



Project Summary

National Surface Water Survey, Western Lake Survey (Phase I – Synoptic Chemistry) Quality Assurance Report

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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 operations and analytical laboratories, daily communications with survey participants, and verification and evaluation of data collected. Quality assurance and quality control samples (e.g., blanks, duplicates, audits) were used to identify, qualify, and quantify sources of sampling and analytical variability in terms of precision, accuracy, bias, and detectability. The relative importance of these sources of variation was assessed statistically.

The final data set represents data of high quality that can be used with confidence in calculating population estimates. Precision, accuracy, and detectability estimates generally met survey data quality objectives. With few exceptions, quality assurance samples adequately characterized the lake water samples for assessment of data quality. 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.

For future surveys, data quality objectives and sampling design should be refined 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.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Survey Design and History

The National Acid Precipitation Assessment Program (NAPAP) was initiated at the request of the Administrator of the U.S. Environmental Protection Agency (EPA) to evaluate the extent of the effects of acidic deposition on aquatic resources within the United States. The National Surface Water Survey (NSWS) program was incor-

porated as part of NAPAP. The National Lake Survey Phase I components of NSWS included the Eastern Lake Survey (ELS-I) and the Western Lake Survey (WLS-I).

The WLS-I portion of NSWS was a synoptic survey of 757 lakes in the West. WLS-I sampling was conducted in 1985 during fall overturn when chemical homogeneity within a lake was expected. The chemical and physical characteristics that were measured during WLS-I are listed in Table 1, along with the data quality objectives (DQOs) for the survey.

Related Documents

The WLS-I quality assurance report provides estimates of WLS-I data quality by reviewing the quality assurance (QA) and quality control (QC) activities and the analytical data. The final report for the survey (Landers et al., 1987) reviews 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) are the major supporting documents.

Data Quality Objectives

The statistical design, sampling and analytical methods, and QA activities for WLS-I were structured to meet the DQOs (measurement criteria) for reporting population estimates and for assessing the variability of sampling, field laboratory, and analytical laboratory performance.

The primary DQOs were measures of precision, accuracy, and detectability (see Table 1). Precision is the capacity of a method to provide reproducible measurements of an analyte. Accuracy is the closeness of a measurement to a true value. Detectability is the capacity to determine a measured value from background concentrations. Three other DQOs (not presented in Table 1), completeness, comparability, and representativeness, also were considered in the survey design and are discussed in the report.

Measurements taken at the lake sites, in the field laboratories, and in the analytical laboratories were compared directly or indirectly to the criteria established for the DQOs. WLS-I and ELS-I DQOs were identical except that the precision requirement for conductance was changed from 1 percent in ELS-I to 2 percent in WLS-I.

Sampling and Analytical Operations

Field sampling activities included locating and describing lake sites, collecting lake water samples, and collecting and recording physical and chemical lake data at the sampling sites. WLS-I sampling support facilities and mobile field laboratories were located in Carson City, Nevada; Wenatchee, Washington; Missoula and Bozeman, Montana; and Aspen, Colorado. Field laboratory operations included receiving samples, preparing sample batches, performing selected chemical and physical analyses, and preserving the integrity of samples until their analysis at the analytical laboratories. WLS-I analytical laboratories received sample shipments from the field laboratories, analyzed the samples, and generated a report on the analytical data. The analytical methods paralleled ELS-I methods to ensure data comparability.

Special Studies

Calibration Study

A random subset of 50 WLS-I wilderness-area lakes was sampled in a calibration study to compare the established sampling method (helicopter access) to the new method (ground access). Data derived from the chemical analyses conducted during the calibration study were used to perform calibration by linear regression. In general, analyses of the calibration study samples showed no significant effects of sampling protocol or sample holding time on analyte concentration. Possible effects of holding time, however, were not adequately tested for samples that had low analyte concentrations (i.e., extractable Al, NO_3^- , and NH_4^+ because concentrations for these samples were near the detection limits.

Nitrate-Sulfate Stability Study

In another special study, splits of samples were collected directly from the Van Dorn sampling apparatus. These samples, preserved with HgCl_2 at the lake site and analyzed for nitrate and sulfate at the EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV) were compared to samples preserved according to standard NSWS protocols and analyzed at the WLS-I analytical laboratories.

Statistical results of the preservation-method comparison indicate that there was little difference between samples

treated with HgCl_2 at the lake site and those preserved later at the field laboratory. Therefore, the difference in preservation procedures should not affect calculation of population estimates for nitrate and sulfate.

Operational Quality Assurance Program

WLS-I QA and QC activities were 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 program included selecting contract analytical laboratories; training field sampling and field laboratory personnel; collecting and analyzing QA and QC data in order to evaluate data quality; maintaining communications with management, sampling, and analytical personnel; and conducting on-site field and laboratory evaluations. Most of the WLS-I QA and QC procedures were used in ELS-I.

Data Base Quality Assurance

Data management and data review activities were coordinated by EMSL-LV, the EPA Environmental Research Laboratory in Corvallis, Oregon (ERL-C), and the Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. The data base management system (DBMS) incorporated the results from data collection, evaluation, verification, and validation. By means of the DBMS, all WLS-I data generated were assembled, stored, and edited. The DBMS also provided basic reports of the survey results, performed certain statistical analyses, and provided data security. An audit performed by an independent contractor revealed excellent data consistency for the data base.

The data verification process, through a rigorous protocol based on principles of aquatic chemistry, identified, corrected, or flagged raw data of questionable or unacceptable quality and identified data that might need to be eliminated during or after validation. The verification process could not identify all potential sources of error. The validation process, then, investigated errors in the chemical analyses not detected in verification and provided a review of the quality of nonchemical variables. After validation, a final data set was prepared that substituted statistically derived values for missing values; population estimates could then be calculated.

Table 1. Chemical and Physical Characteristics Measured, and Associated Data Quality Objectives for Detectability, Precision, and Accuracy, Western Lake Survey – Phase I

Mea- sure- ment Site ^a	Variable (dissolved ions and metals unless noted)	Analytical Method	Unit	Detectability		Intralaboratory (Laboratory Duplicate) Precision		Accuracy Maximum Absolute Bias
				Expected Range (for lake waters)	Required Detection Limit	Percent Relative Standard Deviation (%RSD), Upper Limit ^b		
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. > 0.01 mg/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%	
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 (phosphomolybdate)	mg/L	0.005 - 0.070	0.002	10 (if P conc. > 0.01 mg/L) 20 (if P conc. ≤ 0.01 mg/L)	20%	

Footnotes are at end of table.

(Continued)

Table 1. (Continued)

Mea- sure- ment Site ^a	Variable (dissolved ions and metals unless noted)	Analytical Method	Unit	Detectability		Intralaboratory (Laboratory Duplicate) Precision	Accuracy
				Expected Range (for lake waters)	Required Detection Limit	Percent Relative Standard Deviation (%RSD), Upper Limit ^b	Maximum Absolute Bias
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	0.05	5	10%
A	SO ₄ ²⁻	Ion chromatography	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)	nephelo- metric turbidity units (NTU)	2 - 15	2	10	10%

^aA = analytical laboratory, F = field laboratory, L = lake site.

^bThis limit was the %RSD at concentrations 10 times the required detection limit, unless otherwise noted.

^cAbsolute value of each blank had to be ≤ 10 µeq/L.

^dAtomic absorption spectroscopy used by Laboratory II; inductively coupled plasma atomic emission spectroscopy used by Laboratory I.

^eThe mean of six nonconsecutive blank measurements had to be ≤ 0.9 µS/cm.

^fAlthough 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.

Data Quality Results

QA samples were analyzed during WLS-I to estimate precision (using duplicate pair and audit samples), accuracy (using synthetic audit samples), detectability (using blank samples), and bias (using audit samples). These estimates help determine WLS-I data quality and the reliability of the lake water sample measurements, and, in turn, aid the data user in estimating subregional populations. Conclusions concerning precision, accuracy, and detectability for WLS-I sample data are summarized below. The QA report presents more detailed discussions of the results for these and the other DQOs.

Precision

- For most analytes, systems precision was acceptable. Poor precision for the remaining analytes was attributed to the low analyte concentration levels, to the circumneutrality of most WLS-I lake samples, or to methodological or analytical problems.
- Field laboratory precision was acceptable for analyses performed in all WLS-I field laboratories, and 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 (ionic strengths) and circumneutrality of lake water samples. DQOs must also be developed that differentiate between system precision, which includes field variability, 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. The WLS-I audit sample concentrations did not always bracket the concentrations of WLS-I lakes.

Accuracy

- On the basis of field synthetic audit sample data, accuracy could be estimated for 15 variables; of these, calcium and total aluminum estimates were outside the DQOs.
- 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. The use of different synthetic audit samples that represent the range of analyte concentrations in lake water samples could improve the estimation of accuracy. DQOs for future surveys should account for this relationship.
- It is difficult to ensure the reliability of the theoretical values for WLS-I synthetic audit sample analyte

concentrations. The use of applicable, certified audit samples can ensure the reliability of the theoretical values and of the estimates derived by using them. In addition, synthetic audit samples should be employed in order to evaluate accuracy for acid neutralizing capacity, base neutralizing capacity, dissolved inorganic carbon, and pH.

- Because WLS-I synthetic audit samples were processed in the field laboratory, they do not provide a means of isolating analytical laboratory accuracy. To provide such an estimate, reliable, certified audit samples should be sent directly to the analytical laboratory. Conversely, to estimate system accuracy, a synthetic audit sample must be processed through the sampling apparatus at the lake.

Detectability

- For most analytes, system back-ground contamination was acceptable. Significant exceptions were calcium, nitrate, and silica.
- Background contamination contributed by the field laboratories was negligible for most analytes; nitrate, silica, and sulfate were exceptions. In future surveys, trailer (field laboratory) blanks should be used regularly to allow estimation of the effect of the sample

processing component on lake sample measurements.

- Calibration blank and reagent blank analyses indicate that background contamination and instrumental signal variability contributed by the analytical laboratories 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; these DQOs should be developed for future surveys.
- Matrix spike sample results indicated that matrix effects produced minimal, if any, interference with routine sample analysis.

Lake Water Characteristics

Results and conclusions for the 28 chemical and physical characteristics analyzed during WLS-I are given in detail in the QA report. Conclusions concerning the six primary variables (Landers et al., 1987) are given below.

Acid Neutralizing Capacity

- All QA data estimates indicated that results for acid neutralizing capacity (ANC) 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 ANC.
- For ANC measurements, system precision met the DQOs over the range of routine sample concentrations. A method should be developed for determining a quantitation limit for assessing intralaboratory precision.
- The WLS-I QA program did not include reliable methods for calculating accuracy estimates of ANC. An applicable method should be developed for use in future surveys.

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 calcium (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 slight contamination should not affect population estimates.
- Precision estimates met the DQOs.

- Calibration study data indicated a relative analytical bias of 4 to 8 percent for the two analytical laboratories. Field audit sample data indicated a bias of 8 percent. Measurements from one analytical laboratory were consistently higher than those from the other. When assessing population estimates, knowing which analytical laboratory analyzed the samples from a given subregion may be important to the data user.
- The accuracy estimates calculated from the field synthetic audit sample data indicate that one analytical laboratory exhibited better accuracy than the other for audit samples that had a theoretical concentration of 0.19 mg/L. This accuracy (as absolute bias) is consistent with the relative bias results indicated by field natural audit sample data and calibration study data and may be correlated with an anion deficit described in Landers et al. (1987). However, because the accuracy estimate was based on only one theoretical concentration, confidence in calculating an absolute bias is restricted to 0.19 mg/L and should not be extrapolated across the entire range of routine sample concentrations.

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 sample analyses showed a strong relation between pooled precision and concentration. Precision for field duplicate pair mean concentrations above the quantitation limit met the DQO (except for two pairs). 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.

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. Of

210 field duplicate pairs, 2 had mean concentrations above 0.04 mg/L; 1 of 6 audit sample lots had a mean concentration above 0.01 mg/L.

- Accuracy could not be estimated because of the instability of the extractable Al species in the field synthetic audit sample solution. Alternative methods should be investigated for future survey efforts.

pH (closed system)

- QA data indicated that the field laboratory (closed system) 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 considered in future sampling designs.
- The trailer (field laboratory) duplicate precision for pH measured in the field laboratory (0.03 pH unit) met the DQO.
- When field duplicate pair measurements for all five field laboratories were pooled, 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 of the sample should be considered for use in future sampling efforts.
- The WLS-I QA program did not provide a mechanism for estimating accuracy of closed-system pH; such a method should be developed for use in future surveys.

Sulfate

- The QA data indicated that the routine lake sample data are of acceptable 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 data. Because these biases are relative, the data user should assess the results by the subregions for which each laboratory analyzed samples.

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