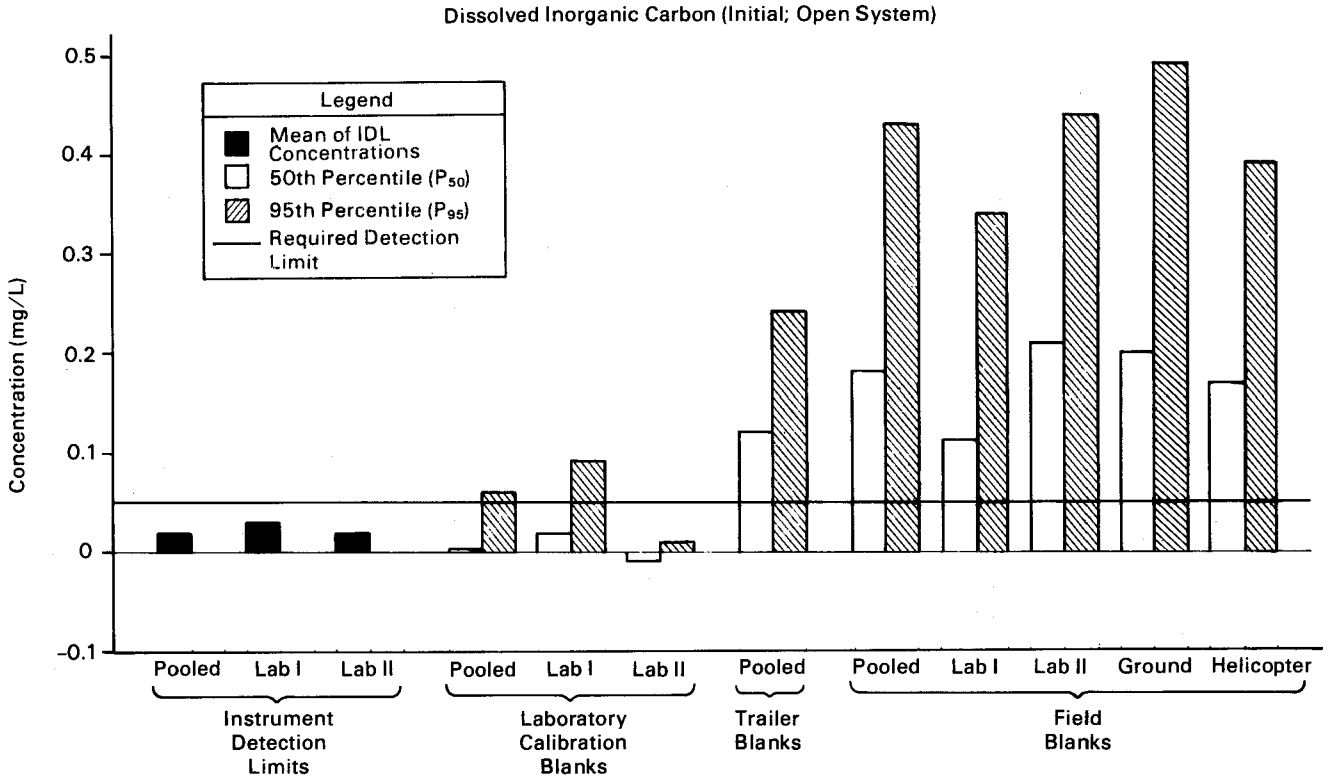


Figure J-10b. ***Dissolved Inorganic Carbon (initial; open system):*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 7 field duplicate pairs were omitted for purposes of resolution.**

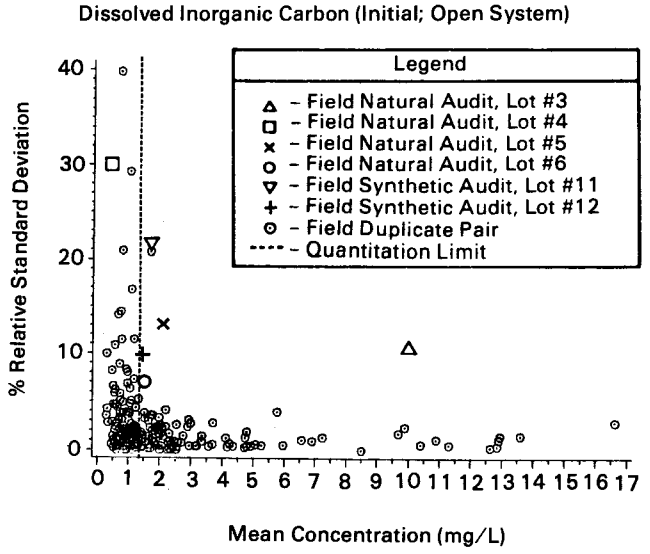


Figure J-11a. ***Dissolved Organic Carbon:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.**

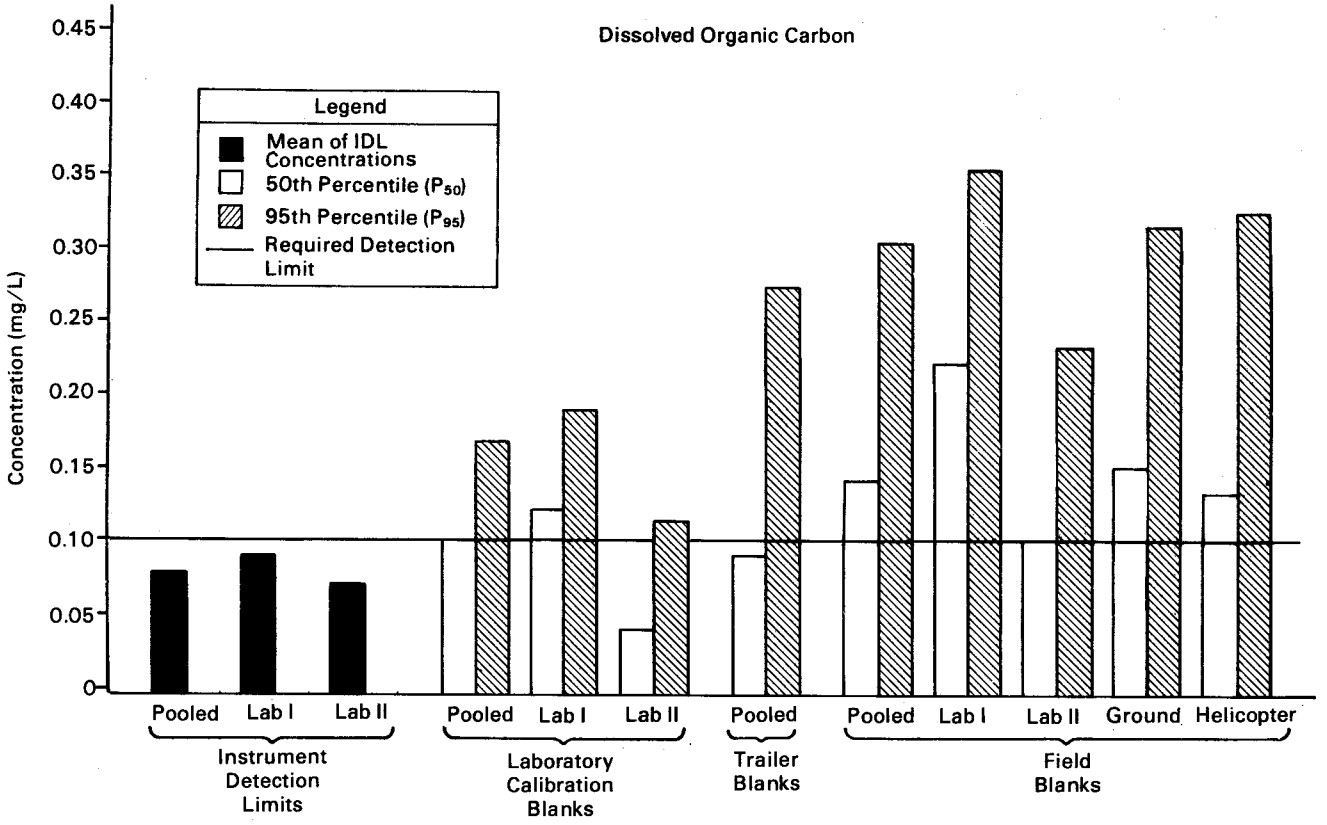


Figure J-11b. ***Dissolved Organic Carbon:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 1 field duplicate pair was omitted for purposes of resolution.**

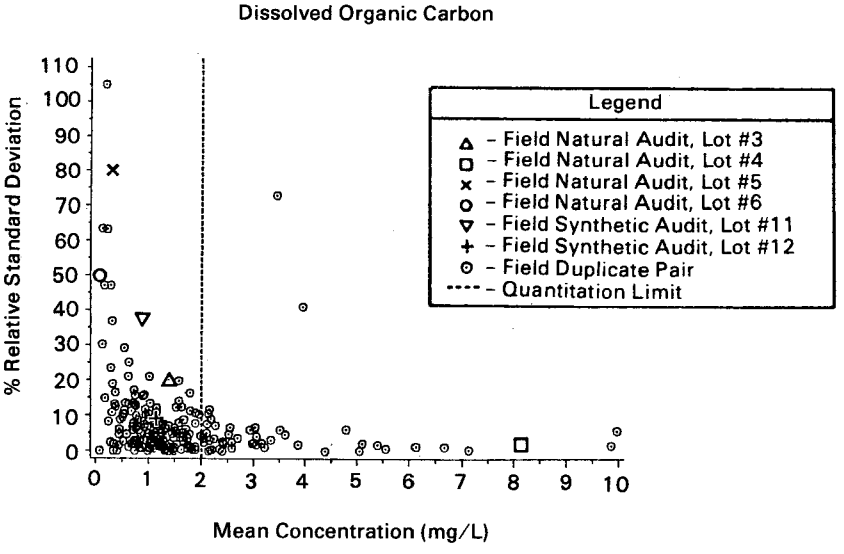


Figure J-12a. ***Fluoride, Total Dissolved:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.**

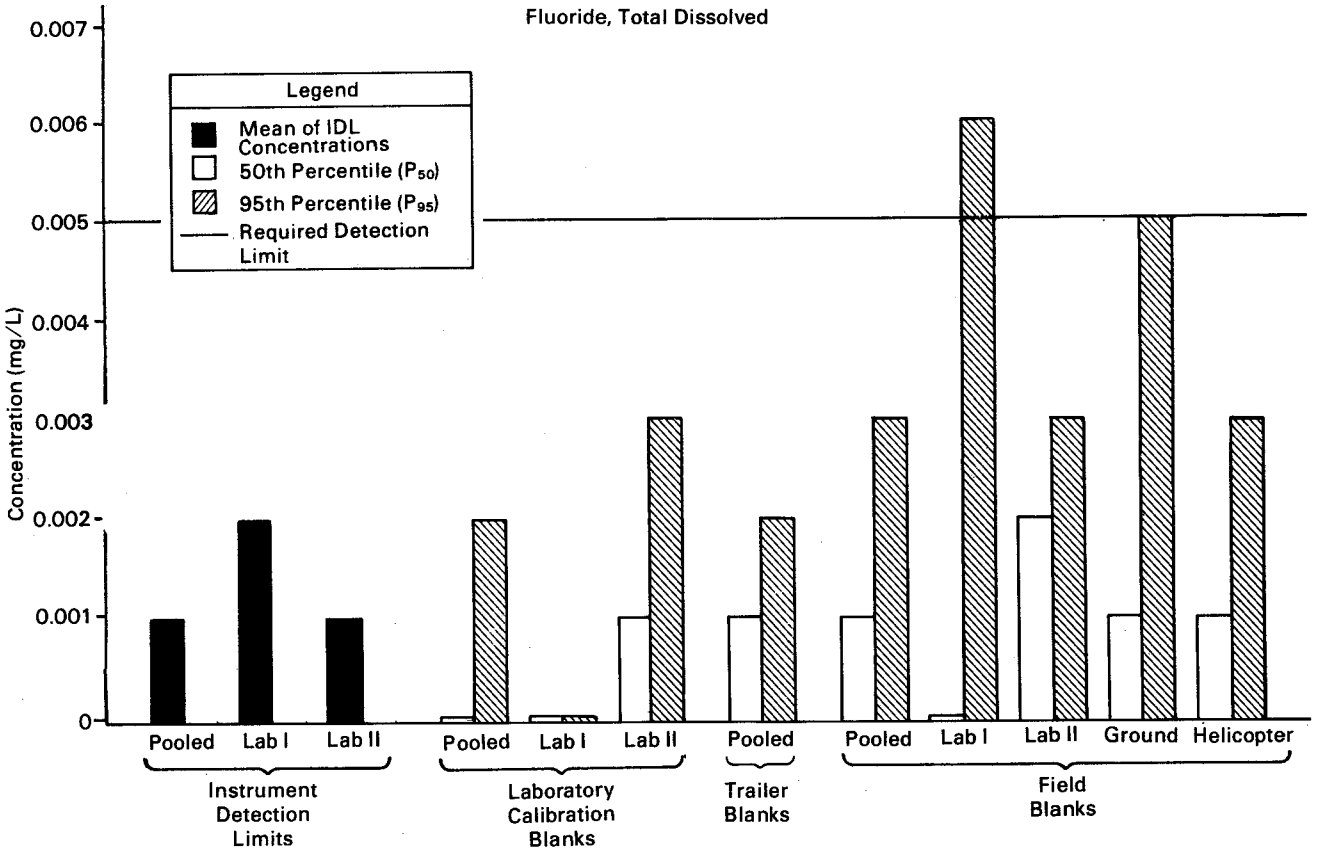


Figure J-12b. ***Fluoride, Total Dissolved:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 6 field duplicate pairs were omitted for purposes of resolution; 2 field duplicate pairs were omitted because their mean concentrations were less than or equal to 0 mg/L.**

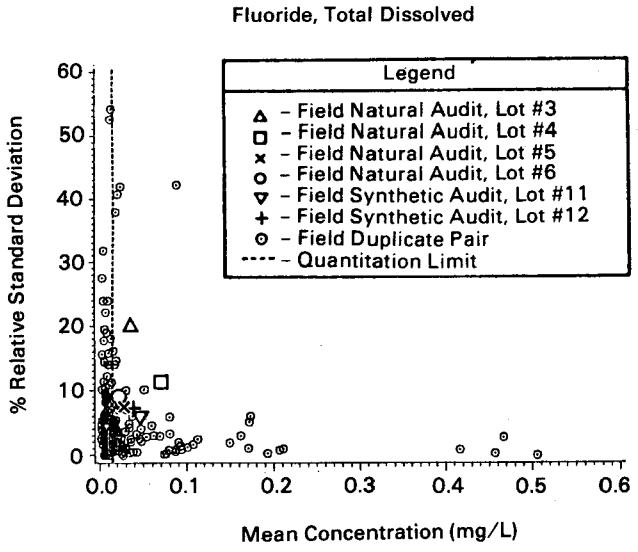


Figure J-13a. *Iron:* **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown. N/A denotes that blank sample data are not available for comparison.**

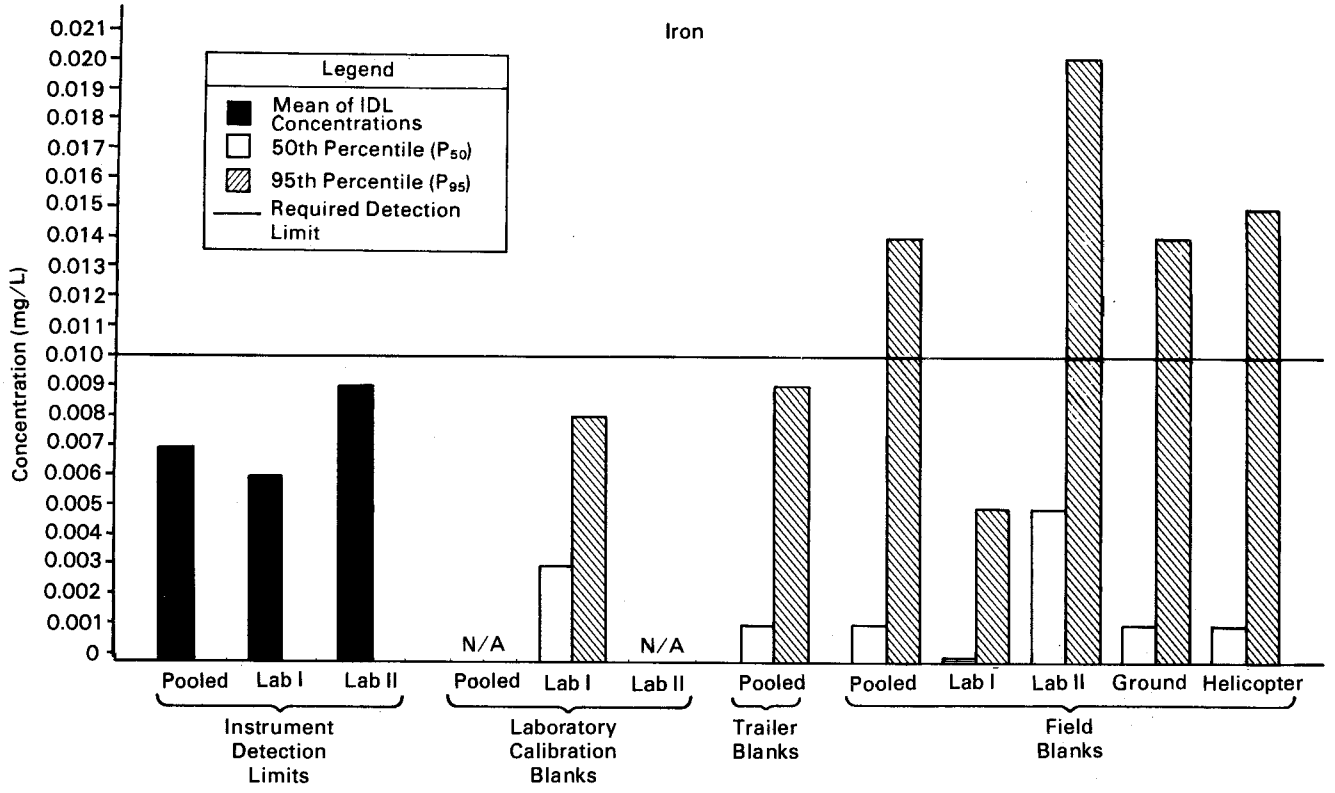


Figure J-13b. *Iron:* **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 11 field duplicate pairs were omitted for purposes of resolution; 18 field duplicate pairs were omitted because their mean concentrations were less than or equal to 0 mg/L.**

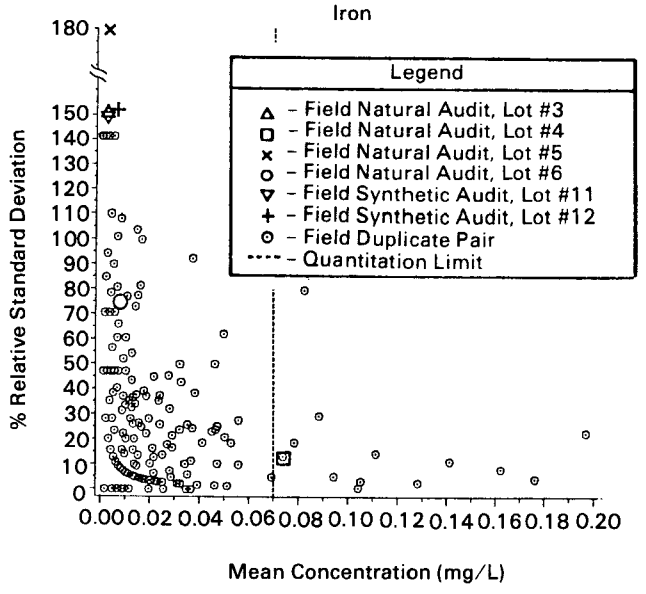


Figure J-14a. ***Potassium:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown. N/A denotes that blank sample data are not available for comparison.**

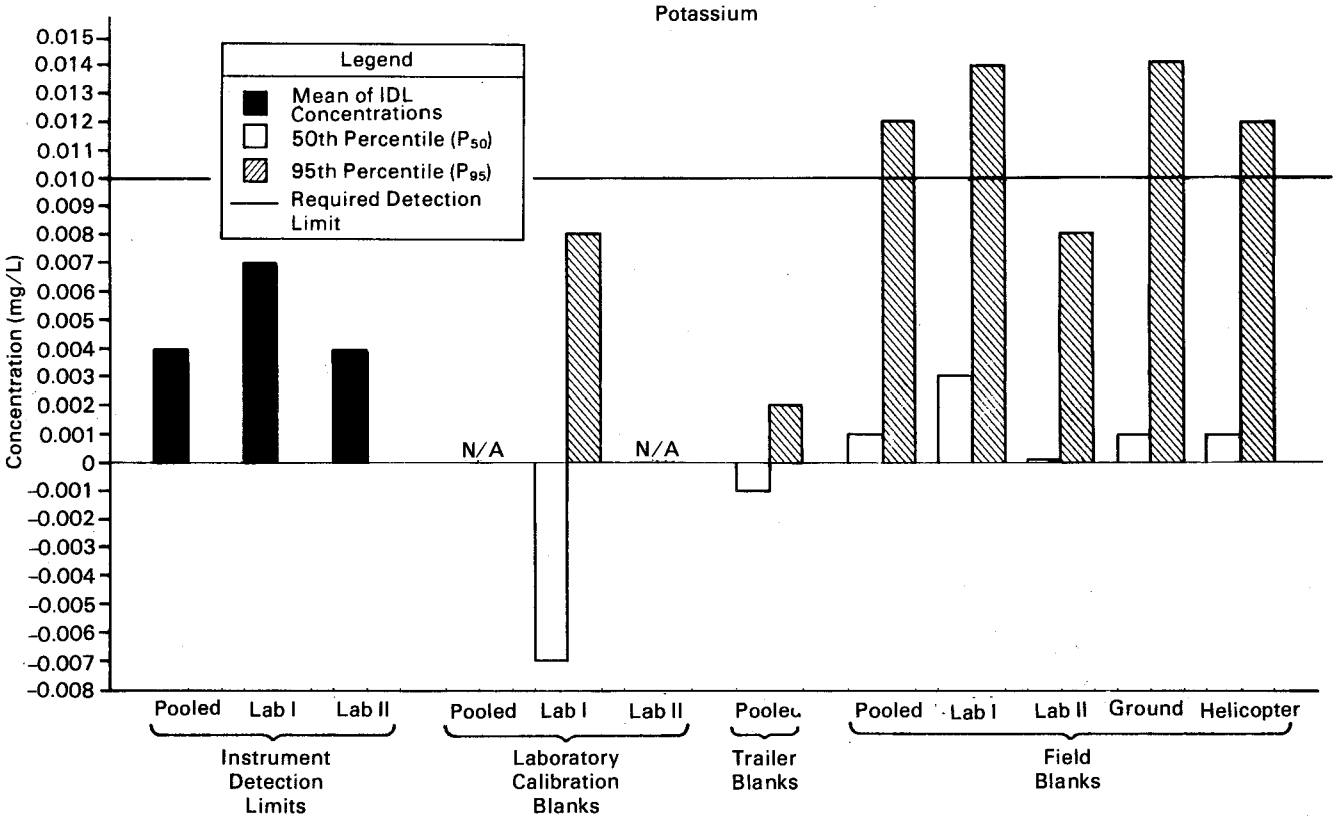


Figure J-14b. ***Potassium:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 4 field duplicate pairs were omitted for purposes of resolution.**

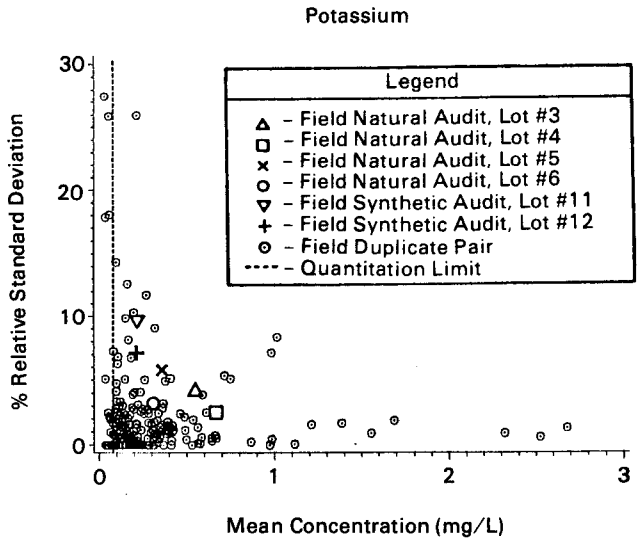


Figure J-15a. ***Magnesium:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown. N/A denotes that blank sample data are not available for comparison.**

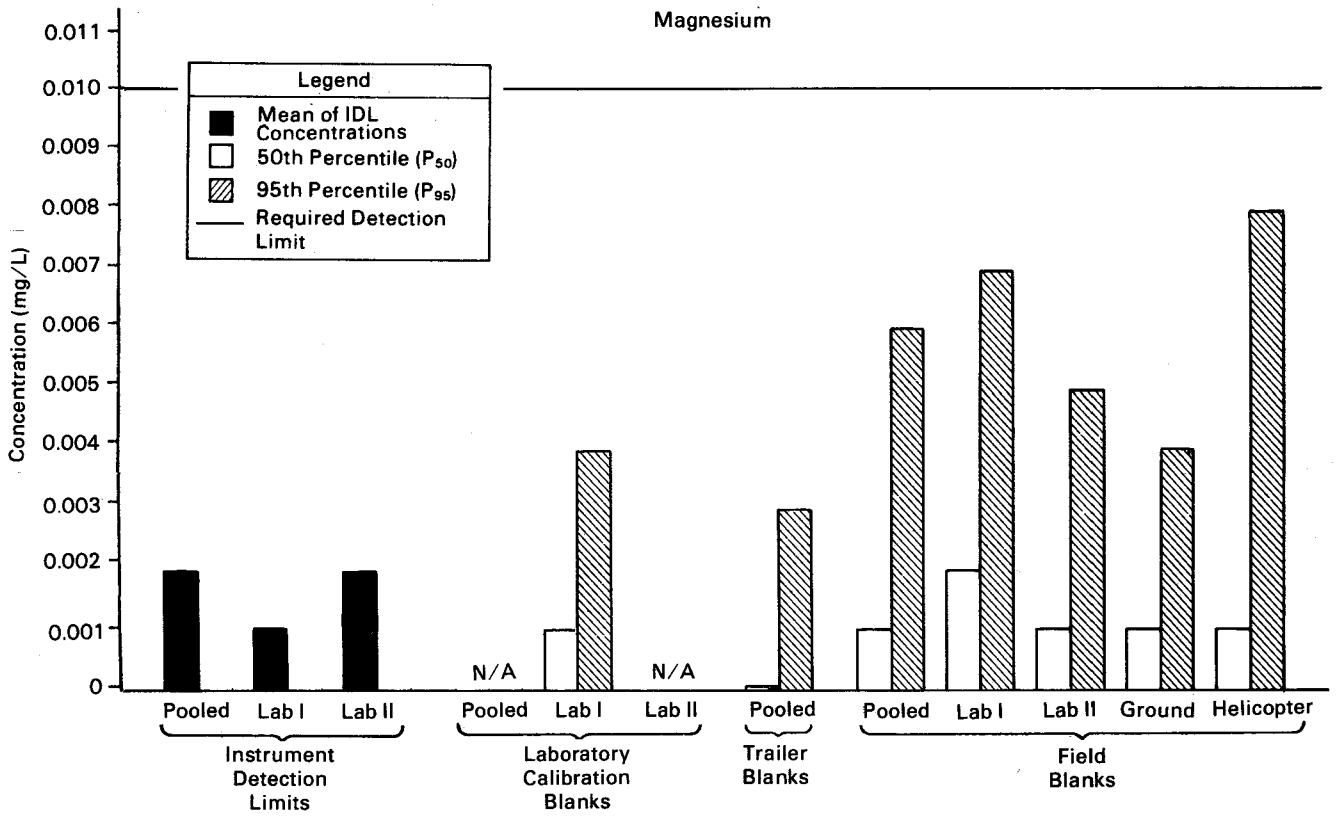


Figure J-15b. ***Magnesium:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 9 field duplicate pairs were omitted for purposes of resolution.**

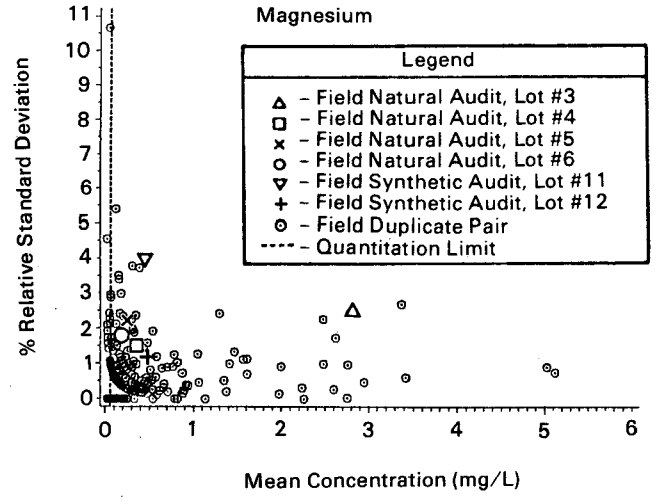


Figure J-16a. ***Manganese:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown. N/A denotes that blank sample data are not available for comparison.**

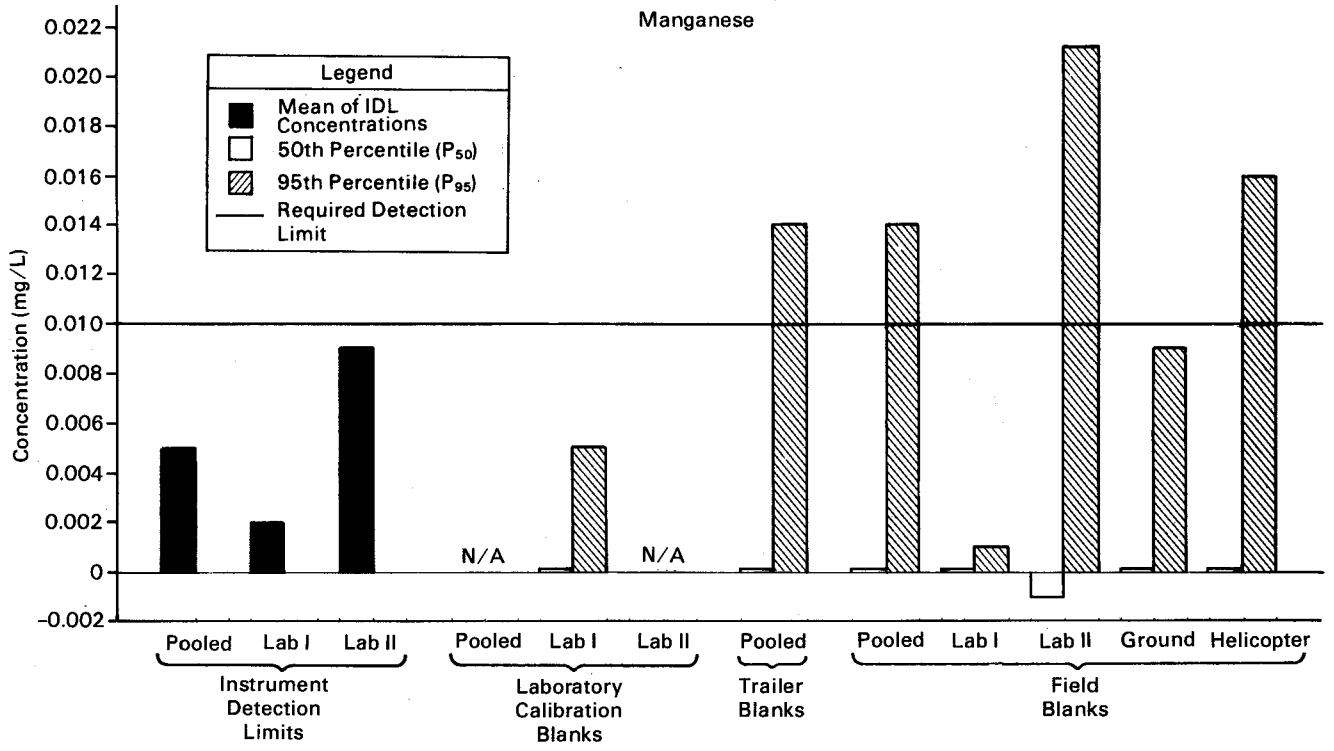


Figure J-16b. ***Manganese:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 12 field duplicate pairs were omitted for purposes of resolution; 78 field duplicate pairs were omitted because their mean concentrations were less than or equal to 0 mg/L.**

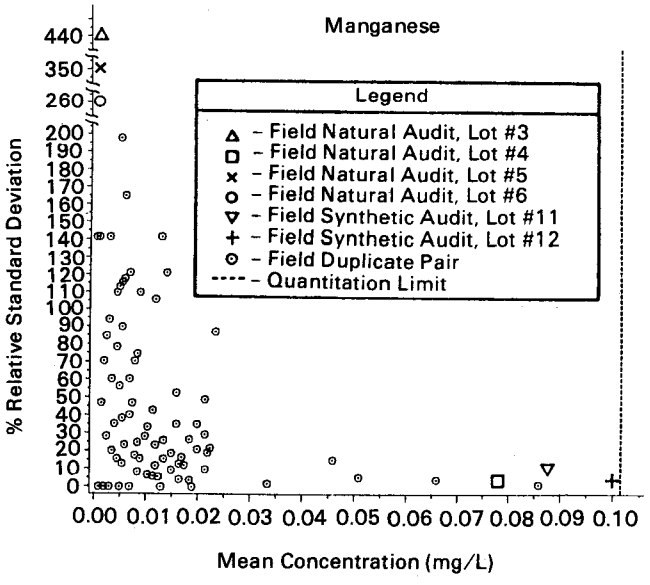


Figure J-17a. ***Sodium:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown. N/A denotes that blank sample data are not available for comparison.**

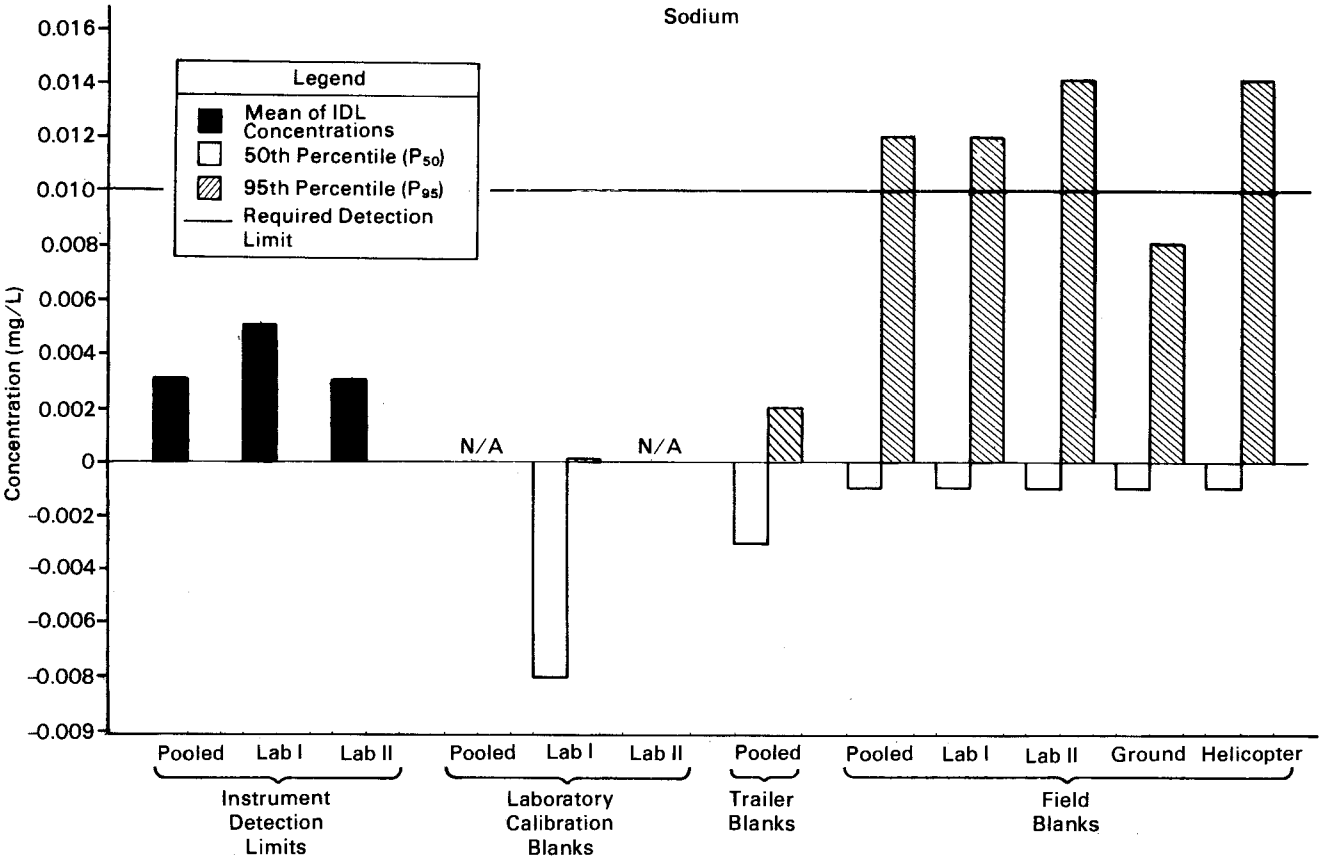


Figure J-17b. ***Sodium:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 4 field duplicate pairs were omitted for purposes of resolution. The %RSD for field synthetic audit lot no. 11 is plotted twice, The lower %RSD indicates the improvement in precision when one known, misreported measurement is corrected; the data base contains the erroneous datum.**

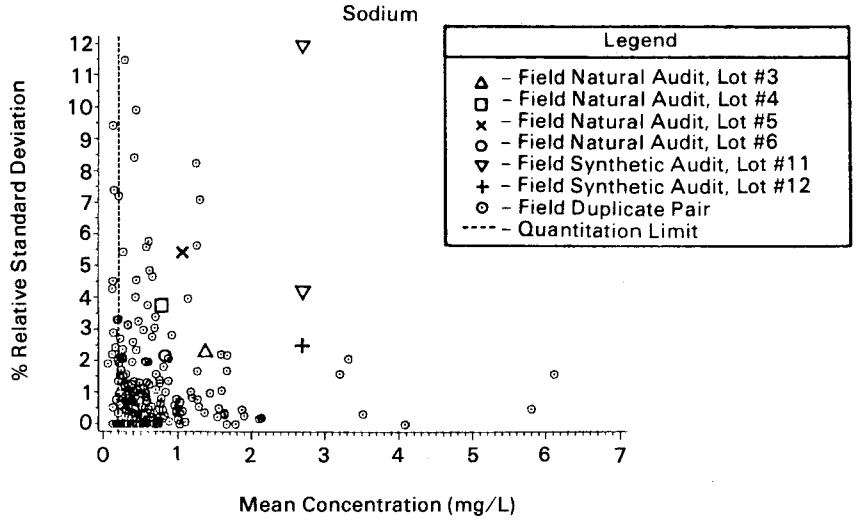


Figure J-18a. *Ammonium:* Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.

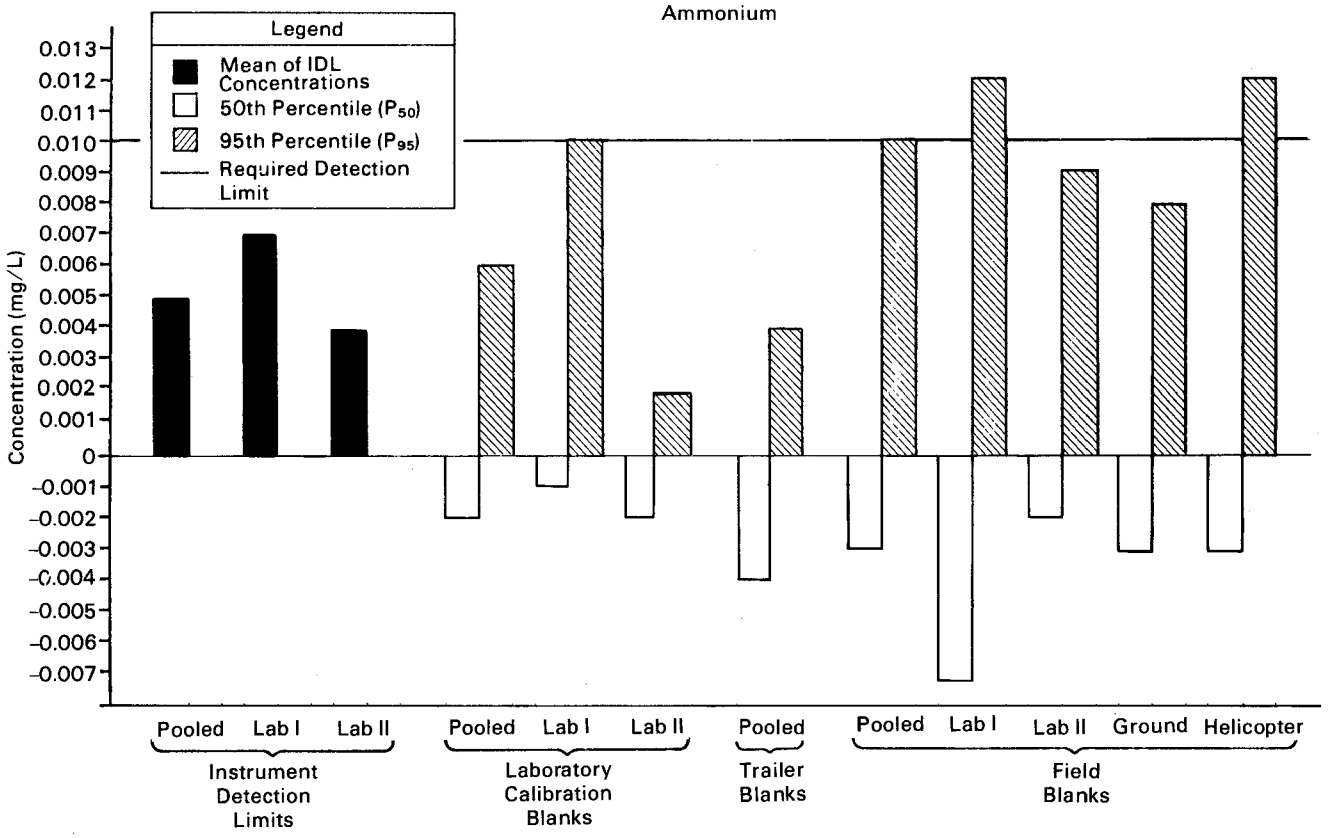


Figure J-18b. *Ammonium:* Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 12 field duplicate pairs were omitted for purposes of resolution; 132 field duplicate pairs were omitted because their mean concentrations were less than or equal to 0 mg/L; field natural audit lot no. 3 was omitted because its mean concentration was less than 0 mg/L.

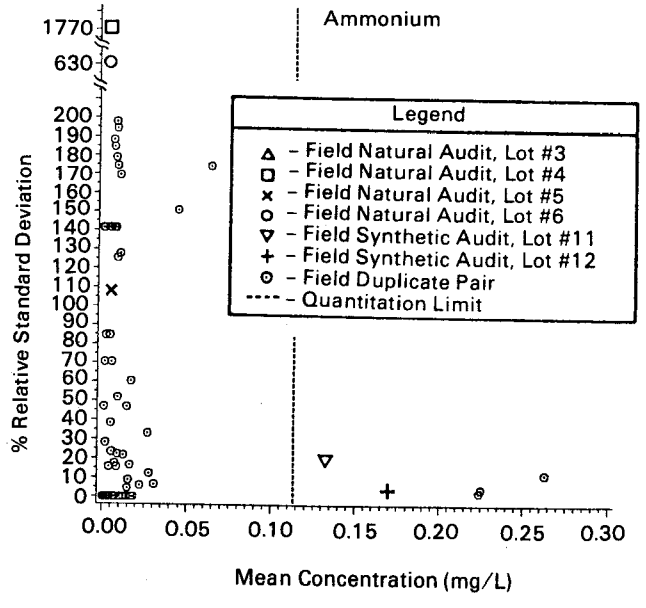


Figure J-19a. ***Nitrate:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.**

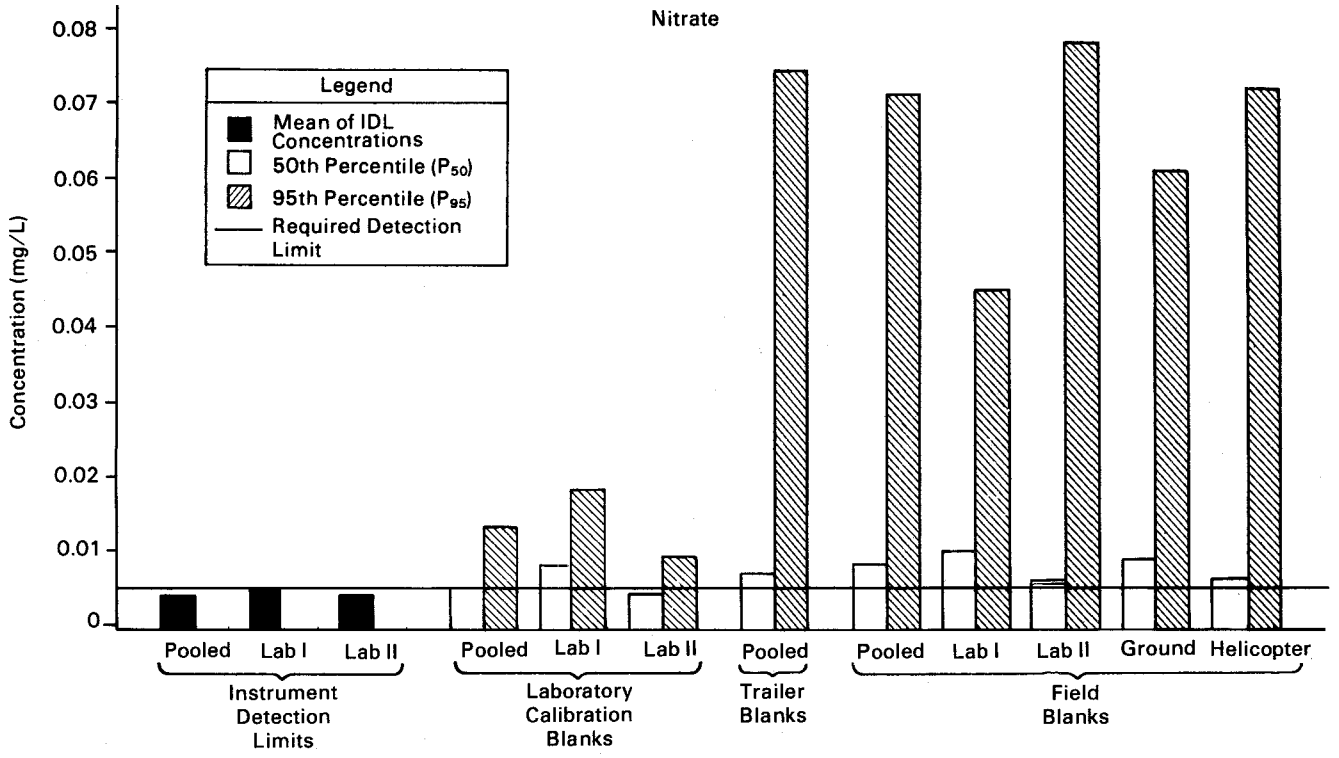


Figure J-19b. *Nitrate:* **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 3 field duplicate pairs were omitted for purposes of resolution.**

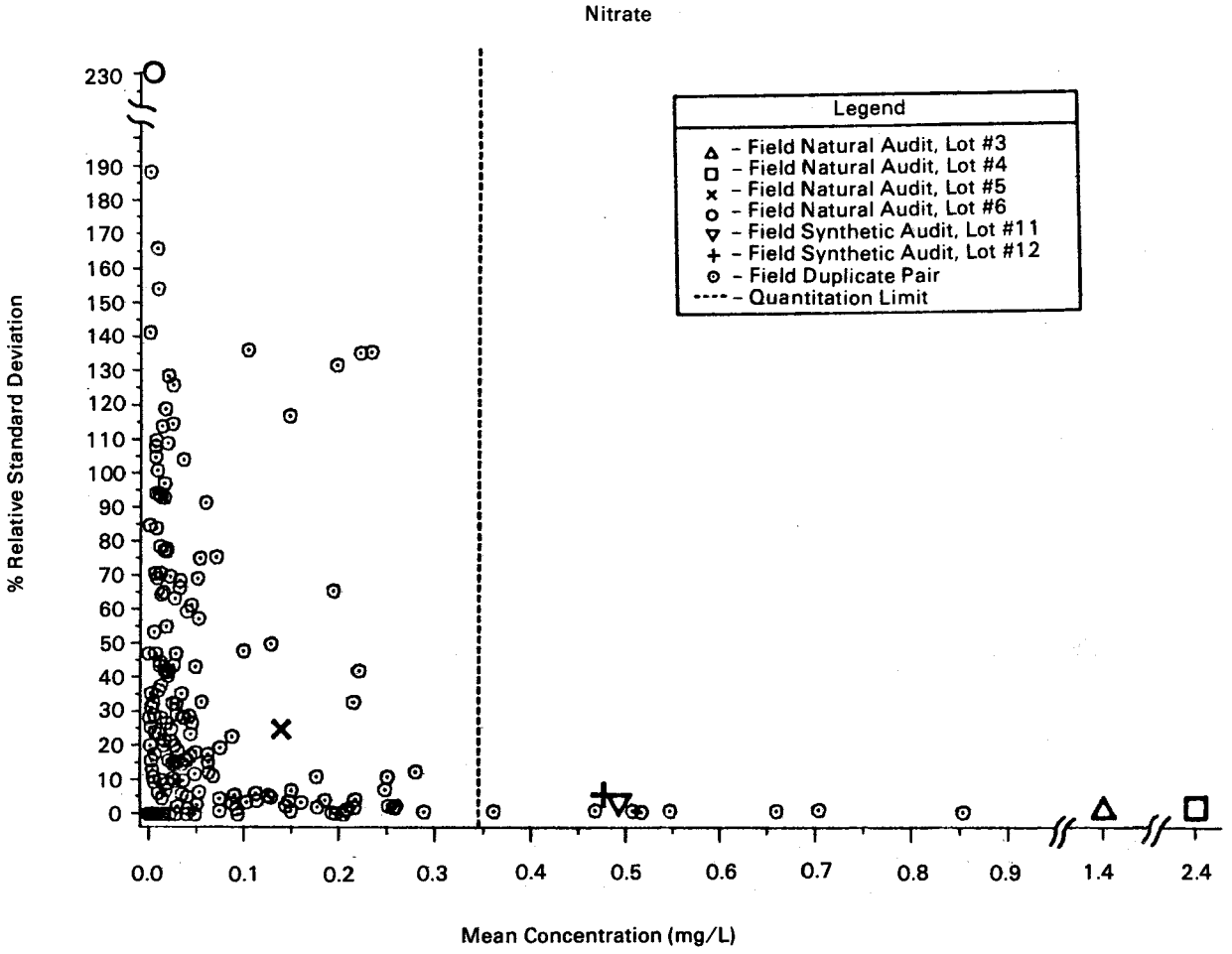


Figure J-20a. ***Phosphorus, Total:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.**

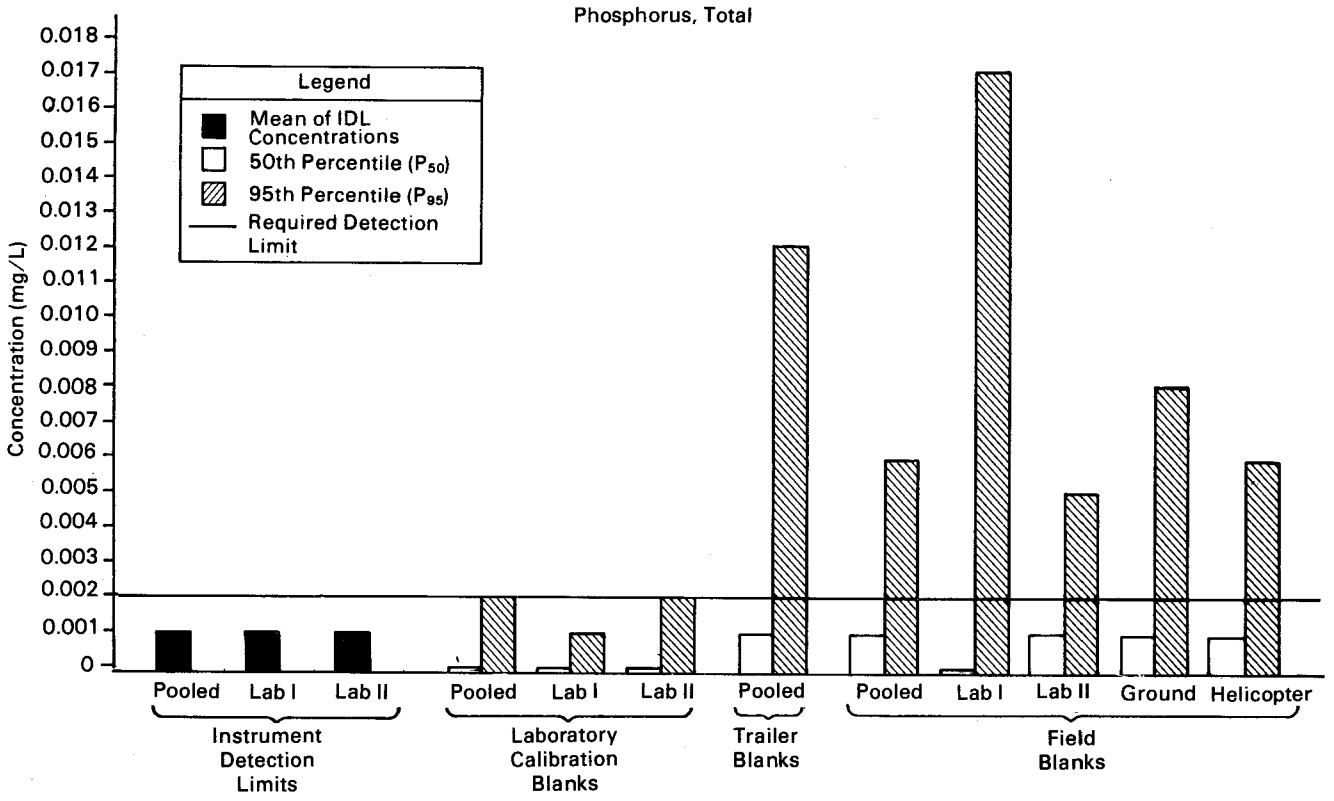


Figure J-20b. ***Phosphorus, Total:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 7 field duplicate pairs were omitted for purposes of resolution; 5 field duplicate pairs were omitted because their mean concentrations were less than or equal to 0 mg/L.**

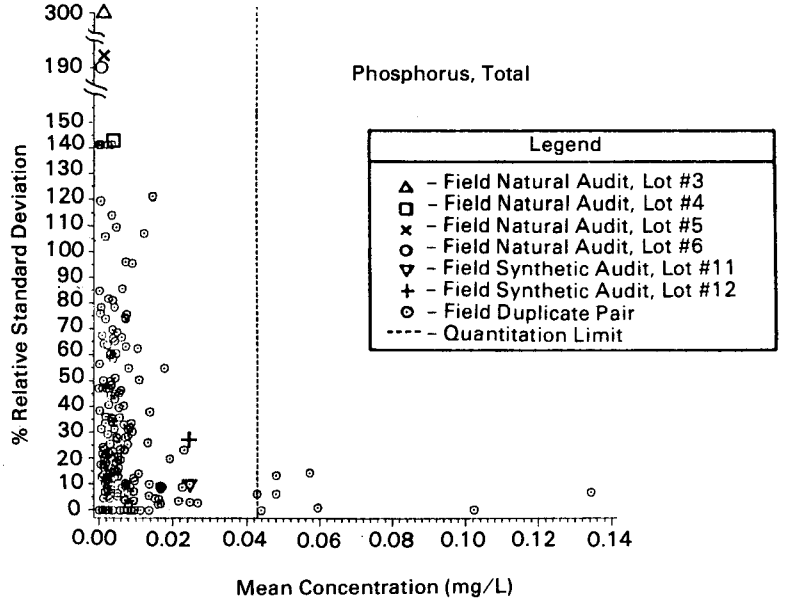


Figure J-21a. ***pH (acidity; open system):*** **Distribution (P_{50} and P_{95}) of the trailer blanks and field blanks. The data are presented pooled and separated by the major components. The theoretical pH of deionized water is shown. N/A denotes that blank sample data are not available for comparison.**

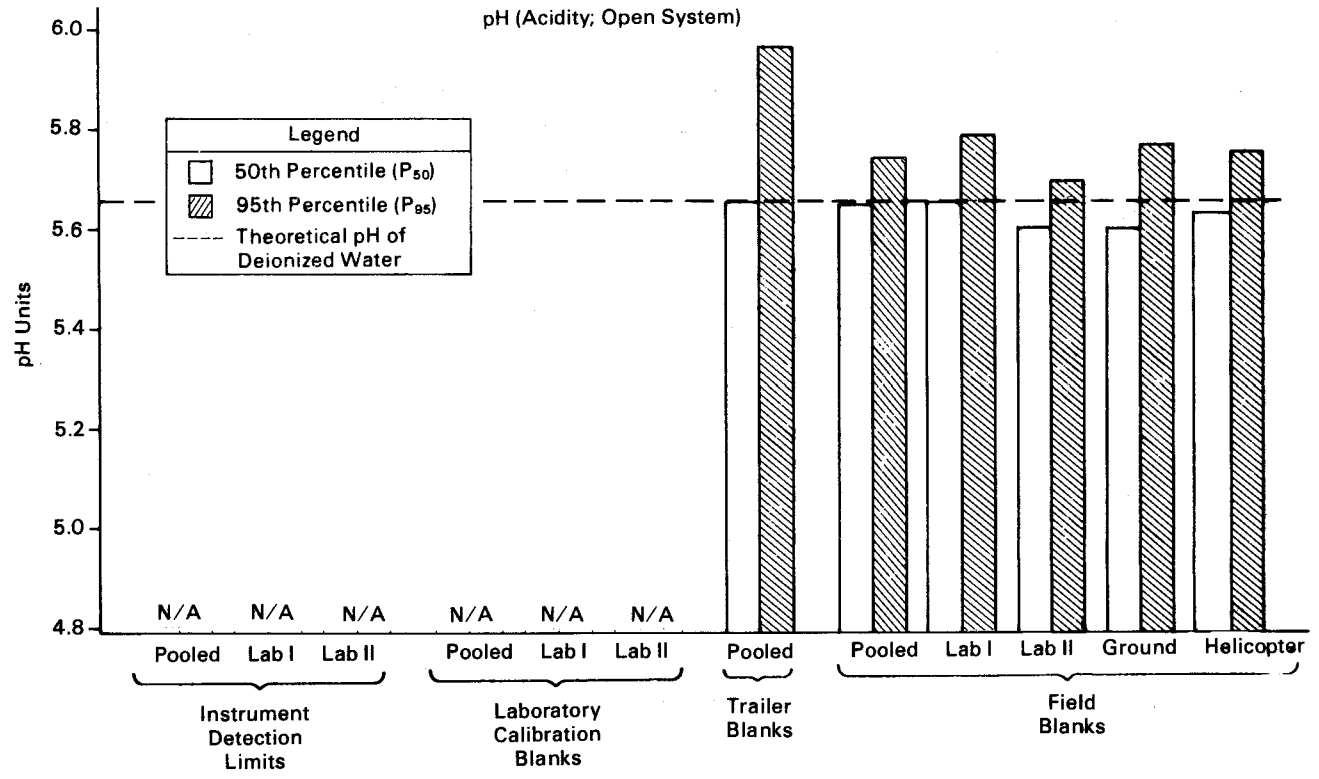


Figure J-21b. ***pH (acidity; open system):*** **Relationship between precision (standard deviation) and mean pH of field duplicate pairs and field audit samples, Western Lake Survey - Phase I.**

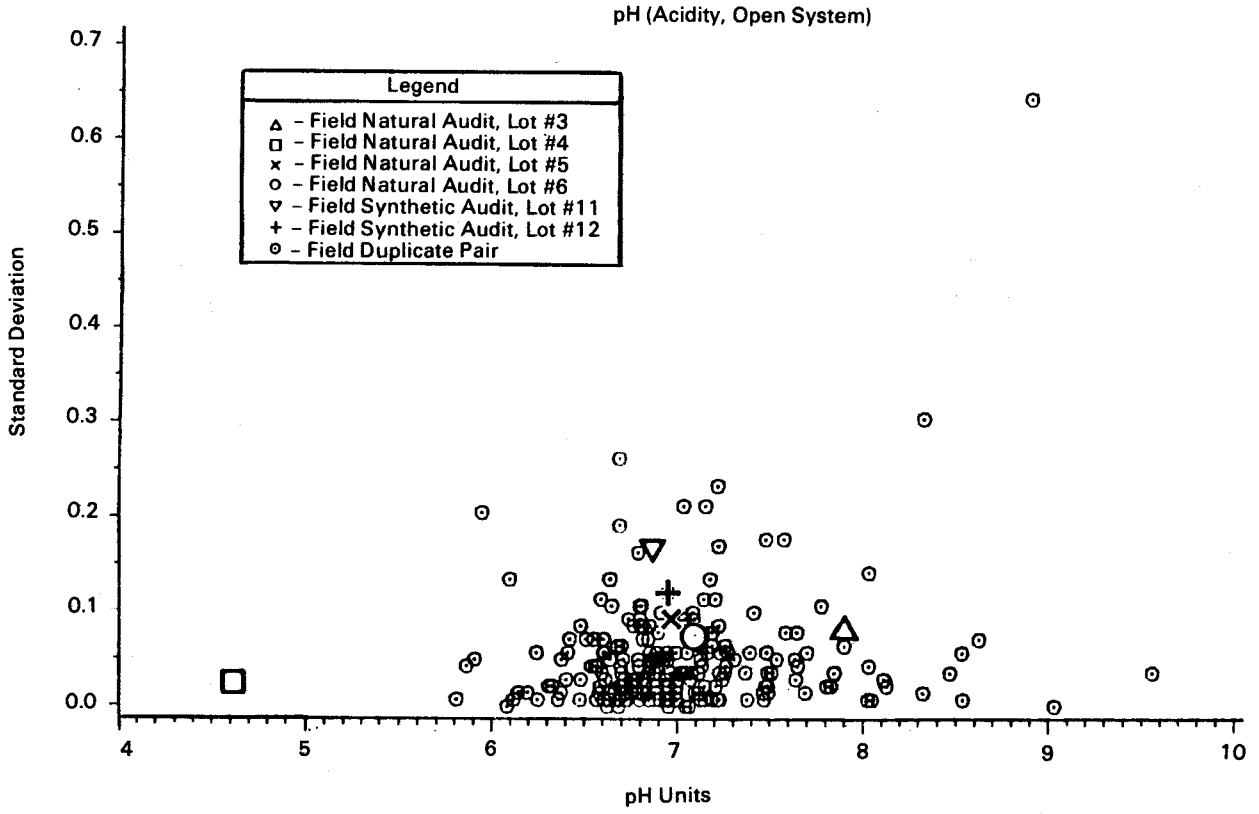


Figure J-22a. ***pH (alkalinity, open system):*** **Distribution (P_{50} and P_{95}) of the trailer blanks and field blanks. The data are presented pooled and separated by the major components. The theoretical pH of deionized water is shown. N/A denotes that blank sample data are not available for comparison.**

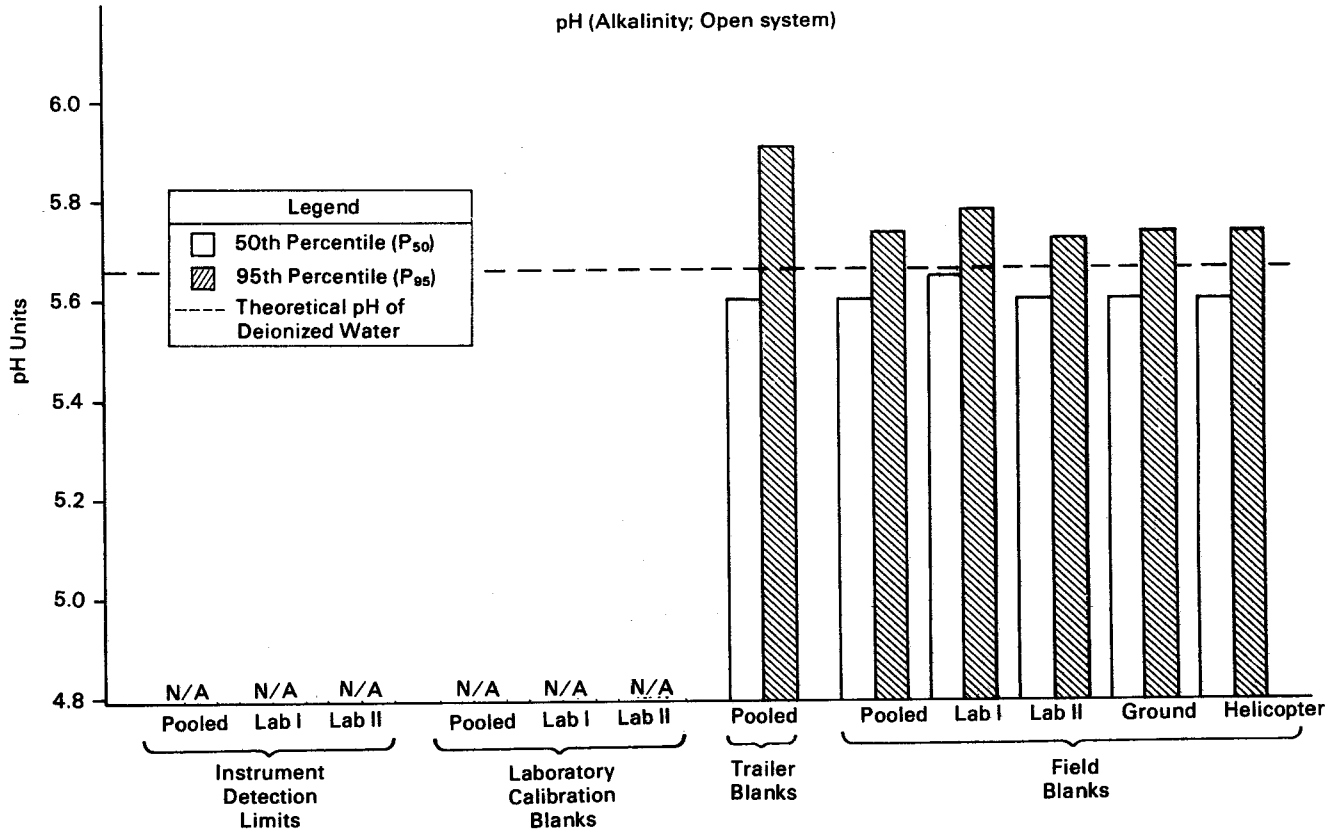


Figure J-22b. ***pH (alkalinity; open system):*** **Relationship between precision (standard deviation) and mean pH of field duplicate pairs and field audit samples, Western Lake Survey - Phase I.**

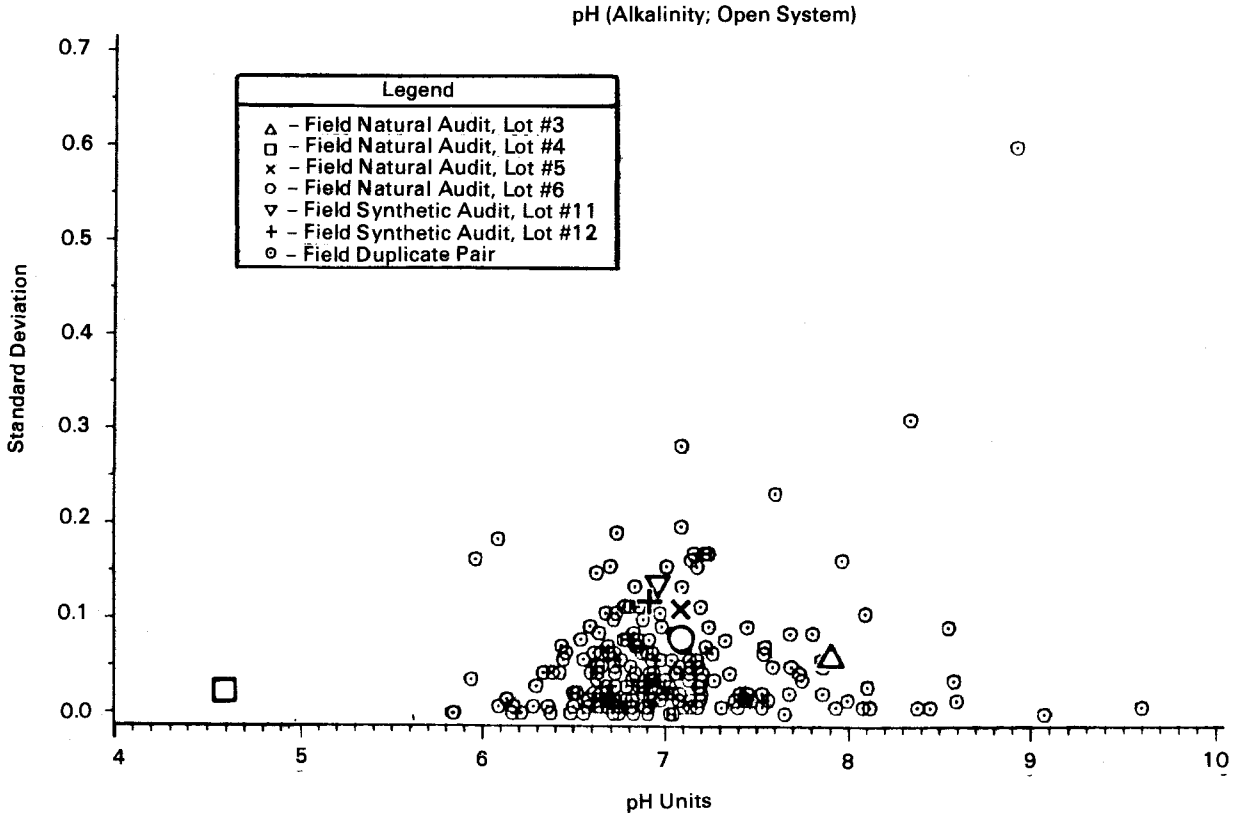


Figure J-23a. ***pH (air equilibrated):*** **Distribution (P_{50} and P_{95}) of the trailer blanks and field blanks. The data are presented pooled and separated by the major components. The theoretical pH of deionized water is shown. N/A denotes that blank sample data are not available for comparison.**

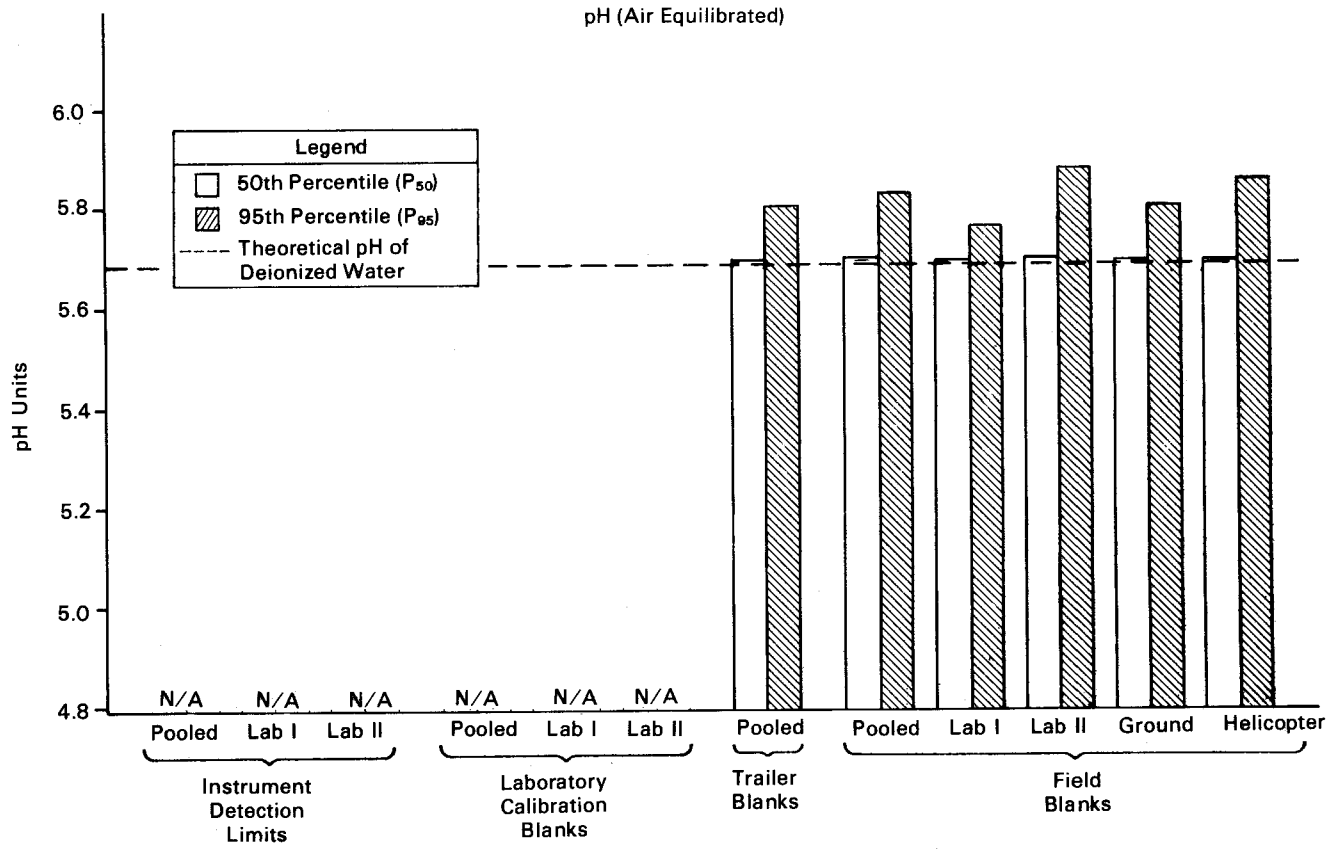


Figure J-23b. ***pH (air equilibrated):*** **Relationship between precision (standard deviation) and mean pH of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. One duplicate pair was omitted for purposes of resolution.**

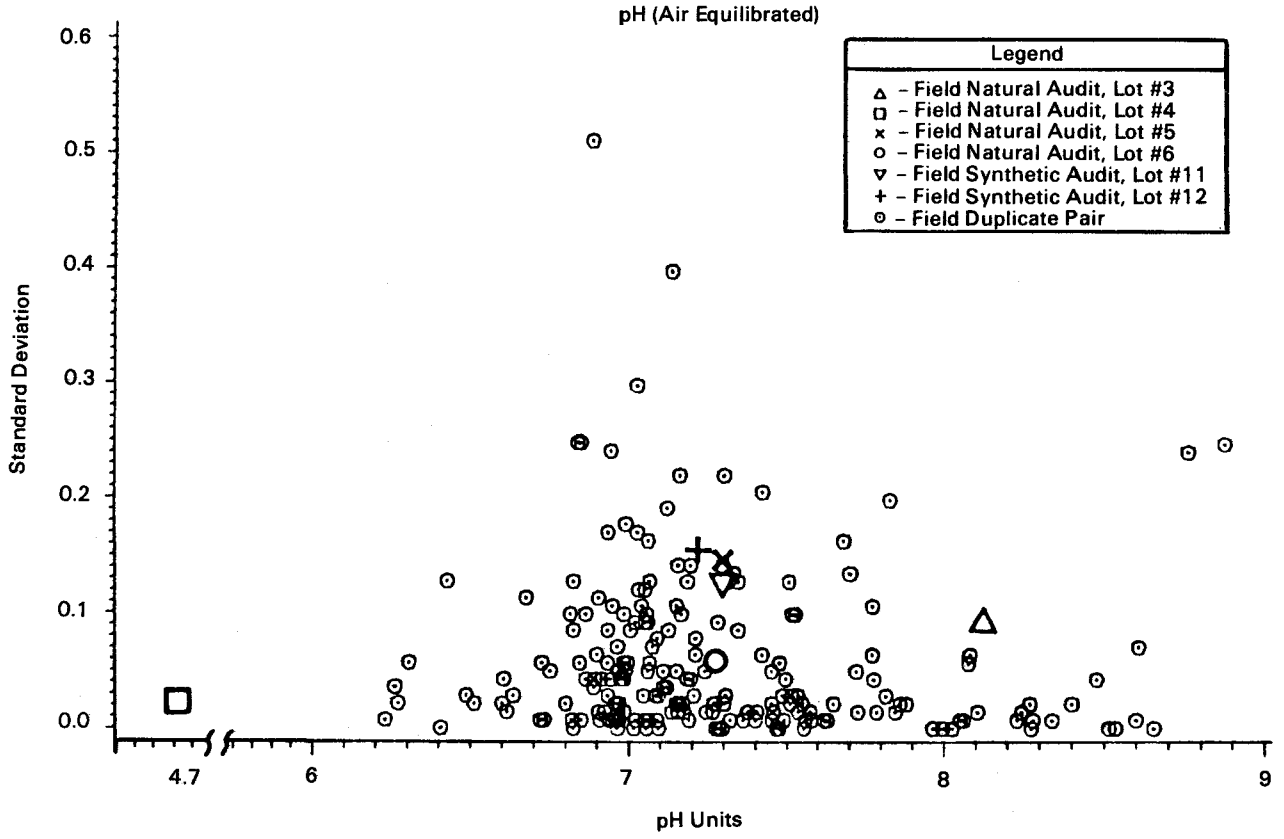


Figure J-24. ***pH (closed system):*** **Relationship between precision (standard deviation) and mean pH of field duplicate pairs and field audit samples, Western Lake Survey - Phase I.**

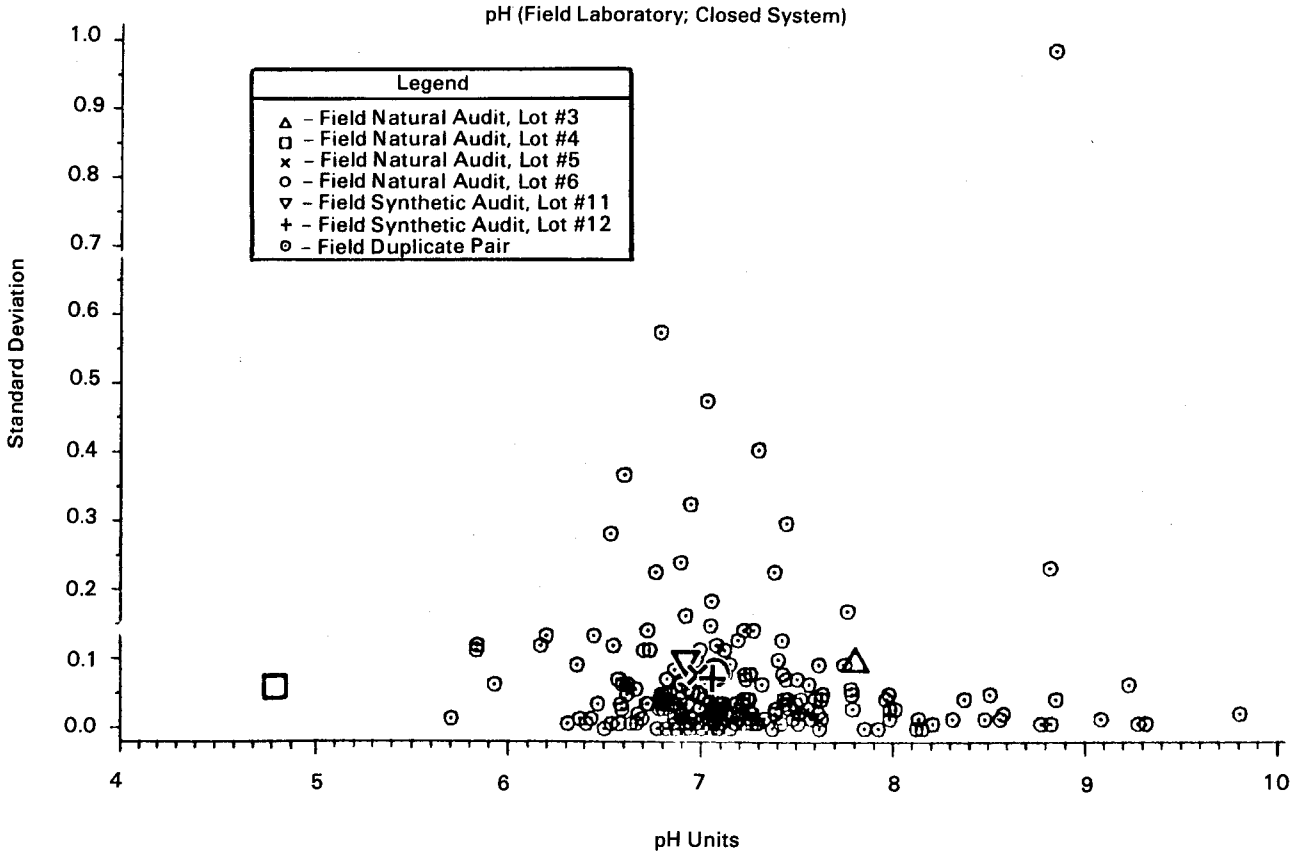


Figure J-25a. ***Silica:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.**

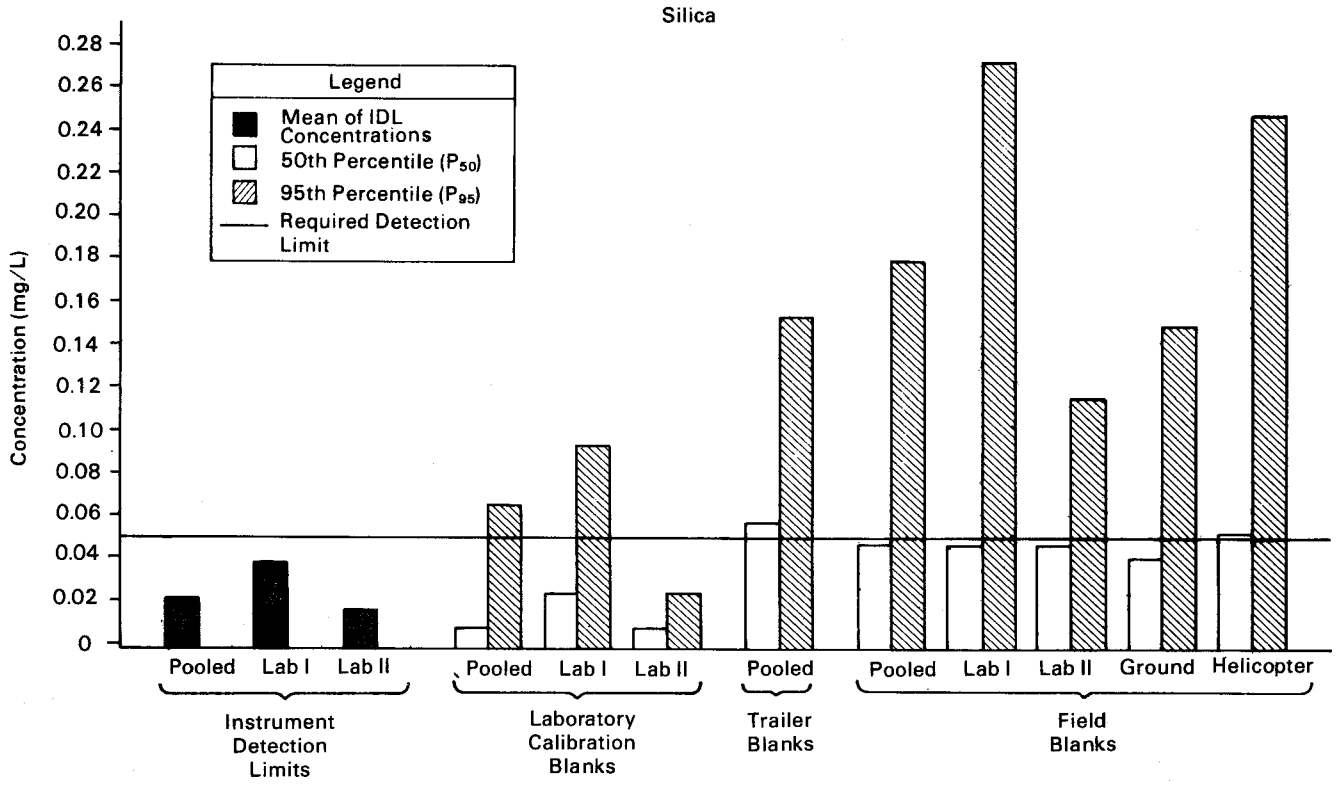


Figure J-25b. ***Silica:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 3 field duplicate pairs were omitted for purposes of resolution.**

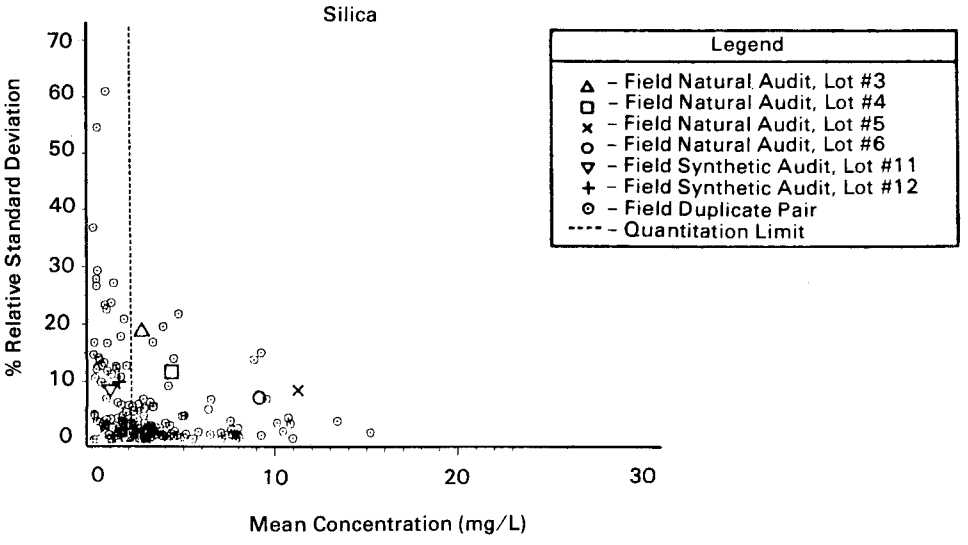


Figure J-26a. ***Sulfate:*** **Comparison of the mean instrument detection limit (IDL) concentrations to the distribution (P_{50} and P_{95}) of the laboratory calibration blanks, trailer blanks, and field blanks. The data are presented pooled and separated by the major components. The required detection limit is shown.**

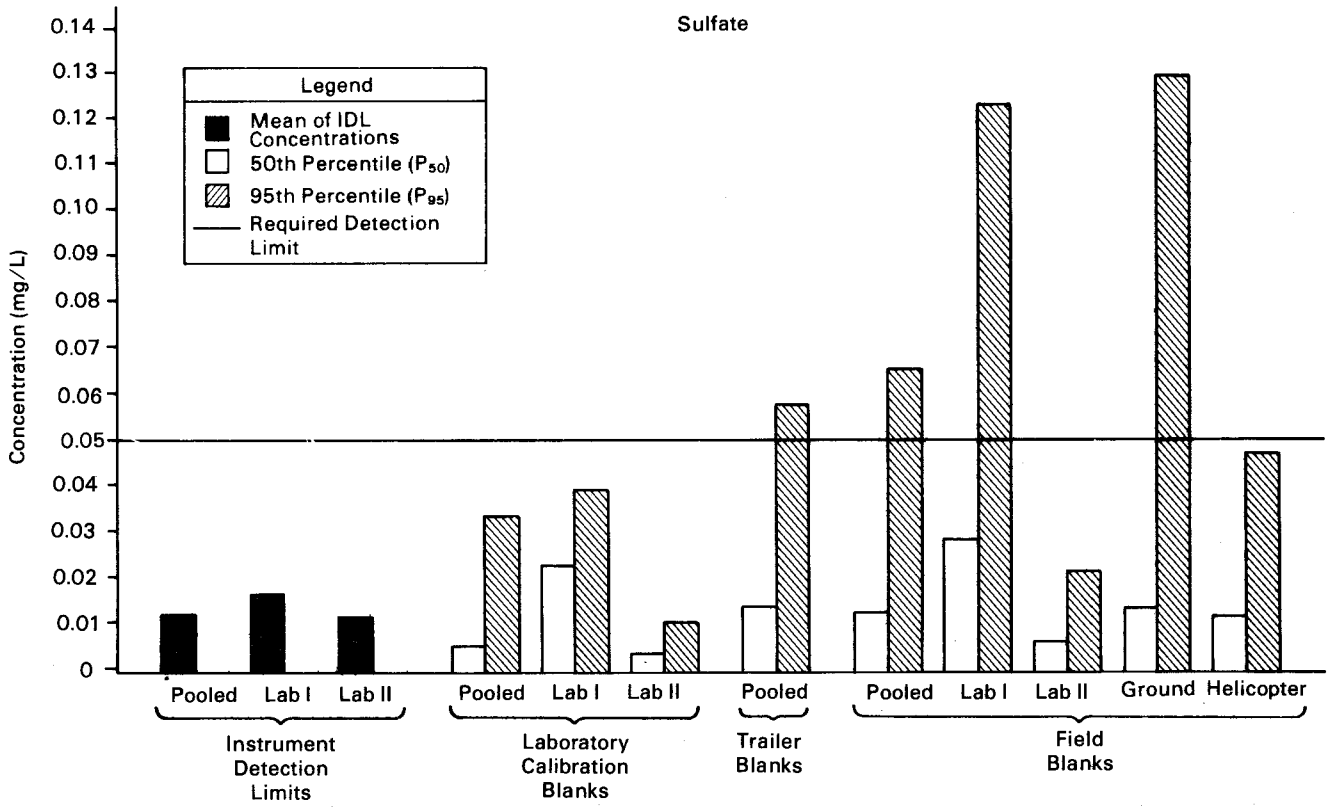
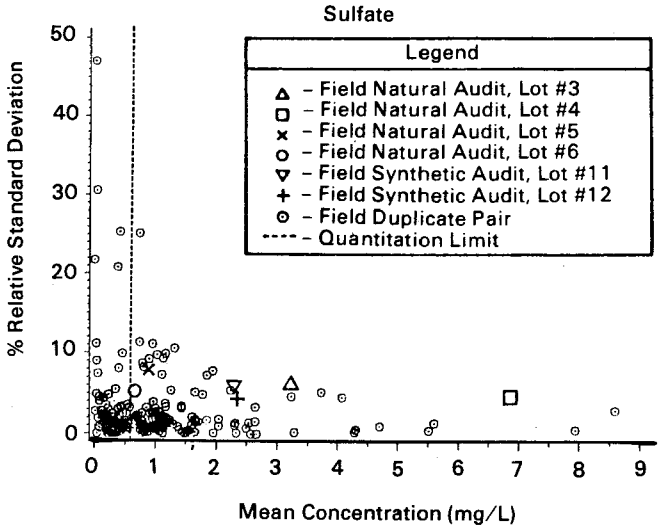


Figure J-26b. ***Sulfate:*** **Relationship between precision (percent relative standard deviation; %RSD) and mean concentrations of field duplicate pairs and field audit samples, Western Lake Survey - Phase I. The quantitation limit is shown; 7 field duplicate pairs were omitted for purposes of resolution.**



Appendix K
Distribution of Analyte Concentrations for Routine Lake Samples

Table K-1 shows the distribution of the analytical measurements for each variable, for all routine lake samples. These data can be useful in interpreting the importance of QA limits and of trends in QA sample data. The lowest and highest values are the endpoints of the range of concentrations measured in WLS-I. The highest value often was associated with a rare high conductance, high ionic strength sample. For comparison, the table also presents median and mean sample concentrations.

Table K-1. Distribution of Analyte Concentrations for Routine Lake Samples, Western Lake Survey - Phase I

Variable[a]	Low Value	Median Value	Mean Value	High Value
Al, extractable	-0.006[b]	0.004	0.006	0.594
Al, total	-0.002[b]	0.024	0.037	1.154
ANC (μeq/L)	-24.0	105.6	270.9	14,140.0
BNC (μeq/L)	-798.5	27.6	23.7	310.9
Ca	0.09	1.67	3.77	95.38
Cl^-	0.011	0.14	0.87	187.50
Conductance (μS/cm)	1.6	14.6	44.5	6,601.0
DIC, air equilibrated	0.14	1.36	3.74	485.4
DIC, initial	0.16	1.44	3.82	462.60
DOC	0.05	1.3	1.9	32.0
F^-, total dissolved	0.000	0.015	0.062	6.233
Fe	-0.009[b]	0.015	0.034	0.974
K	0.00	0.21	0.85	269.40
Mg	0.02	0.28	1.06	126.00
Mn	-0.043[b]	0.001	0.004	0.212
Na	0.02	0.54	3.79	1,205.00
NH_4^+	-0.083[b]	-0.002[b]	0.000	0.240
NO_3	-0.013[b]	0.022	0.105	2.669
P, total	-0.003[b]	0.005	0.008	0.188
pH, acidity (pH units)	4.55	6.94	7.03	9.93
pH, alkalinity (pH units)	4.60	6.92	7.03	9.93
pH, air equilibrated (pH units)	4.65	7.21	7.29	9.92
SiO_2	-0.05[b]	2.27	3.76	98.74
SO_4^{2-}	0.00	0.82	3.87	1,726.00

[a] Concentrations are in mg/L unless otherwise indicated. Each variable includes 811 routine sample analyses, except for ANC, BNC, total dissolved F^-, SiO_2,and SO_4^{2-}, each of which includes 810 routine sample analyses.
[b] Negative values are a result of analytical laboratory instrument calibration.

Appendix L

Collection and Preparation of Nitrate-Sulfate Split Samples

Collection Procedure (Lake Site)

1. Complete an aliquot label and affix it to a 125-mL Nalgene bottle.

2. Fill the bottle to the shoulder with sample that has been processed through the Van Dorn sampler.

3. Use a dropper bottle to add 2 drops (0.1 mL) of 5 percent $HgCl_2$ to the aliquot. Note the amount of preservative used on the aliquot label.

4. Cap the aliquot bottle tightly. Invert it several times to mix the contents. Tape the cap with electrician's tape, then place it in a plastic bag for transport with the Cubitainers and syringes.

Field Natural Audit Preparation Procedure (Field Laboratory)

1. Prepare nitrate-sulfate aliquot labels. Enter the audit sample code in the lake ID field on the label. Do not record a crew ID. Check the line indicating that the sample is an audit.

2. Rinse the 125-mL Nalgene bottles (not acid-washed) three times with 5 to 10 mL of audit sample.

3. Fill each bottle with field natural audit sample. Refrigerate it at 4°C until needed (1 to 10 days later).

Appendix M

Proposed Procedure for Use of Low Ionic Strength, Circumneutral, Mid-Range pH and DIC Quality Control Check Samples

During ELS-I and NSS Phase I Pilot, precision and accuracy data showed that pH values in the range pH 6 to 8 were the most difficult to determine. The readings in this range were more variable and took more time. Also, when an electrode is malfunctioning or is incorrectly calibrated, readings for near-neutral, low-ionic-strength samples are affected most (see Best et al., 1987). It is not always possible, however, to detect instrument problems with the quality control check sample (QCCS) used (10^{-4} N H_2SO_4, pH = 4) or with commercial pH buffers (high-ionic-strength). For this reason, the use of a low-ionic-strength QCCS with a pH in the range 6 to 8 was investigated.

In August 1985, experiments were performed at EMSL-LV with a low-ionic-strength pH QCCS (ionic strength = 4.5 x 10^{-5}, conductance < 5 µS). The sample also may be used as a low-level DIC QCCS. Preparation instructions are given in Table M-1. Sample results of the experiment are given in Table M-2. The average ΔpH (difference from theoretical) was 0.002 ± 0.069 and average ΔDIC (relative difference from theoretical) was -1.3 ± 7 percent.

As a result of this experiment, during WLS-I, two new QCCS solutions for pH and DIC were proposed, in addition to those used previously in NSWS. The use of these solutions was to provide the following benefits:

- independent checks of the neutral calibration point and mid-range linearity in pH analysis
- independent analysis of low-range sensitivity at two levels in DIC analysis
- a field-determined cross-check between pH and DIC analyses which would enable early detection of suspect measurements

The protocol for measurement of pH was to be the standard closed method used for routine lake samples in the field laboratory, as described in the methods manuals (Hillman et al., 1986; Kerfoot and Faber, 1987).

Table M-1. Preparation of the Experimental, Circumneutral, Mid-Range, Low Ionic Strength pH/DIC Quality Control Check Sample (pH 7, DIC 0.7 ppm)

Temp (°C)	pH	DIC (mg/L)
10	6.91	0.734
15	6.93	0.715
20	6.97	0.685
25	7.00	0.665
30	7.03	0.643
35	7.08	0.640
40	7.11	0.618

a. Dilute 0.270 mL of the 1,000-ppm DIC stock QC solution to 1.000 L.
b. Sparge with 300 ppm CO_2 for 20 to 30 minutes. The exact pH and DIC values are given above
c. Store in sealed syringes at 4°C.

The theoretical pH values of these solutions are 7.00 and 5.67 at 25°C, and the theoretical DIC values are 0.665 mg/L and 0.148 mg/L at 25°C. These solutions were to be made weekly and held under refrigeration until used.

The procotol for the QCCS measurements is as follows.

Weekly:

1. Prepare all reagents for 4.00, 5.67, and 7.00 QC check solutions.
2. Draw 18 syringes each of the 5.67 and 7.00 solutions, seal with syringe valves, date and label 6 of the 5.67 pH solution syringes "0.148 ppm DIC," date and label the remaining 12 5.67 pH syringes "pH 5.67," date and label 6 of the 7.00 pH syringes "0.665 ppm DIC," date and label the remaining 12 7.00 pH syringes "pH 7.00.

Table M-2. Results from Analysis of Low Ionic Strength Quality Control Sample

Day	pH Theoretical	pH Measured	Δ	DIC (mg/L) Theoretical	DIC (mg/L) Measured	Δ(%)
1	7.09	6.97	-0.12	--	--	--
2	7.09	7.13	+0.04	0.634	0.604	-4.7
3	7.04	7.00	-0.04	--	--	--
6	7.08	7.03	-0.05	0.640	0.623	-2.7
7	7.06	6.99	-0.07	0.641	0.669	+4.4
8	7.00	7.07	+0.07	--	--	--
8	7.01	7.03	+0.02	--	--	--
8	7.01	7.23	+0.22[a]	0.658	0.571	-13[a]
9	7.02	7.01	-0.01	0.646	0.655	+1.4
10	6.99	7.01	+0.02	0.671	0.657	-2.1
10	7.00	7.06	+0.06	0.665	0.654	-1.7
13	7.03	6.76	-0.27[b]	0.643	0.625	-2.8
13	7.03	6.72	-0.31[b]	0.643	0.633	-1.5
14	7.02	7.05	+0.03	0.651	0.661	+1.5
15	7.01	6.94	-0.07	0.657	0.630	-4.1
15	7.01	6.91	-0.10	0.653	0.637	-2.4
15	7.02	7.07	+0.05	--	--	--
15	7.02	7.12	+0.10	--	--	--
15	7.02	7.09	+0.07	--	--	--
15	7.02	7.12	+0.10	--	--	--
15	7.02	6.96	-0.06	--	--	--

[a] Possible incomplete equilibration (DIC low, pH high) or preparation error.
[b] Possible pH error (possibly due to calibration; pH low, DIC acceptable).

3. Store all syringes in the refrigerator and use them in determinations throughout the daily sample analysis.

Daily (by batch):

1. Calibrate the pH meter with the pH 7.00 buffer and the pH 4.00 buffer.

2. Analyze the 7.00, 5.67, and 4.00 pH QCCS solutions, in that order. NOTE: If initial QCCS values are out of range for any solutions, reanalyze the solutions. If the measurement is still out of range, recalibrate the instrument and reanalyze the QCCS solutions.

3. Analyze 5 samples in the batch.

4. Analyze the 4.00 pH QCCS.

5. Repeat steps 3 and 4 until all samples have been analyzed.

6. Analyze the final 4.00 pH QCCS.

7. Analyze the 7.00 and 5.6 pH QCCS in that order.

8. Enter the 4.00 pH QCCS value on the batch form. Enter the 5.67 and 7.00 values in the logbook only.

If at any time the value of a 4.00 pH QCCS solution falls outside the acceptance criteria of ±0.10 pH unit, analyze a fresh QCCS solution. If the QCCS value still fails to meet the criteria, recalibrate the instrument and reanalyze the affected samples, available volume permitting. If the value of the 5.67 or the 7.00 pH QCCS solutions falls outside the acceptance window, analyze a fresh sample of the QCCS solution. If the value still falls outside criteria, enter a note in the pH logbook documenting the circumstances, including the DIC values associated with the variant QCCS solutions. Because the 7.00 and 5.67 pH QCCS checks are only conducted before the first sample in the batch is analyzed and after the last sample in the batch is analyzed, do not reanalyze samples based solely on failure to meet acceptance criteria for one of these solutions.

Reanalysis of an entire batch of samples would be prohibitively time consuming, because pH is usually the slowest procedure conducted in the field laboratory.

The protocol for analysis of DIC was to be identical to that described in the methods manual (Hillman et al., 1986; Kerfoot and Faber, 1987), with the exception that two new QCCS analyses were to be added before the first sample in the batch was analyzed and

after the last sample in the batch was analyzed. The protocol for DIC analysis is as follows.

Weekly:

1. Prepare DIC stock solutions.
2. Prepare 7.00 and 5.67 pH QCCS solutions, as described above.

Daily:

1. Prepare calibration and QCCS solutions as specified in the methods manual.
2. Calibrate the DIC at 10.00 mg/L.
3. Using 0.148 mg/L DIC and 0.665 mg/L DIC syringes from the refrigerator, analyze samples of the DIC QCCS solutions.
4. Check linear dynamic range of the calibration curve by analyzing a 20.00-ppm DIC calibration solution.
5. Analyze a 2.00-mg/L DIC QCCS.

   NOTE: If any of the QCCS or linearity check concentrations vary from the theoretical value by more than 10%, reanalyze the solution. If the measurement still fails to meet the "QC criteria, recalibrate the instrument.

6. Analyze a calibration blank sample.
7. Analyze batch samples and QC check samples as described in the field laboratory methods manual (Morris F. A., D. V. Peck, D. C. Hillman, K. J. Cabble, S. L. Pierett, and W. L. Kinney, 1985. *National Surface Water Survey, Western Lake Survey - Phase I, Field Training and Operations Manual* [internal report], U.S. Environmental Monitoring Systems Laboratory, Las Vegas, Nevada).
8. Analyze a 2.00-mg/L QCCS.
9. Analyze a 0.665-mg/L DIC QCCS.
10. Analyze a 0.148-mg/L DIC QCCS.

If at any time any QCCS value differs from the expected value for that QCCS solution by more than 10 percent, a fresh QCCS sample will be analyzed. If the QC check is still outside the acceptance criteria for a 2.00 QCCS, the samples associated with the acceptance QCCS measurements will be reanalyzed. If the QC check sample for a 0.148 or 0.665 mg/L QC solution is still outside acceptance criteria, the values will be noted in the logbook, along with the pH values based solely on failure to meet criteria for these two solutions.

Glossary

Abbreviations

ANOVA	analysis of variance
AQUARIUS	Aquatics Quality Assurance Review, Interactive Users' System
ASTM	American Society for Testing and Materials
%CD	percent conductance balance difference
CLP	Contract Laboratory Program
DBMS	data base management system
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
DQO	data quality objective
ELS-I	Eastern Lake Survey - Phase I
EMSI	Environmental Monitoring and Services, Inc.
EMSL-LV	U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada
EPA	U.S. Environmental Protection Agency
ERL-C	U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, Oregon
Forest Service	U.S. Department of Agriculture, Forest Service
%IBD	percent ion balance difference
ICPAES	inductively coupled plasma atomic emission spectroscopy
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
NSS	National Stream Survey
NSWS	National Surface Water Survey
ORNL	Oak Ridge National Laboratory
QA	quality assurance
QC	quality control
QCCS	quality control check sample
RMS	root-mean-square
%RSD	percent relative standard deviation
SAI	Systems Applications, Inc.
SAS	Statistical Analysis System
SMO	Sample Management Office
SOW	Statement of Work
USGS	U.S. Geological Survey
WLS-I	Western Lake Survey - Phase I

Definitions

Absolute Bias — The difference between a measured value and the true value. (See Accuracy.)

Acceptance Criteria — The range in which the analytical measurement of a quality assurance or quality control sample is expected to be; measurements outside that range (also referred to as control limits) are considered suspect.

Accuracy — The closeness of a measured value to the true value of an analyte. For this report, accuracy is calculated as:

$$\frac{\bar{X} - T}{T} 100$$

where:

$\bar{X}$ = the mean of all measured values, T = the true value.

Acid Neutralizing Capacity — Total acid-combining capacity of a water sample determined by titration with a strong acid. Acid neutralizing capacity includes alkalinity (carbonate species) as well as other basic species (e.g., borates, dissociated organic acids, alumino-hydroxy complexes.

Air Equilibration — The process of bringing a sample aliquot to equilibrium with standard air (300 ppm CO_2) before analysis; used with some pH and dissolved inorganic carbon measurements.

Aliquot — Fraction of a sample prepared for the analysis of particular constituents, sent in a separate container to the analytical laboratory.

Alkalinity Class — One of three categories to which each lake in the survey was designated before sampling activities began. The alkalinity class estimated the acid neutralizing capacity of the lake. The three classes are < 100 µeq/L, 100 µeq/L < 200 µeq/L, and 200 µeq/L ≤ 400 µeq/L.

Among-Batch Precision — The estimate of precision that includes effects of different laboratories and day-to-day difference within a single laboratory, calculated from field audit sample data (as percent relative standard deviation).

Analyte — A chemical species that is measured in a water sample.

Analytical Laboratory

In this report, a laboratory under contract with the U.S. Environmental Protection Agency to analyze water samples shipped from the field laboratories.

Analytical Laboratory Duplicates

Aliquots of a sample that is split in the analytical laboratory. The aliquots are analyzed in the same batch.

Anion

A negatively charged ion.

Anion-Cation Balance

In an electrically neutral solution such as water, the total charge of positive ions (cations) equals the total charge of negative ions (anions). In this report, anion-cation balance is expressed as percent ion balance difference (% IBD) and is calculated as follows:

$$\frac{\Sigma\, anions - \Sigma\, cations + ANC}{\Sigma\, anions - \Sigma\, cations + ANC + 2[H^+]} 100$$

where:

Σ anions = $[Cl^-] + [F^-] + [NO_3^-] + [SO_4^{2-}]$

Σ cations = $[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + NH_4^+]$

ANC $\simeq$ Alkalinity (the ANC value is included in the calculation to account for the presence of unmeasured ions such as organic ions)

$[H^+] = (10^{-pH}) \times 10^6$ µeq/L

Anion Deficit

The concentration (in microequivalents per liter) of measured anions less the measured cations.

ASTM Type I Reagent-Grade Water

Deionized water (which meets American Society for Testing and Materials [ASTM] specifications for Type I reagent-grade water) that has a measured conductance of less than 1 µS/cm at 25°C. This water is used in the preparation of blank samples and reagents.

Audit Sample

A standardized water sample submitted to an analytical laboratory for the purpose of checking overall performance in sample analysis. Natural audit samples were lake water; synthetic audit samples were prepared by diluting concentrates of known chemical composition in ASTM Type I reagent-grade water.

Base Cation

A nonprotolytic cation that does not affect acid neutralizing capacity; usually calcium or magnesium.

Batch

A group of samples processed and analyzed together. A field batch of samples is defined as all samples (including quality assurance and quality control samples) processed at one field laboratory in one day. A laboratory batch is defined as all samples processed and analyzed at one analytical laboratory, associated with one set of laboratory quality control samples.

Batch ID

The numeric identifier for each batch.

Bias

The systematic difference between values or sets of values.

Blank Sample	A sample of ASTM Type I reagent-grade water analyzed as a quality assurance or quality control sample in WLS-I. (See calibration, reagent, trailer, and field blanks.)
Calculated Conductance	The sum (as µS/cm) of the theoretical specific conductances of all measured ions in a sample.
Calibration Blank	A solution used in standardizing or checking the calibration of analytical instruments; also used to determine instrument detection limits.
Calibration Curve	The linear regression of the analytical instrument response to a set of calibration standards (varying in concentrations) from which the linear dynamic range is determined.
Calibration (Lake) Study	Study conducted during WLS-I to determine whether or not the methods of sample collection (helicopter crew versus ground crew) affected the chemistry of the water samples; samples collected during this study were also used to evaluate analytical laboratory bias.
Carryover	An artifact of the analyte carried from a sample of high concentration to a subsequent sample or samples as a result of incomplete rinsing of an instrument or apparatus.
Cation	A positively charged ion.
Circumneutral	Close to neutrality in pH (near pH 7).
Closed System	Method of measurement in which a water sample is collected and analyzed for pH and dissolved inorganic carbon without exposure to the atmosphere. These samples were collected in syringes directly from the Van Dorn sampling apparatus and were analyzed in the field laboratory.
Comparability	A measure of data quality that allows the similarity within and among data sets to be established confidently.
Completeness	A measure of data quality that is the quantity of acceptable data actually collected relative to the total quantity that was attempted to be collected.
Component (of a system)	For this report, any of the sets of procedures used to get a sample from the lake to analysis. Major components include sample collection, sample processing, and sample analysis. Other components include sample transport, sample shipment, and data reporting. Together, these components are the system.
Conductance	A measure of the electrical conductance (the reciprocal of the electrical resistance) or total ionic strength of a water sample expressed as µS/cm at 25°C.
Conductance Balance	A comparison of the measured conductance of a water sample (in µS/cm) to the equivalent conductances (in µS/cm) of each ion measured in that water sample at infinite dilution. In this report, conductance balance is expressed as percent conductance difference (%CD) and is calculated as follows: $$\frac{calculated\ conductance - measured\ conductance}{measured\ conductance} 100$$ The ions used to calculate conductance are Ca^{2+}, Cl^-, CO_3^{2-}, H^+, HCO_3^-, K^+, Mg^{2+}, Na^+, NO_3^-, OH^-, and SO_4^{2-}.
Confidence Limit (95%)	A value that, in association with statistics, has a 95 percent chance of being above the true value of the population of interest.

Cubitainer	A 3.8-L container made of semirigid polyethylene used to transport field samples (routine, duplicate, blank) from the lake site to the field laboratory.
Data Base	All computerized results of the survey, which include the raw, verified, validated, and final data sets as well as back-up and historical data sets.
Data Base Audit	An accounting of the data and of the data changes in the data base; includes changes made within a data set and among all data sets.
Data Package	A report, generated by an analytical laboratory for each batch of samples analyzed, that includes analytical results, acid neutralizing capacity titration data, ion chromatography specifications, analysis dates, calibration and reagent blank data, quality control check sample results, matrix spike recovery results, and analytical laboratory duplicate results, and standard addition results.
Data Qualifier	Annotation applied to a field or analytical measurement related to possible effects of the quality of the datum. (See flags and tags).
Data Quality Objectives	Accuracy, detectability, and precision limits established before a sampling effort. Also includes comparability, completeness, and representativeness.
Data Set 1	Set of files containing raw data.
Data Set 2	Set of files containing verified data.
Data Set 3	Set of files containing validated data.
Data Set 4	Set of files containing final, enhanced lake data: missing values or errors in the validated data set were replaced by substitution values; duplicate values were averaged; negative values (except for acid neutralizing capacity) were set equal to zero.
Detectability	The capacity of an instrument or method to determine a measured value for an analyte above background levels.
Detection Limit Quality Control Check Sample	A quality control check sample with a theoretical concentration designed to check instrument calibration at the low end of the linear dynamic range.
Dilute Lake	For this report, a lake with a conductance of less than 10 µS/cm.
Dissolved Inorganic Carbon	A measure of the dissolved carbon dioxide, carbonic acid, bicarbonate and carbonate anions that constitute the major part of acid neutralizing capacity in a lake.
Dissolved Organic Carbon	The organic fraction of carbon in a water sample that is dissolved or unfilterable (for this report, 0.45-µm pore size).
Equivalent	Unit of ionic charge; the quantity of a substance that either gains or loses one mole of protons or electrons.
Exception	An analytical result that does not meet the expected quality assurance or quality control criteria for which a data flag is generated.
Exception Program	A computer program in AQUARIUS that identifies or flags analytical results classified as exceptions.

Extractable Aluminum	Operationally defined aluminum fraction that is extracted by the procedure used in WLS-I; this measurement is intended to provide an indication of the concentration of the aluminum species that may be available in a form toxic to fish.
Field Audit Sample	A standardized water sample submitted to field laboratories to check overall performance in sample analysis by field laboratories and by analytical laboratories. Natural field audit samples were lake water; synthetic field audit samples were prepared by diluting concentrates of known chemical composition into ASTM type I reagent-grade water.
Field Base	A location providing support for helicopters, sampling personnel, and field laboratories during field sampling operations.
Field Blank Sample	A sample of ASTM Type I reagent-grade water prepared at the field laboratory and transported to the lake site by the field sampling crews. At the lake site, the blank was processed through the Van Dorn sampling apparatus. These samples were analyzed at field laboratories (except for pH and DIC) and at analytical laboratories and were employed in the calculation of system decision and system detection limits and quantitation limits.
Field Duplicate Sample	Second sample of lake water collected by the sampling crew at the same location and depth at the lake site immediately after the routine sample, in accordance with standardized protocols.
Field Duplicate Pair	A routine lake water sample and a second sample (field duplicate sample) collected from the same lake, by the same sampling crew, during the same visit, and according to the same procedure.
Field Inter-laboratory Bias	The systematic difference in measurement of an analyte between two or more field laboratories.
Field Laboratory	Mobile laboratory (trailers) in which sample processing and measurement of selected variables were performed. One field laboratory was located at each field base.
Field Laboratory Among-Batch Precision	The estimate of day-to-day variability of the analytical measurements performed in the field laboratory for a particular audit sample lot, calculated as percent relative standard deviation (for turbidity, true color and closed-system DIC) and standard deviation (for closed-system pH).
Field Natural Audit Sample	See field audit sample.
Field Synthetic Audit Sample	See field audit sample.
Final Data Set	Data Set 4. (See definition for Data Set 4.)
Flag	Qualifier of a data point that did not meet established acceptance criteria that were assigned during the verification and validation procedures.
Gran Analysis	A mathematical procedure used to identify the equivalence point or points of the titration of a carbonate system and subsequently for acid and base neutralizing capacities of that system.
Ground Crew	A team of lake sampling personnel who gained access to the lake site on foot or with pack animals and who sampled the lake from an inflatable boat.
Ground Sample	A lake sample (routine or duplicate) or a field blank sample collected by the ground crew.

Helicopter Crew	A team of lake sampling personnel who gained access to and sampled the lake from a pontoon-equipped helicopter.
Helicopter Sample	A lake sample (routine, duplicate, or triplicate) or a field blank sample collected by the helicopter crew.
Holding Time	(1) In the field laboratory,the time elapsed between sample collection and sample preservation. (2) In the analytical laboratory, the elapsed time between sample processing in the field laboratory and final sample analysis or reanalysis.
Hydrolab	In situ water quality analytical instrument for the measurement of pH, conductance, and temperature.
Imprecision	The degree of irreproductibility or deviation of a measurement from the expected or average of a set of measurements for a particular analyte; the variation about the mean.
In Situ	Referring to measurements taken within the water column of a lake.
Initial DIC	A measurement of dissolved inorganic carbon made on an aliquot immediately before it is titrated for acid neutralizing capacity.
Instrumental Detection Limit	For each chemical variable, value calculated from laboratory calibration or reagent blank samples that indicates the minimum concentration reliably detectable by the instrument(s) used; calculated as three times the standard deviation of 10 nonconsecutive blank analyses (on the same calibration curve).
Interlaboratory Bias	Systematic differences in performance between laboratories estimated from analysis of the same type of samples.
Intralaboratory Bias	The degree of imprecision or uncertainty of measurement in the analysis of an analyte in the laboratory.
Intralaboratory Precision Goal	A precision goal based on the data quality objectives for the analysis of laboratory duplicate pairs within a single laboratory.
Ionic Strength	A measure of the interionic effect resulting from the electrical attraction and repulsion between different ions. In very dilute solutions, ions behave independently of each other, and the ionic strength can be recalculated from the measured concentrations of anions and cations present in the solution.
Laboratory Bias	The degree of uncertainty of the measurement of an analyte within a laboratory or between laboratories; see intralaboratory bias and interlaboratory bias.
Laboratory Blank Sample	A sample of ASTM Type I reagent-grade water prepared and analyzed by analytical laboratories. (See calibration blank, reagent blank.)
Laboratory Duplicate Sample	Sample aliquot that is split and prepared at the analytical laboratories and that is analyzed in a batch.
Lake ID	An identification code assigned to each lake in the survey which indicates subregion, alkalinity characteristics, and map coordinates.
Linear Dynamic Range	The range of analyte concentration for which the calibration curve is a straight line.
Loran-C	A system of long-range navigation that uses paired radio signals to determine the geographic position of a target lake.

Management Team	EPA personnel responsible for overseeing the WLS-I sampling and quality assurance design and the subsequent interpretation of lake data results.
Matrix	The physical and chemical composition of a sample being analyzed.
Matrix Spike	A quality control sample, analyzed at an analytical laboratory, that was prepared by adding a known concentration of analyte to a sample. Matrix spike samples were used to determine possible chemical interferences within a sample that might affect the analytical result.
Nitrate-Sulfate Split	A 125-mL fraction of the sample taken directly from the Van Dorn sampling apparatus, immediately preserved with $HgCl_2$, and subsequently analyzed at EMSL-LV for NO_3^- and SO_4^{2-}.
On-Site Evaluation	A formal on-site review of field sampling, field laboratory, or analytical laboratory activities to verify that standardized protocols are being followed.
Open System	A measurement of pH or dissolved inorganic carbon obtained from a sample that was exposed to the atmosphere during collection, processing, and preparation before measurement.
Outlier	Observation not typical of the population from which the sample is drawn.
P_{50}	The median value of blank sample analyses.
P_{95}	The 95th percentile of the blank sample analysis.
Percent Ion Balance Difference	A quality assurance procedure used to check that the sum of the anion equivalents equals the sum of the cation equivalents (see anion-cation balance).
Percent Recovery	A calculation of the matrix spike sample which indicates the effect of the sample matrix on the analytical measurement (also termed matrix interference).
Percent Relative Standard Deviation (% RSD)	The standard deviation divided by the mean, multiplied by 100, expressed as percent. Also known as the coefficient of variation.
pH	The negative logarithm of the hydrogen-ion activity. The pH scale runs from 1 (most acidic) to 14 (most alkaline); the difference of 1 pH unit indicates a 10-fold change in hydrogen-ion activity.
pH, acidity	A measurement of pH made in the analytical laboratory immediately before the BNC titration procedure and before the KCl spike has been added.
pH, alkalinity	A measurement of pH made in the analytical laboratory immediately before the ANC titration procedure and before the KCl spike has been added.
Platinum Cobalt Unit	Measure of the color of a water sample defined by a potassium hexachloroplatinate and cobalt chloride standard color series.
Population Estimate	A statistical estimate of the number of lakes (target lakes) with a particular characteristic (i.e., alkalinity class of a subregion) extrapolated from the number of lakes sampled (probability sample).
Practical Difference	Judgemental difference between a measurement result and an expected result (usually expressed in absolute terms as units of measure).

Precision	A measure of the capacity of a method to provide reproducible measurements of a particular analyte.
Primary Variables	Variables of foremost concern in the survey (pH, acid neutralizing capacity, extractable aluminum, sulfate, calcium, dissolved organic carbon).
Protolyte	That portion of a molecule that reacts with either H^+ or OH^- in solution.
Protolyte Analysis Program	An exception-generating computer program of AQUARIUS that evaluates in situ, field laboratory, and analytical laboratory measurements of pH, DIC, ANC, BNC, and DOC in light of known characteristics of carbonate equilibria.
Quality Assurance	Steps taken to ensure that a study is adequately planned and implemented to provide data of the highest quality, and that adequate information is provided to determine the quality of the data base resulting from the study.
Quality Assurance Sample	A sample (other than the routine lake sample) that is analyzed in the analytical laboratory and that has an origin and composition unknown to the analyst.
Quality Control	Steps taken during sample collection and analysis to ensure that the data quality meets the minimum standards established by the quality assurance plan.
Quality Control Check Sample	A sample of known concentration used to verify continued calibration of an instrment.
Quality Control Sample	Any sample used by analysts to check immediate instrument calibration or response; the measurement obtained from a quality control sample is expected to fall within specific acceptance criteria or control limits.
Quantitation Limit	For each chemical variable (except pH), a value (calculated from blank samples) that represents the lowest concentration that can be measured with reasonable precision; determined as 10 times the standard deviation of a type of blank sample.
Raw Data Set	The initial data set (Data Set 1) that has received a cursory review to confirm that data are provided in proper format and are complete and legible.
Reagent	A substance added to water (because of its chemical reactivity) to determine the concentration of a specific analyte.
Reagent Blank	A laboratory blank sample that contained all the reagents required to prepare a sample for analysis of silica and total aluminum.
Relative Bias	The expected difference between a measured value and the true value, expressed as a percentage of the true value.
Remote Base Site	Location serving as a base of operations for sampling crews working more than 150 miles from the field laboratory; samples collected by these crews had to be flown to the field laboratory daily.
Representativeness	A measure of data quality; the degree to which sample data accurately and precisely reflect the characteristics of a population.
Required Detection Limit	For each chemical variable, the highest instrument detection limit allowable in the analytical laboratory contract.

Root-mean-square	A summary statistic of the relative or absolute standard deviation (SD); a pooled standard deviation of the percent relative standard deviation (%RSD), calculated by the formula: $\sqrt{[\bar{X}^2_{\%RSD} + SD^2_{\%RSD}\ (n\text{-}1/n)]}$
Routine Sample	The first lake sample collected at a site in accordance with standardized protocols.
Sample ID	The numeric identifier given to each lake sample and quality assurance sample in each batch.
Sampling Method Bias	Systematic difference between analytical results of samples collected by helicopter access and samples collected by ground access.
SAS	Statistical Analysis System, Inc. (Cary, NC). A statistical data file manipulation package that has data management, statistical, and graphical analysis abilities. The WLS-I data base was developed and analyzed primarily using SAS software and is distributed in SAS format.
Secondary Variables	Chemical variables measured during WLS-I considered to be important in providing additional data in quantifying the chemical status of lakes, e.g., sodium, magnesium, potassium, nitrate, chloride, and total aluminum.
Sparging	A sample preparation procedure that involves bubbling a gas into an aliquot.
Spike	A known concentration of an analyte introduced into a sample or aliquot.
Split Sample	A subsample (aliquot) of a field batch sample that was sent for analysis to a laboratory other than an analytical laboratory; also a procedure of separating one aliquot (or sample) into two.
Standard Additions	An analytical procedure in which equal volumes of a sample are added to a series of known and varied concentrations of the analyte. This procedure is utilized only when there is a suspected matrix interference indicated with the matrix spike sample.
Standard Deviation	The square root of the variance of a given statistic, calculated by the equation: $\sqrt{\Sigma\,(X - \bar{X})^2 / (n - 1)}$
Statistical (significant) Difference	A high probability that two sets of measurements did not come from the same population of measurements.
Stratified Lake	In this report, a lake with a temperature difference greater than 4°C between the water layers at 1.5 m below the surface and 1.5 m above the lake bottom. If the temperature difference is also greater than 4°C between the water layers at 1.5 m below the surface and 60 percent of site depth, then the lake is strongly stratified; if not, it is weakly stratified.
Synoptic	Relating to or displaying conditions as they exist simultaneously over a broad area.
System Decision Limit	For each chemical variable except pH, a value that reliably indicates a concentration above background, estimated as the 95th percentile (P_{95}) of the field blank sample concentration.

System Detection Limit	For each chemical variable, except pH, a value indicating the highest concentration of analyte that could be present in a routine lake sample in which the analyte was not detected, estimated as $2(P_{95} - P_{50})$ where P_{95} is the 95th percentile and P_{50} is the 50th percentile (median) of the field blank sample concentration.
System Precision	Cumulative variability associated with sample collection, transport, processing, preservation, shipment, analysis, and data reporting. An estimate of data certainty for each analyte and the amount of variability associated with analyte concentration; the estimate is based on the statistical evaluation of field duplicate pairs.
Systematic Error	A consistent error introduced in the measuring process. Such error commonly results in biased estimations.
Systematic Random Sampling	The technique used in the survey to select the lakes to be sampled.
Tag	Code on a data point that is added at the time of collection or analysis to qualify the datum.
Titration Data	Individual data points from the Gran analysis of acid neutralizing capacity and base neutralizing capacity.
Trailer Blank	An ASTM Type I reagent-grade water sample prepared and processed at the field laboratory but analyzed at an analytical laboratory.
Trailer Duplicate	Split sample prepared and analyzed at the field laboratory.
Triplicate Lake Sample	The third sample of lake water collected by the helicopter crew at a lake immediately after the routine and duplicate samples are collected in accordance with standardized protocols; this third sample was used only as part of the calibration study.
True Color	The color of water that has been filtered or centrifuged to remove particles that may impart an apparent color; true color ranges from clear blue to blackish-brown.
Tuple	A SAS observation generated by an exception program or by a QA auditor. Used to record changes to existing data sets or to qualify a data point.
Turbidity	A measure of light scattering by suspended particles in an unfiltered water sample.
Van Dorn Sampler	A water collection apparatus with a volume of 6.2 L used to sample a water column in the lake.
Validation	Process by which data are evaluated for quality with reference to the intended data use; includes identification of outliers and evaluation of potential systematic error after data verification.
Verification	Process of ascertaining the quality of the data in accordance with the minimum standards established by the quality assurance plan.
Withheld Sample	One of the three samples collected from a lake by the helicopter crew during the calibration study. As part of holding time experiment, this sample was held in the dark at 4°C for a specified period prior to processing and preservation.