



Project Summary

Eastern Lake Survey - Phase II Quality Assurance Report

T. E. Mitchell-Hall, A. C. Neale, S. G. Paulsen, J. E. Pollard, and D. W. Sutton

The Eastern Lake Survey - Phase II (ELS-II) was designed primarily to assess seasonal variability in regional surface water chemistry. This report describes and evaluates the quality assurance program employed during the survey. The operations component included quality assurance and quality control procedures to ensure that all samples were collected and analyzed consistently and to estimate the accuracy and precision of the reported values with a known degree of confidence. The data management component established a means to store and track data; to identify and correct entry, reporting, and analytical errors; and to keep a record of such changes. The survey designed identified 24 physical and chemical characteristics of lake water for measurement. Data quality objectives for detectability, accuracy, precision, representativeness, completeness, and comparability for ELS-II were based on previous related surveys. During data verification and validation activities, several issues (concentrated primarily on the data from the chloride, nitrate, sulfate, and alkalinity analyses) prompted a Special Data Assessment. This process produced a list of recommendations and justifications for changes to be made to the official verified data base.

Overall, the quality assurance program was successful in identifying and resolving a number of data quality issues and assuring that the

data were of known and documented quality. For ELS-II as a whole, the data are of acceptable quality and every effort was made to correct any deficiencies. The accuracy and precision of data for four analytes of primary interest in acidic deposition research (acid neutralizing capacity, pH, nitrate, and sulfate) were close to or better than the goals set for intralaboratory performance. The representativeness, completeness, and comparability of the data meet the project objectives. Special attention should be given to the data quality objectives for surveys with multiple components, including consideration of specific objectives for each component.

This report is submitted in partial fulfillment of contract number 68-03-3249 by Lockheed Engineering and Sciences Company under the sponsorship of the U.S. Environmental Protection Agency. This report covers a field work period from March 25 to May 3, 1986, for the Spring Seasonal subsurvey; from July 23 to August 11, 1986, for the Summer Seasonal subsurvey; and from October 8 to November 14, 1986, for the Fall Seasonal subsurvey. Data verification was completed in September 1987. The Special Data Assessment began in February 1988 and ended in March 1989.

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 docu-

mented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This report describes and evaluates the quality assurance (QA) program employed during the Eastern Lake Survey - Phase II (ELS-II). This survey was designed primarily to assess seasonal variability in regional surface water chemistry. The ELS-II is one of a series of surveys conducted as part of the National Surface Water Survey (NSWS), a component of the National Acid Precipitation Assessment Program. The ELS-II QA program was designed to ensure that all samples were collected and analyzed consistently, to verify the report results, and to inform data users of the quality and potential limitations of the data base. In addition to summarizing the results of the QA program for ELS-II, this report includes an assessment of analytical data quality.

In ELS-II a subset of the lakes samples in Phase I of the Eastern Lake Survey was resampled to assess chemical variability and biological status. Lakes included in the ELS-II were restricted to those lakes considered susceptible to acidification. To assess this chemical variability, a subset of 150 lakes that had been sampled in the northeast region during Phase I was sampled during each of the ELS-II seasonal subsurveys. To produce comparable data, procedures for sample collection, sample analysis, and data reporting were based on the protocols established during Phase I.

The ELS-II, which took place in 1986, consisted of three major components—the Spring Seasonal, Summer Seasonal, and Fall Seasonal subsurveys. The assessment of analytical data quality discussed in this report applies to these three subsurveys as well as the data generated by the Fall Variability study which was conducted during the Fall Seasonal subsurvey.

Design and Operations of the Quality Assurance Program

The ELS-II quality assurance and quality control program was a multifaceted design to reduce uncertainty in the data quality. Monitoring techniques were incorporated at each stage of collecting, processing, and analyzing the lake samples. On-site evaluations also were performed to monitor the system. Data quality objectives were established to determine the relative quality of the data

in terms of representativeness, completeness, comparability, detectability, accuracy, and precision. A data base management system established a means to store and track data; to identify and correct entry, reporting, and analytical errors; and to keep a record of such changes. Table 1 lists the analytes selected for measurement and the location of the measurements.

Table 1. Chemical and Physical Variables Measured During the Eastern Lake Survey - Phase II

Field Site	
Conductivity ($\mu\text{S}/\text{cm}$)	
Depth (m)	
Dissolved oxygen (mg/L)	
pH, field (pH units)	
Temperature ($^{\circ}\text{C}$)	
Processing Laboratory	
Aluminum (mg/L)	
Total monomeric	
Nonexchangeable monomeric	
pH, closed system (pH units)	
Dissolved inorganic carbon, closed system (mg/L)	
True color (PCU)	
Turbidity (NTU)	
Analytical Laboratory	
Acid-neutralizing capacity ($\mu\text{eq}/\text{L}$)	
Aluminum, (mg/L)	
Total extractable	
Total	
Ammonium (mg/L)	
Base-neutralizing capacity ($\mu\text{eq}/\text{mL}$)	
Calcium (mg/L)	
Chloride	
Conductivity ($\mu\text{S}/\text{cm}$)	
Dissolved inorganic carbon (mg/L)	
Initial	
Equilibrated	
Dissolved organic carbon (mg/L)	
Fluoride, total dissolved (mg/L)	
Iron (mg/L)	
Magnesium (mg/L)	
Manganese (mg/L)	
Nitrate (mg/L)	
pH (pH units)	
Equilibrated	
Initial (acid titration for ANC)	
Initial (base titration for BNC)	
Phosphorus, total dissolved (mg/L)	
Potassium (mg/L)	
Silica (mg/L)	
Sodium (mg/L)	
Sulfate (mg/L)	

ELS-II sampling activities included field operations that were conducted from field base sites by helicopter and ground crews. They collected lake samples and associated data on the physical and chemical characteristics of the lake. After collection, the samples were sent to a centrally located processing laboratory in Las Vegas, NV. Processing laboratory activities included organizing the samples into batches; analyses for selected physical and chemical characteristics; splitting the samples into aliquots; and preserving, packing, and shipping the samples to analytical laboratories.

Two analytical laboratories participated in ELS-II. The QA program provided laboratories with explicit instructions, sample analysis protocol for ELS-II samples. Each laboratory was to use the same protocols to measure the 24 analytes of interest.

The QA program used a variety of field and quality control (QC) samples to monitor activities during the survey, assist in verification, and finally to assure data quality. The data quality objectives for ELS-II were based on those established for previous NSWS surveys. (Quality site system audits evaluated the field processing laboratory, and analytical laboratory facilities, equipment, and operations such as record keeping, data reporting, sample analysis, and procedures.

The data management system was designed to assemble, modify, and store data collected during the NSWS survey. An independent data management company provided these services for ELS-II. A number of data bases were created for ELS-II. The raw data base consists of information derived from the field forms, the processing laboratory form, and the analytical laboratory data package. The survey data were entered into the raw data base twice, the two sets of data were compared for inconsistencies, and any errors were corrected.

The QA staff at the U.S. Environmental Protection Agency (EPA) laboratory in Las Vegas verified the data by checking the internal consistency of sample results and by evaluating the QA and QC sample results. Much of the verification process was computerized. Changes to the raw data base that were necessary as a result of verification activities were sent to the data base administrator where the official verified data base was created. That data base was compared to the QA staff data base to ensure accuracy. Other data bases were created by the data base management administrator at the direction

tion of the EPA laboratory in Corvallis, OR, which was responsible for validating the data.

The modified verified data base is the product of a Special Data Assessment which occurred after verification and validation were completed. This assessment was conducted to address a number of issues identified during data verification and validation. The modified verified data base was created by copying the official verified data base and making any changes resulting from the Special Data Assessment.

The objective of data evaluation and verification was to identify and they correct or qualify suspect data as well as to maintain continuous control over the data acquisition process. The steps in this process included:

- Communicating with the field base coordinators and the laboratories.
- Reviewing field and processing laboratory data forms.
- Evaluating the preliminary QA data from each analytical laboratory.
- Checking on the completeness of each data package and on the consistency of sample data.
- Confirming or correcting suspect data.
- Requesting reanalysis of samples for which data remained suspect after confirmation or correction.
- Assigning data qualifier tags and flags to data when necessary.
- Entering the corrected values and data qualifiers into a copy of a copy of the raw data base to create the official verified data base.

Many concepts developed during ELS-I were implemented in ELS-II. In addition, further modifications based on the experience gained from previous NSWIS surveys were made to improve the ELS-II. These changes include: eliminating the requirement to analyze a matrix spike sample; implementing daily direct data transfers via electronic media between the analytical laboratories and the QA staff; conducting an Interlaboratory Bias Study; developing an improved system for use by the QA staff to edit the data; using boats for lake access; measuring dissolved oxygen at the site; establishing the processing laboratory in a central location; measuring dissolved and non-exchangeable monomeric aluminum at the processing laboratory; using two pH meters for one batch; submitting final data packages from the analytical laboratories electronically; and changing the precision requirement for conductivity

from 1% to 2% relative standard deviation.

Assessment of Operations

Field operations for ELS-II successfully completed collection and shipping of samples according to protocol. On-site evaluations monitored all field operations. The evaluations concluded that a checklist for field equipment should be used by field crews prior to departure from the base site and identified a need for more care in completing forms correctly and concisely. The on-site evaluations concluded that the field sampling personnel were adhering to QA and QC protocols and none of the findings had an adverse effect on data quality.

The processing laboratory successfully processed and analyzed the ELS-II samples. Samples were prepared for shipment to the analytical laboratories within the specified holding times in all cases. Two on-site evaluations of the processing laboratory indicated that processing laboratory operations were satisfactory and that laboratory personnel performed their duties well.

Standard EPA contract laboratory program procedures were used to secure the services of two analytical laboratories to perform sample analyses for the ELS-II. Laboratory 1 performed the sample analyses for the Spring Seasonal subsurvey. Laboratory 2 performed the sample analyses for the Fall Seasonal subsurvey. Both laboratories analyzed samples for the Summer Seasonal subsurvey. During the Summer Seasonal subsurvey, both laboratories analyzed samples designed to evaluate inter-laboratory bias.

An on-site evaluation of Laboratory 1 during the Spring Seasonal subsurvey resulted in several findings: sample receipt, storage, and labelling procedures were adequate; the ion chromatograph system was not fully automated with respect to controlling the pump and detector, requiring two analyses per sample i.e., one for nitrate and one for chloride and sulfate; the instrument detection limit for chloride exceeded the contract-required detection limit; the laboratory was well equipped to analyze metals, but experienced aluminum contamination in the total aluminum digestion; and laboratory personnel were preparing control charts for percent relative standard deviation (%RSD), not QCCS control charts as required by the contract. In summary, Laboratory 1 had some deficiencies at the time of the on-

site evaluation but was performing adequately.

The on-site evaluation of Laboratory 2 during the Summer Seasonal subsurvey resulted in several findings: sample receipt, storage, and labelling procedures were adequate; the laboratory was reporting a calculated pH value instead of the measured pH value; and analysts were not warming samples in a temperature-controlled water bath to 25°C before performing conductivity measurements as required by the contract. The evaluation team concluded that the overall performance of Laboratory 2 was acceptable and that the laboratory was operating within the contractual framework.

During data review and verification, sample reanalysis was only requested as a final corrective action when there was no other alternative for correcting data problems identified by the QA staff. Reanalyses were requested at two different times. A nominal number of reanalyses were requested in 1986 as a result of analytical problems detected during actual sample analyses. These analyses were performed either within or just outside of the maximum required holding time. The QA staff requested the majority of the reanalyses during data verification in 1987. The number of these reanalyses was kept to a minimum.

The review and verification process identified several significant problems at the analytical laboratories. Appropriate changes or notations were made in the verified data base. Some of these problems are: four batches of samples required reanalyses for dissolved organic carbon during the Spring Seasonal subsurvey; one Spring Seasonal batch of samples and one Fall Seasonal batch of samples required reanalyses for total aluminum; chloride, sulfate, and nitrate values for two batches were reported incorrectly by one laboratory because of an error in preparing standard solutions; one laboratory experienced difficulty in many instances in meeting the contract-required instrument detection limit for chloride; ammonium values were reported as nitrogen values by one laboratory during the Summer Seasonal subsurvey; one laboratory did not calculate anion and cation balances and conductivity balances as required by the contract; inconsistencies in the calculation of ANC and BNC by both analytical laboratories were resolved by the development of an improved calculation procedure; and one laboratory made errors in the sample log-in procedure.

Special Data Assessment

During data verification and validation activities, several issues (concentrated primarily on the data from the chloride, nitrate, sulfate, and alkalinity analyses) prompted a Special Data Assessment. This special assessment took place after the completion of the official verified data base and during the final phase of data validation. This assessment included an extensive examination of the raw data from both analytical laboratories for many parameters. Samples were targeted as outliers by various QA and QC sample programs, the verification programs, and the validation process. This method of identifying problem samples provided a mechanism for the QA auditor to determine if an analyte had multiple problems.

All outliers were prioritized by analyte. Chloride, sulfate, nitrate, and alkalinity were of the highest priority. If a sample was considered an outlier, then the entire batch was reviewed using the analytical raw data. This process produced a list of recommendations and justifications for changes to be made to the official verified data base. The data base created by these changes is referred to as the modified verified data base.

Assessment of Data Quality

The quality assurance program was successful in reducing to acceptable levels errors associated with the acquisition and reporting of data, as well as in identifying and correcting potential problems associated with data quality.

Completeness, Comparability, and Representativeness

The ELS-II data base was at least 90 percent complete based on the ratio of lake samples collected to the lake samples targeted for collection and on the percentage of acceptable data generated from those samples. The use and documentation of standardized sampling and analytical procedures allow for a quantitative evaluation of the data from ELS-I and ELS-II and other past and future studies. Standardized protocols helped to ensure that each of the samples collected was representative of the chemical condition existing in the lake at the time of sampling. From the quality assurance perspective, representativeness can be defined by how well the audit samples reflected the matrices and the concentration ranges of the routine samples. Natural audit samples were composed of characterized, stabilized

lake water from a dilute lake with moderate ANC and from a lake representative of an acidic system. Experimental synthetic audit samples were designed to represent the expected concentration ranges of the ELS-II routine samples and were prepared at five concentrations.

Detectability

Detectability can be addressed at two levels. The first is the detectability associated with a particular instrument or analytical method. These limits are generally determined by calibration or reagent blanks that are not blind to the analyst. The second level evaluates the system detectability, i.e., the lowest value of an analyte that can be detected when the entire process, from sample collection through laboratory analysis, is taken into consideration. Field blank samples consist of reagent grade distilled water that is passed through the sampling device and the entire processing and analytical procedure. Within each of these two levels, there are two specific limits which can be distinguished—the decision limit and the detection limit. The decision limit represents the lowest measured sample value that can be distinguished from a blank sample or background noise. The detection limit represents the lowest true or theoretical concentration above the decision limit that can be measured with a specified level of reliability. For most data users, the system decision limit will be of primary interest. This assessment concentrates on system-level detectability because it is of most interest for the purposes of routine data interpretation.

Evaluation of detectability for the ELS-II data is complicated by the apparent difference in the results of the two analytical laboratories. Laboratory 1 consistently had a larger system decision limit, as a result of either larger values, poorer precision, or both, for non-exchangeable monomeric aluminum, chloride, conductivity, initial and equilibrated dissolved inorganic carbon, potassium, magnesium, and sulfate. The importance of this apparent problem depends entirely on the relative levels of these analytes in the routine samples. Several of the analytes were present at relatively low levels in the lakes surveyed. In some cases this is not surprising because the lakes under consideration are, in general, dilute, oligotrophic systems that usually have low buffering capacity corresponding to low DIC values. Thus, it is not unexpected to

find a high percentage of samples below the decision limit. These results do not necessarily indicate poor data quality, rather reflect the systems being studied. These results do mean that analysis and interpretation of trends in these data require more attention to the issue of detectability, and differing levels of performance from participating laboratories can be a problem.

The analysis of concentrations found in audit samples with respect to system detection limits indicates that great care must be taken in creating and selecting audit samples. The quantity of DIC, chloride, nitrate, and total dissolved phosphorus present in the natural audit samples was low relative to the system detection limits. The lowest concentrations in these audit samples should be less than the expected system detection limits.

Accuracy and Precision

The ELS-II QA report presents a different approach to assessing accuracy and precision than that used in previous QA reports for the NSWS. In this report, summary statistics from QA data for each analyte are presented by seasonal appendices. The procedures and calculations that can be used to interpret the statistics are presented within the appendices. The data user is then provided with the tools for evaluation of the level of error associated with survey data without a reference to pre-set data quality objectives.

Based on the data from both audit and routine-duplicate pair samples, the ELS-II data base reflects high quality data for most analytes of interest. For example, ANC, pH, nitrate, and sulfate values are of high quality with accuracy and precision well below or near the DQC. Nitrate values were very close to the upper bounds of the DQOs for Spring. Seasonal subsurvey data and should be evaluated carefully by the data user to determine if the quality is adequate to answer the question being asked. Analytes that did not meet pre-established DQOs included Laboratory 1 chloride data and all analytical laboratory measurements of extractable aluminum, DIC, and DOC. Processing laboratory measurements for DIC should be used because those values meet the DQC. Extractable aluminum data are comparable in quality to that produced on other NSWS projects. High levels of total aluminum imprecision are a function of one or two outlying data points for seasonal subsurveys. These data should

be closely examined by the data user to determine if the associated variability and bias would limit the interpretability of the data.

Interlaboratory Bias

Because the ELS-II survey design used two laboratories over the course of the three seasonal subsurveys, the issue of interlaboratory bias is an especially critical one. Three sets of samples can be used to analyze the QA and QC data for interlaboratory bias. The first set consists of the triplicate-routine samples taken during the summer subsurvey. Equal portions of these samples were sent to each analytical laboratory. The two kinds of natural audit samples make up the second and third sets. The results of the analyses indicate that the most clear instances of interlaboratory bias exist for measurements of conductivity, DIC-eq, DIC-initial, and iron. There is somewhat weaker evidence to indicate potential problems with interlaboratory bias for ANC, calcium, chloride, total fluoride, potassium, pH-eq, and turbidity. There are other instances of interlaboratory bias which appear to be supported by either the split analyses or the natural audit sample data, but not both. The scientific implications of the biases which are indicated depend almost entirely on the magnitude of differences which one is trying to detect between the seasonal data.

Other Methods of Assessing Data Quality

Three checks of overall sample data quality are provided by comparison of measured ANC values and calculated carbonate alkalinity, comparison of the total ionic charge of anions and cations, and comparison of measured and calculated specific conductance values. Comparison of measured ANC values to calculated carbonate alkalinity values

provides an indication of the reliability of pH, DIC, and ANC measurements and an indication of the presence of unmeasured noncarbonate protolytes. The anion and cation balance provides an estimate of the internal consistency of the sample composition. Comparison of the measured and calculated values for specific conductivity values provides an additional check on analytical errors in the measurements or on the presence of unmeasured ionic species.

Figures in the report show plots of measured ANC versus calculated alkalinity. These plots show that ANC results measured by Laboratory 1 (Spring Seasonal Subsurvey) may be slightly lower than those measured by Laboratory 2 (Fall Seasonal subsurvey). The plots also show that the DIC-initial measurements performed by Laboratory 1 have a high bias. The DIC data from the processing laboratory would provide a better estimate of the DIC content of the sample.

Both the plots of the sum of anions versus the sum of cations and of the measured versus calculated conductivities illustrate the problems related to chloride analyses made at Laboratory 1. When only chloride values of less than 7.0 mg/L are included in the plots, almost all the data points fall in close proximity to the 1:1 line.

Based on internal consistency checks, the results of ELS-I and the ELS-II Fall Seasonal subsurvey appear to be comparable. ELS-I and the Fall Seasonal subsurvey plots for measured ANC versus calculated carbonate alkalinity, sum of anions versus sum of cations, and measured versus calculated conductivity display similar patterns.

Conclusions and Recommendations

Overall, the QA program was successful in identifying and resolving a number of data quality issues. The program also

was effective in assuring that the data were of known and documented quality. The majority of the data are of acceptable quality and every effort was made to correct any deficiencies. The data for nineteen of the analytes indicate no interlaboratory bias, and the data for six analytes indicate only slight interlaboratory bias. The issue of detectability should be considered in the context of the routine sample values. Analyte values in low concentration ranges cannot be evaluated using the pre-established data quality objectives. The accuracy and precision of data for four analytes of primary interest in acidic deposition research (ANC, pH, nitrate, and sulfate) were close to or better than the goals set for intralaboratory performance. In a few cases, data interpretation may be limited by considerations of data quality in terms of precision, accuracy and detectability. The representativeness, completeness, and comparability of the data are adequate to meet the project objectives.

In future studies of this type, on-site evaluations at the analytical laboratories should be scheduled early in the process of sample analysis and at least two should be required. The addition of certain requirements to laboratory contracts would improve the QA program; and special attention should be given to the requirements for surveys with multiple components. Data quality objectives should be developed for both the total and analytical systems. Natural audit samples should be well characterized for use in a QA program.

T. E. Mitchell-Hall, A. C. Neale, J. E. Pollard, and D. W. Sutton are with Lockheed Engineering and Sciences Company, Las Vegas, NV 89119; S. G. Paulsen is with the University of Nevada, Las Vegas, NV 89119.

D. T. Heggem is the EPA Project Officer (see below).

The complete report, entitled "Eastern Lake Survey - Phase II Quality Assurance Report," (Order No. PB 89-224 919/AS; Cost: \$28.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

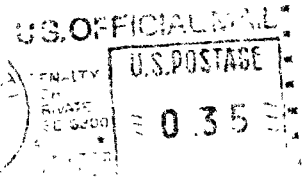
The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Las Vegas, NV 89193-3478

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use \$300

EPA/600/S4-89/029



000085833 PS
U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604