Research and Development

EPA/600/S4-88/010 Mar. 1988

**ŞFPA** 

# **Project Summary**

# Guide to the Application of Quality Assurance Data to Routine Survey Data Analysis

S. G. Paulsen, C. L. Chen, K. J. Stetzenbach, and M. J. Miah

The National Surface Water Survey at the National Acid Precipitation Assessment Program was designed to evaluate the present status of our nation's surface waters with regard to the problem of acidic precipitation. In this program, extensive effort has been directed toward assuring and quantifying the quality of the data produced during the surveys. This report provides assistance in utilizing the quality assurance data when interpreting the routine survey data.

The quality assurance reports for each of the surface water surveys, Eastern Lake Survey-Phase I, Western Lake Survey-Phase I, National Stream Survey—Phase I and Eastern Lake Survey-Phase II provide detailed information on the detectability, accuracy and precision of the routine lake data collected within each of these surveys. The data contained in the quality assurance reports pertaining to each of these issues can provide additional information which can enhance the analysis of the routine lake data and extend the applicability of the survey data beyond the original intent by providing future investigators the kind of detailed information about the quality of the data which is necessary when applying the data to studies for which it was not designed.

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

This document is designed to assist the end user of the National Surface Water Survey (NSWS) data with the interpretation and application of the quality assurance data within each survey. A quality assurance program is used not only to ensure that the data produced from these surveys meet some predetermined standards, but also measure its accuracy and precision so that inter and intra survey comparisons are possible. Most users of the survey data will be concerned with the accuracy and precision of any given measurement. The precision of a measurement cannot be changed, however, lack of accuracy resulting from an identifiable error may be correctable. This report is designed to help the user understand and apply the information available in the QA reports. It is hoped that the reader will be able to use the methods provided in this document to evaluate the bias in sample data and correct for it when possible, and apply precision data to population estimates and to temporal and spatial comparisons.

The information in this report will also provide the users of these QA data with ideas of what can or cannot be accomplished with QA data. We will try to identify components of error and their relative magnitude. All of the data (with the exception of chapter 5) used for this report comes from the quality assurance data collected during the Eastern Lake Survey Phase-1 (ELS-I) and Western Lake Survey Phase-1 (WLS-I) of the Aquatic Effects Research Program (AERP).

The QA/QC data collected in these surveys have three major functions:

- Ensure and identify the precision, accuracy, representativeness, completeness, and comparability of the survey data,
- 2. Improve the interpretation of the survey data, and
- Provide a means of assessing the risk of altering current QA/QC procedures and improving future sampling efforts.

The types of quality assurance and quality control samples collected, their intended function and general frequency of collection are presented in Table 1.

Currently the QA/QC data have been used primarily for the first function, identifying and ensuring data quality. This report is designed to provide guidance in using the QA/QC data in interpreting lake sample data and is directed primarily at the data users. A second report will follow in which the QA/QC data are used to optimize furture sampling efforts and will be directed toward program managers and planners.

The "Guide to the Application of Quality Assurance Data to Routine Survey Data Analysis" is divided into five chapters to better assist the users of the Aquatic Effects Research Program (AERP) quality assurance data. A summary of each chapter is listed below.

### Chapter Two—Detection Limits

Two major classifications of limits appear in the NSWS Quality Assurance reports: method limits and system limits. Method limits identify detection limits

Table 1. Quality Assurance and Quality Control Samples Used During Phase I Surveys of the NSWS

Sample Type	Description	Function	Frequency of Use
Quality Assurance			
Field Blank	Reagent-grade deionized water subjected to sample colleciton, processing and analysis	Used in estimating background due to sample colleciton, processing and analysis	One per sampling crew per day
Field Duplicate	Duplicate lake or stream sample	Used in estimating overall within- batch precision	One per field station per day
Field Audit	Synthetic sample or natural lake samples processed at field lab	Used in estimating overall among- batch precision and lab bias	As scheduled
Laboratory Audit	Synthetic sample or natural lake sample; prepared at support lab	Used in estimating analytical among-batch precision and lab bias	As scheduled
Quality Control			
Calibration Blank	Reagent-grade deionized water	Used in identifying signal drift and contamination of sample	One per lab batch
Reagent Blank	Reagent-grade deionized water plus reagents for total AI, SiO <sub>2</sub> analyses	Used in identifying contamination of reagents	One per lab batch
Quality Control Check Sample (QCCS)	Standard solution from source other than calibration standard	Used in determining accuracy and consistency of instrument calibration	Before the first measurement and as specified
Detection Limit (QCCS)	Standard solution at 2 to 3 times the required detection limit	Used in determining accuracy at lower end of linear dynamic range of measurement method	One per lab batch
Field Laboratory (Trailer) Duplicate	Split of lake or stream sample	Used in determining analytical within-batch precision of field lab measurements	One per field batch
Analytical Laboratory Duplicate	Split of sample aliquot	Used in determining analytical within-batch precision of analytical lab measurements	One per lab batch
Matrix Spike	Sample aliquot plus known quantity of analyte	Used in determining sample matrix effect on analytical lab measurement	One per lab batch

applicable to a method under laboratory conditions and represent the lowest level of analyte detectable. Instrumental detection limits are an example of method detection limits and are determined by using reagent or calibration blanks. They are primarily of interest to program and laboratory managers and are used to determine if the analytical laboratory is meeting required specifications.

System limits are those limits which apply to the complete measurement process from sample collection in the field through laboratory analysis. The system decision limit and the system detection limit are two examples of system level limits. Some confusion existed during the NSWS about the use of decision and detection limits. In general, the decision limit, as used during NSWS, applies to a conceptual point which allows one to distinguish individual sample measurements from the measurements found for blank samples. The confusion arose because this conceptual point has most frequently been referred to in the past by others simply as the limit of detection. However, the detection limit, as used during NSWS, is somewhat different and refers to the conceptual point which allows the user to determine the lowest true or theoretical concentration which can be distinguished with 95% confidence from blanks. It cannot be used to determine if measurements which have already been taken are different from background. It is recommended that in future reports the current usage of decision and detection limits be abandoned in favor of the more standard and accepted definitions.

#### Chapter Three—Inaccuracy

When repeated measurements are taken on a sample, the difference between the mean of the repeated measurements and the true (theoretical) concentration is defined as bias, and bias implies inaccuracy. In NSWS, synthetic audit samples are used to estimate inaccuracy. Synthetic audit samples are prepared in a laboratory by using different dilutions of standard materials, so the true (theoretical) concentrations are known. Inaccuracy can be estimated by substracting the theoretical concentration from the mean of the measurements on each sample. When consistent inaccuracy exists between laboratories it is considered interlaboratory bias. If this interlaboratory bias is consistent and can

be quantified then the routine data can be analyzed taking into account the bias.

### Chapter Four—Imprecision

A measurement from the analytical laboratory is the combination of the true value, systematic biases (determinate errors), and random errors (indeterminate errors). Repetitive measurements of the same sample will not normally result in the same answer because of measurement imprecision. Commonly used measures of imprecision are variance, coefficient of variation (relative standard deviation) and fourth spread (the difference of the upper and lower quartiles).

When the magnitude of the precision varies with concentration of analyte then some adjustments must be made in order to use the standard statistical techniques which assume constant variance. One approach is to stabilize the variance with data transformation techniques. The use of the quality assurance data in identifying suitable data transformations which tend to stabilize the variance is examined in this chapter.

Measurement precision consists of a variety of components. When evaluating the analytical results from a survey, these components of variance can provide some indication of steps along the processing and analytical procedure which are contributing the most to the variance. Efforts can be directed toward reducing or tightening these procedures to reduce the variance in future studies.

# Chapter Five—Comparison of Analyte Concentration

The QA/QC plan is a strategy to monitor laboratory performance and an attempt to guarantee the quality of the measurements. The ultimate purpose of the survey is to compare analyte concentrations from different regions or different times using the routine field samples. A preliminary nested model is proposed in this chapter to describe the field routine samples collected in ELS-I.

# Chapter Six—Comparison of Surveys

Four surveys were conducted during Phase I of the AERP (ELS-I, WLS-I, NSS-P, and NSS-I). This chapter presents the data on detectability, precision and accuracy from these surveys so that the data can be more easily examined and compared. The ideal situation is when the estimates of detectability, precision, and accuracy are the same across

surveys or similar enough so that the QA data can be pooled for all surveys. But if, for example, the decision limits differ significantly between surveys, then analysis and comparison of the routine lake data across surveys will be a more involved process. The data for all Phase I Surveys are presented for comparative purposes.

### References

Best, M. D., S. K. Drouse, L. W. Creelman, and D. J. Chaloud. 1986. 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.

Box, G. E. P., Hunter, W. G., and Hunter, J. S. 1978. Statistics for Experimenters.

Christian, Gary. 1986. Analytical Chemistry, p. 64. J. Wiley & Sons, New York, 4th ed.

Draper, N. R. and Smith, H. 1981. *Applied Regression Analysis*.

Drouse, 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. U. S. Environmental Protection Agency, Las Vegas, Nevada.

Hoaglin, D. C., F. Mosteller, and J. W. Tukey. 1983. *Understanding Robust and Exploratory Data Analysis*.

Hubaux, A. and G. Vox. 1970. Decision and detection limits for linear calibration curves. Anal. Chem. 42:849-855.

Keith, L. H., W. Crummett, J. Deegan, Jr., R. A. Libby, J. K. Taylor, and G. Wentler. 1983. Principles of environmental analysis. Anal. Chem. 55:2210-2218.

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.

Long, G. L. and J. D. Winefordner. 1983. Limit of detection: a closer look at the IUPAC definition. Anal. Chem. 55:712-724.

Miller, J. C. and J. N. Miller. 1984. Statistics for Analytical Chemistry. Ellis Horword, Ltd. Chicester, U.K. 202 pp. SAS Institute Inc. 1985. SAS Procedures Guide for Personal Computers, Version 6 Edition. Cary, NC: SAS Institute Inc. 373 pp.

Silverstein, M. E., M. L. Faber, S. K. Drouse, and T. E. Mitchell-Hall. 1987. National Surface Water Survey Western Lake Survey (Phase I—Synoptic Chemistry) Quality Assurance Report. U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

S. G. Paulsen, C. L. Chen, and K. J. Stetzenbach are with the University of Nevada, Las Vegas, NV 89154; M. J. Miah is with Lockheed Engineering and Management Services Company, Las Vegas, NV 89119.

Robert D. Schonbrod is the EPA Project Officer (see below).

The complete report, entitled "Guide to the Application of Quality Assurance Data to Routine Survey Data Analysis," (Order No. PB 88-166 863/AS; Cost: \$14.95, 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

P.O. Box 93478

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/S4-88/010

0000329 PS
USENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO





