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USGS Blind Sample Project—Monitoring and Evaluating Laboratory Analytical Quality

Branch of Quality Systems

U.S. Department of the Interior–U.S. Geological Survey

The U.S. Geological Survey (USGS) collects and disseminates information about the Nation's water resources. Surface- and ground-water samples are collected and sent to USGS laboratories for chemical analyses. The laboratories identify and quantify the constituents in the water samples. Random and systematic errors occur during sample handling, chemical analysis, and data processing. Although all errors cannot be eliminated from measurements, the magnitude of this uncertainty can be estimated and tracked over time. Since 1981, the USGS has operated an independent, external, quality-assurance project called the Blind Sample Project (BSP). The purpose of the BSP is to monitor and evaluate the quality of laboratory analytical results through the use of double-blind quality-control (QC) samples. The information provided by the BSP assists the laboratories in detecting and correcting problems in the analytical procedures. The information also can aid laboratory users in estimating the extent that laboratory errors contribute to the overall errors in their environmental data.

What is a "Double-Blind Sample"?

A "double-blind sample" is a QC sample submitted for analysis for which the identity of the sample as well as its concentration levels are unknown to the analyst. Double-blind QC samples containing selected inorganic and nutrient constituents at various levels of concentrations are prepared and disguised as routine environmental samples. The BSP submits these samples to the National Water Quality Laboratory (NWQL) in Arvada, Colorado, and Quality of Water Service Unit (QWSU) in Ocala, Florida. The NWQL provides analytical services for all USGS national programs and many local or regional projects conducted by the USGS. The QWSU provides analytical services for many USGS projects in the Southeastern United States.

Standard reference samples (Farrar and Long, 1997) are used to make the QC samples for the BSP. They are used diluted with deionized water, undiluted, and mixed in varying proportions with other standard reference samples. This sample-mixing procedure produces a large number of unique samples available for quality-assurance purposes. The standard reference samples are usually natural matrix samples collected from different sources such as snowmelt, streams, and ground water.

The BSP samples are made to appear as much like environmental samples as possible and are subjected to identical laboratory handling, processing, and analytical procedures. After the laboratories analyze the samples, BSP personnel compile and review the analytical results. The resulting data are stored in the USGS National Water Information System data base.

Analytical Bias and Variability

The laboratories are evaluated by how closely their analytical results approximate the most probable value of the blind QC samples. Most probable values are the median concentrations reported for each constituent in the round-robin evaluation of the standard reference sample. The assessment of whether an analytical result is acceptable is based on the number of standard deviations that the measured concentration differs from the most probable value. Analytical results that are within two standard deviations of the most probable value are considered acceptable.

Analytical errors fall into two major categories: bias and variability. Bias is systematic error that causes consistently positive or negative deviation in the results from the most probable value. Variability is random error that affects the ability to reproduce results. Repeated measurements of the BSP samples over time provide estimates of both systematic bias and random variability in the laboratory analytical procedures. The BSP uses a variety of graphical and statistical tools to evaluate laboratory analyses of the blind QC samples. These tools include control charts, relative standard deviation charts, boxplots of error distributions, Wilcoxon signed-rank test for bias, binomial-probability distribution test for variability, and statistical summaries.

Control charts are produced for each analytical method as a review of the laboratory performance. They are a graphical display of the analytical deviation from the most probable value with respect to time. Control charts show if analytical results are within the expected control limits. The BSP sets control limits at ±2 standard deviations of the most probable value. These charts can illustrate a systematic or sudden shift in bias or variability. The control chart (fig. 1) for whole water-recoverable iron analyses indicates a change from a positive bias in February 1996 to a negative bias in September 1996.

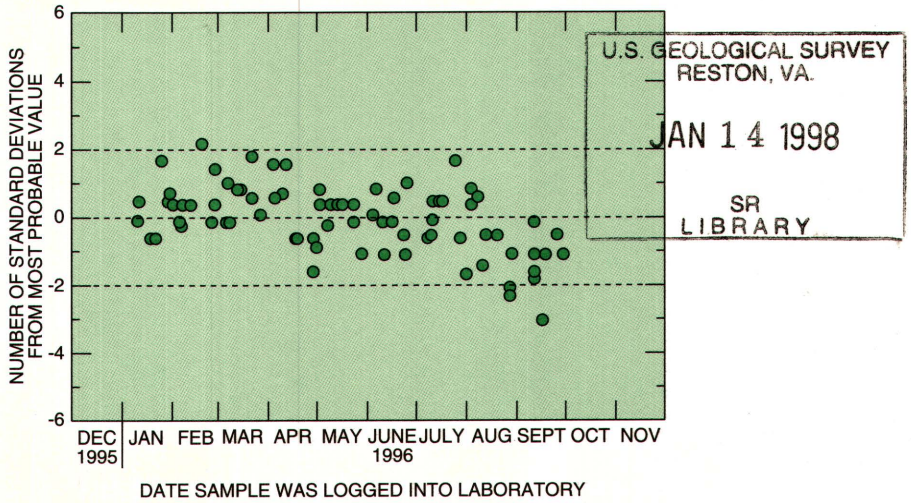

Figure 1. *Control chart for whole water-recoverable iron analyses of blind quality-control samples.*

Another graphical tool used by the BSP is the relative standard deviation chart, which displays analytical variability with respect to concentration. These charts allow a data reviewer to estimate analytical variability at a given concentration. The relative standard deviation chart (fig. 2) for dissolved zinc analyses is typical in showing that variability decreases with increasing concentrations.

Online Results Aid in Water-Quality Interpretation

The BSP maintains an interactive online computer program and data base, QADATA, for the retrieval and assessment of blind QC sample analytical results. Currently, the QADATA data-base system contains more than 160,000 QC analyses for inorganic and nutrient constituents, and physical-property measurements dating from October 1984 to the present (1997). New analytical data released from the laboratories are added weekly to the QADATA data base. Data retrievals from the QADATA system can be customized to document the laboratories' analytical bias and variability relative to the time period, analytical procedures, and concentration ranges of individual water-quality projects or programs. The QADATA system is available through the USGS computing environment. Instructions for accessing the QADATA system are available on the Internet at:

http://btdqs.usgs.gov/bsp/qadatanew.htm

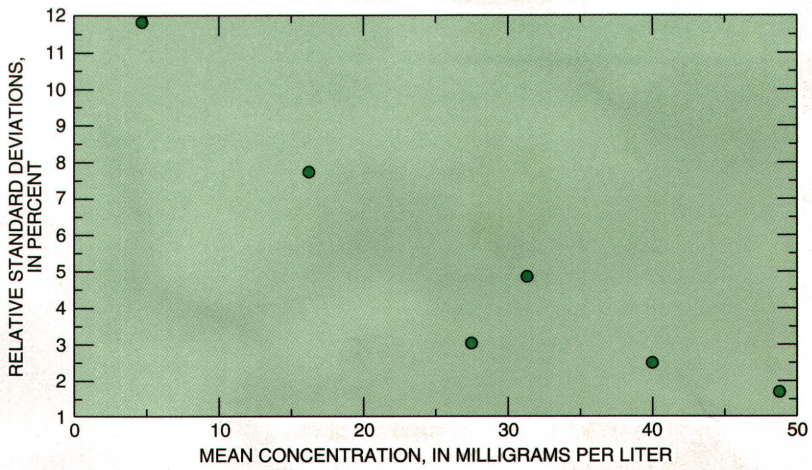

Figure 2. *Relative standard deviation chart for dissolved zinc analyses of blind quality-control samples.*

Reference Cited

Farrar, J.W., and Long, H.K., 1997, Report on the U.S. Geological Survey's evaluation program for standard reference samples distributed in September 1996—T–143 (trace constituents), T–145 (trace constituents), M–140 (major constituents), N–51 (nutrient constituents), N–52 (nutrient constituents), P–27 (low ionic strength constituents), and Hg–23 (mercury): U.S. Geological Survey Open-File Report 97–20, 145 p.

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Information on technical reports and data related to the Blind Sample Project can be obtained from:

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