Participation in Performance-Evaluation Studies by U.S. Geological Survey National Water Quality Laboratory

U.S. Department of the Interior

U.S. Geological Survey

INTRODUCTION

Performance-evaluation studies provide customers of the U.S. Geological Survey National Water Quality Laboratory (NWQL) with data needed to evaluate performance and to compare or select laboratories for analytical work. The NWQL participates in national and international performance-evaluation (PE) studies that consist of samples of water, sediment, and aquatic biological materials for the analysis of inorganic constituents, organic compounds, and radionuclides. These studies are administered by the following organizations:

- U.S. Environmental Protection Agency (USEPA)
- U.S. Geological Survey (USGS) Branch of Quality Systems (BQS)
- National Research Council of Canada
- National Oceanic and Atmospheric Administration (NOAA)

To carry out the analytical work, the NWQL employs about 150 chemists, biologists, technicians, and support personnel, plus some 30 contract employees, at a laboratory near Denver. The staff determines physical properties, major ions, nutrients, trace metals, pesticides, volatile organic compounds, industrial organic compounds, explosives, and radionuclides, in addition to identifying and enumerating species of algae and invertebrates.

This Fact Sheet provides a summary of PE study results from January 1993 through April 1997. It should be of particular interest to USGS customers and potential customers of the NWQL, water-quality specialists, cooperators, and agencies of the Federal Government. In addition, individual PE study results are routinely provided to USGS customers and are frequently posted to the NWQL Website at

wwwnwql.cr.usgs.gov/USGS.

Statistical techniques used to calculate acceptance limits vary among studies and are often changed throughout the course of a study. Since this Fact Sheet presents data from multiple PE studies over a period of several years, it would be impractical to define the acceptance limit calculations used for each study. Instead, the authors have summarized the NWQL results based on definitions provided by the study administrators.

INORGANIC ANALYSIS

Water Samples

The Laboratory participates in the USEPA water-supply (WS) and water-pollution (WP) performance-evaluation studies. These national studies are conducted twice annually. The WS study is used to maintain certification for the determination of drinking-water constituents. The WP study assesses laboratory performance for measuring concentrations of constituents greater than those found in WS studies.

The Laboratory analyzes about 30 constituents for the WS study and about 70 constituents for the WP study. As indicated in figure 1, the NWQL has had a high rate of successful determinations for the analysis of WS and WP samples according to predefined study acceptance criteria. This consistent performance is especially significant in light of changes in analytical techniques from 1993 to 1997. For the July 1996 and subsequent WS studies, the NWQL used analytical methods that meet the requirements of the USEPA's drinking-water regulations. Study dates accompanied by an asterisk indicate the

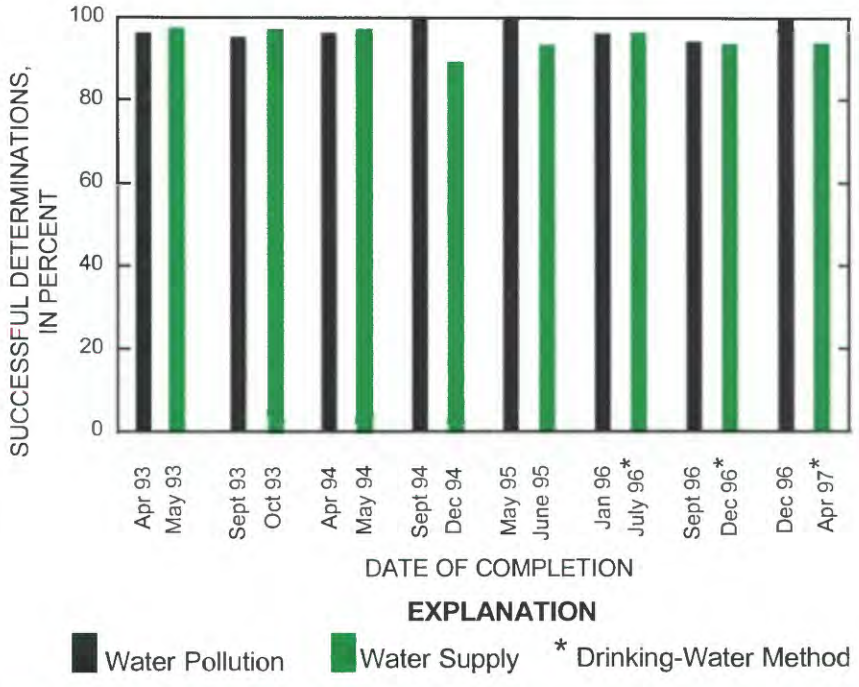


Figure 1. Results of National Water Quality Laboratory water-supply and water-pollution inorganic constituent performance-evaluation studies administered by U.S. Environmental Protection Agency from 1993 to 1997.

use of these analytical methods (fig. 1). In addition, the NWQL undergoes an in-depth on-site review every 3 years to maintain Drinking-Water Certification, although this review is not part of the PE studies.

BQS administers a national standard reference program to evaluate over 200 participating laboratories. The results of these evaluations are published by USGS (Long and Farrar, 1993, 1994a, 1994b, 1995a, 1995b, 1996, 1997a, 1997b). Participating laboratories are first evaluated for each constituent analyzed. The constituent rating scale is from 0 to 4, with 0 being poor and 4 excellent. This rating scale is related to the z-value, which indicates statistically how far away the reported value is from the sample mean. As shown in equation 1, the z-value is the difference of the expected concentration from the NWQL reported concentration relative to the standard deviation for the constituents in the study:

$$\text{z-value} = \frac{\text{NWQL reported concentration} - \text{expected concentration}}{\text{standard deviation for study constituents}} \quad (1)$$

Overall laboratory ratings are then calculated by averaging the individual constituent ratings. The NWQL has consistently received overall ratings of 3 and above and has analyzed a high percentage of the selected constituents from 1993 to 1997 (fig. 2).

The NWQL also participates in the National Water Research Institute study administered by the National Research Council of Canada. This study -- a combination of the former Federal Provincial Great Lakes Action Plan and the Long Range Transport of Atmospheric Pollutants studies -- is conducted twice a year. The focus of the National Water Research Institute study is the analysis of major ions, nutrients, total phosphorous, and trace elements in water. For the last four studies, which were administered in 1995 and 1996, the NWQL reported an average of 37 constituents per study. The NWQL has been rated as satisfactory ("quite acceptable") or above for 74 percent of the analyses. The remaining 26 percent showed either a slightly high or slightly low bias as defined by the Canadian study.

Biological Tissues

NWQL methods for determining inorganic constituents in biological tissue are evaluated by participation in the intercomparison study for trace metals. The study is administered annually by the National Research Council of Canada for NOAA. The participating laboratories analyze a certified reference material in addition to the unknown tissue sample and perform five replicate analyses of each material. From 1993 through 1996, 76 percent of the constituents analyzed by the NWQL have been within study acceptance limits. In general, for those constituents that have been outside acceptance limits, the recoveries have

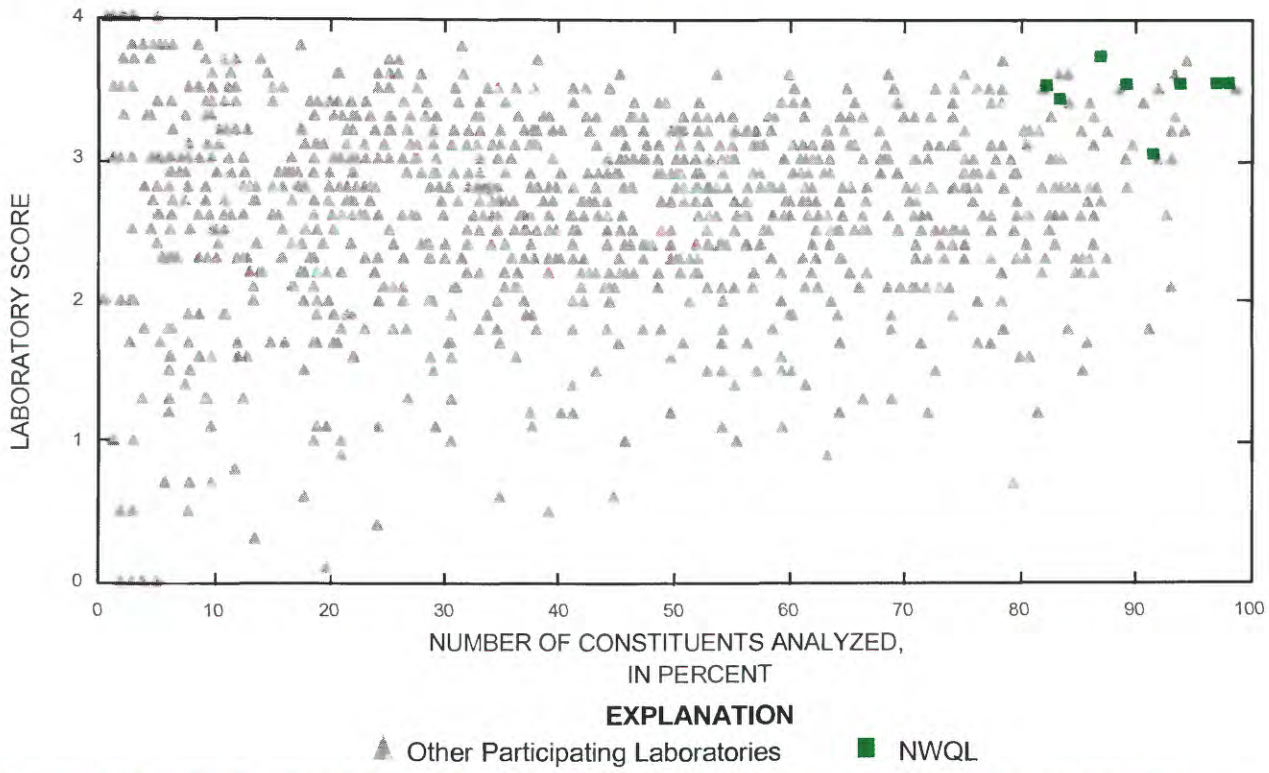


Figure 2. Results of National Water Quality Laboratory performance in relation to other participating laboratories in the inorganic sample-evaluation studies administered by the U.S. Geological Survey Branch of Quality Systems from 1993 to 1997.

been low. This apparent low bias might be due, in part, to the less rigorous digestion procedure developed and used by the NWQL (Hoffman, 1996). Recoveries for the NOAA studies from 1993 through 1996 are shown in figure 3. There are fewer PE studies to evaluate inorganic method performance for the analysis of biological tissues than there are available for other less complex sample types. For this reason, the NWQL routinely analyzes a certified reference material with each batch of environmental samples. Much of this information has been summarized and can be obtained by contacting the Chief, Quality Management Program, at the NWQL.

Sediment Samples

Sediment materials analyzed for inorganic constituents are sent to the Geologic Division laboratory, which participates in several national and international PE studies. Information may be obtained by contacting the Chief, Minerals Resource Program, Geologic Division, U.S. Geological Survey, at the Denver Federal Center.

ORGANIC ANALYSIS

Performance-evaluation studies for organic compounds in samples are more difficult to administer than those for inorganic constituents. Organic compounds may be degraded by many mechanisms, including heat, light, and microorganisms. Because many of the compounds are unstable, special measures must be taken to ensure that PE studies evaluate method performance and are not biased by natural compound degradation. These measures include chilling samples and protecting them from heat and light. Along with the high cost for organic analyses, these special measures make national PE studies expensive.

Water Samples

The NWQL participates in several nationally and internationally recognized programs, including the

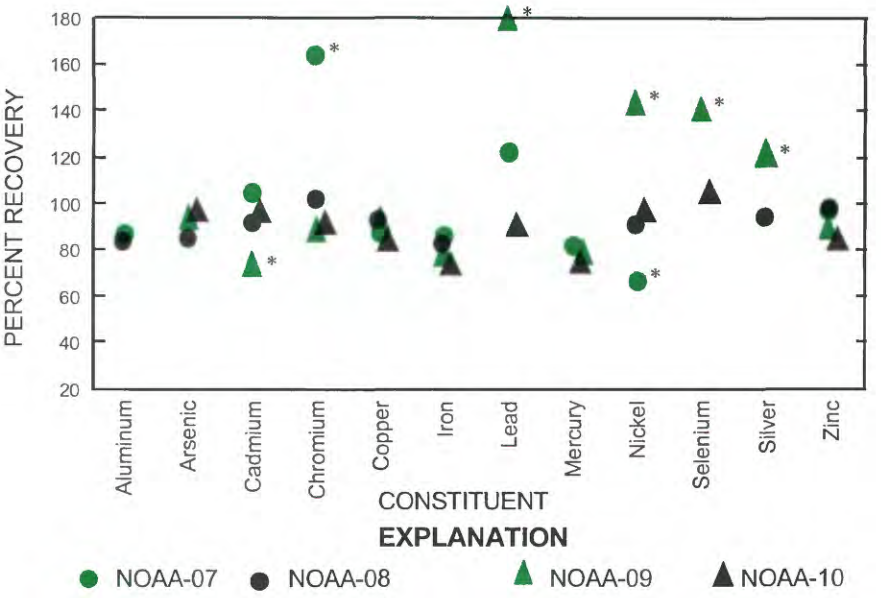


Figure 3. Results of National Water Quality Laboratory performance-evaluation studies for constituents in biological tissues from 1993 to 1996. The studies are administered by the National Research Council of Canada for the National Oceanic and Atmospheric Administration. Data points with an asterisk indicate that more than 25 percent of the participating laboratories had difficulty determining the constituent in that particular study. These problems are generally related to either low constituent concentrations or fine sediment particles within the tissue.

USEPA water-supply (WS) and water-pollution (WP) studies, which are administered biannually. The WS study allows the NWQL to maintain certification for the analysis of drinking-water compounds. Along with this evaluation, the NWQL must pass a rigorous laboratory review every 3 years. The WP study assesses laboratory performance for measuring high concentrations of organic compounds that might be found at a contaminated site.

Results of NWQL organic determinations for WS and WP studies from 1993 to 1997 are shown in figure 4. The

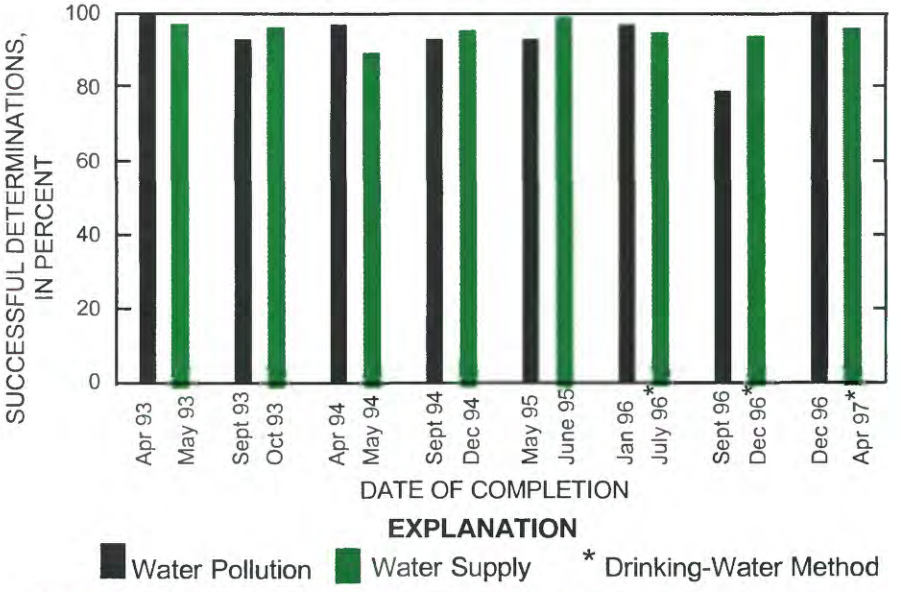


Figure 4. Results of National Water Quality Laboratory water-supply and water-pollution organic compound performance-evaluation studies administered by U.S. Environmental Protection Agency from 1993 to 1997.

NWQL analyzes an average of 60 compounds as part of each of these studies. The September 1996 data point (fig. 4) indicates an anomalous result because some analytical instruments were inoperable during the study. The percentage of successful determina-tions has been extremely high for these studies. Since July 1996, the NWQL has adopted USEPA's drinking-water analytical methods for WS studies. Study dates accompanied by an asterisk indicate results obtained by use of the drinking-water analytical methods (fig. 4).

The NWQL also analyzes samples submitted from the National Water Research Institute of Canada. This internationally recognized study is aimed at determining only one specific organic compound: dissolved organic carbon. The study is administered twice annually. In the last four studies, for samples submitted from 1995 through 1997, the NWQL consistently received ratings of satisfactory or above.

To supplement the limited availability of national PE studies, the NWQL has implemented an in-house blind-sample program to routinely evaluate the broad range of organic compounds. As part of this internal program, blind samples are submitted for about two-thirds of all water-matrix analytical methods performed by the NWQL Organic Chemistry Program. Sample submission constitutes about 3 percent of the environmental sample load. The blind-sample program is designed to collect bias and variability information across the calibration range for all organic methods and to provide this information to NWQL customers.

Results from this program are too numerous to display or discuss in this Fact Sheet. Blind-sample data summaries may be obtained by contacting the Chief, Quality Management Program, at the NWQL.

Sediment and Tissue Samples

Although primarily a water-analysis laboratory, the NWQL has developed expertise for the determination of organic compounds in sediment and tissue. Several methods that cover a variety of compound classes are available. The range includes methods for the determination of organo-chlorine and organophosphorous compounds, volatile and semivolatile compounds, and gross organic determinations, such as total carbon.

Quality assurance for these methods is a high priority at the NWQL. Both sediment and tissue methods are monitored in the NOAA Inter-comparison Evaluation for Organics in Biological Tissue and Marine Sediment study. Performance-evaluation samples for this study are distributed annually by the National Institute for Standards and Technology.

NWQL performance (z-value results) for the most recent NOAA studies for organochlorine compounds in marine sediment samples is shown in figure 5.

Control limits were not defined as part of these studies. Frequently, a control limit is set at three times the standard deviation of the expected value. If only normal random errors are present, then 99.7 percent of the values will fall within this limit (Friedman and Erdmann, 1982, p. 91). NWQL reported concentrations for these studies have all been less than 1.5 standard deviations from the mean, with the exception of hexachlorobenzene in the 1995 study, which appears anomalous when compared with other historical and on-line quality-control data.

In addition to the organochlorine compounds, the NWQL analyzed the marine sediment samples for polycyclic aromatic hydrocarbons (PAHs) in the 1994 and 1995 studies. The compounds analyzed as part of these studies consist of 23 PAHs of which the NWQL determined 17. The NWQL is within 3 standard deviations of the study mean 94 percent of the time. Only two compounds exceeded 3 standard deviations in the 1994 study.

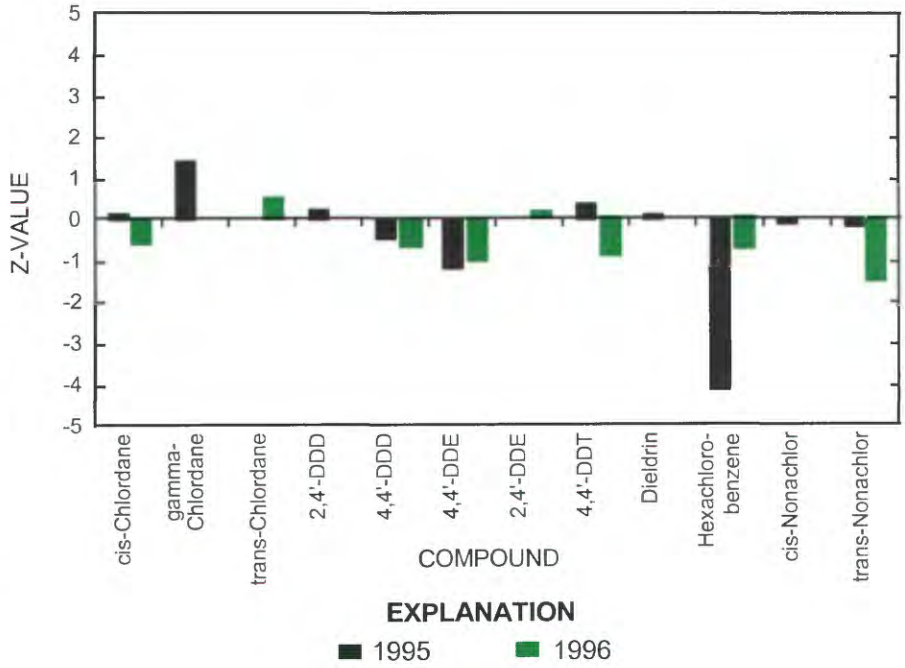
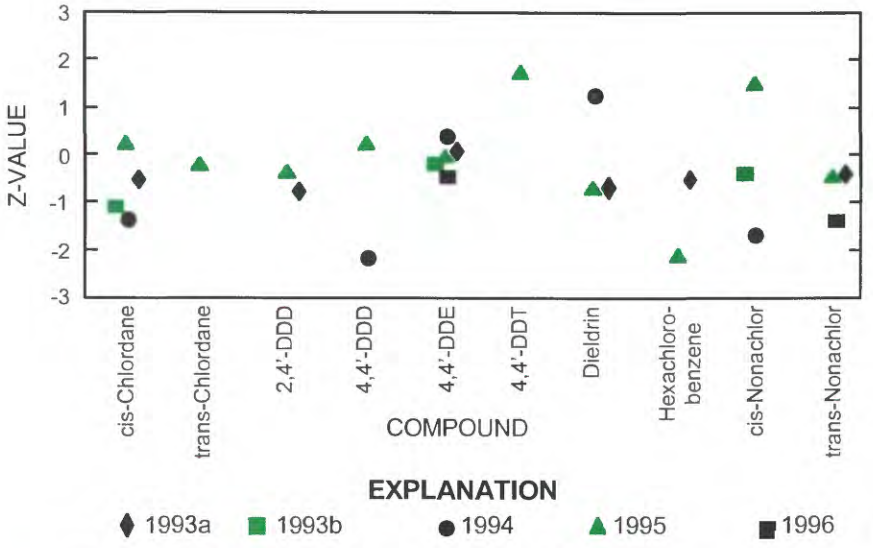


Figure 5. Results of National Water Quality Laboratory marine sediment performance-evaluation studies administered by the National Institute for Standards and Technology for the National Oceanic and Atmospheric Administration, 1995 and 1996.



1993a = Fish homogenate. 1993b = Mussel tissue.

Figure 6. Results of National Water Quality Laboratory biological tissue performance-evaluation studies administered by the National Institute for Standards and Technology for the National Oceanic and Atmospheric Administration, from 1993 to 1996.

Laboratory results for analyses of the NOAA biological tissue samples in two separate data sets for the 1993 study are shown in figure 6. During this study, fish homogenate and mussel tissue samples were provided to the participating laboratories (see 1993a and 1993b in fig. 6). Some compounds that are charted along the x-axis of the graph in figure 6 were not present in samples from every study; as a result, fewer data points for these compounds are shown in the figure.

As previously discussed, the control limits for these studies were not provided to the NWQL. Z-values have been calculated for all reported compounds. The control limits were set at 3 standard deviations from the mean of samples from the NOAA study. All NWQL results for these studies from 1993 through 1996 have been within acceptance limits. [At the time this Fact Sheet was published, the 1997 NOAA study assessment was still underway.]

Performance-evaluation studies for sediment and tissue methods, especially for organic compounds, can be difficult and costly to administer. For these reasons, several certified reference materials are routinely analyzed with each batch of environmental samples to ensure data quality. Reference material results may be obtained by contacting the Chief, Quality Management Program, at the NWQL.

RADIOCHEMISTRY OF WATER

The radiochemistry section of the NWQL participates five times a year in PE studies that are administered by USEPA and mandated by the Safe Drinking Water Act (U.S. Environmental Protection Agency, 1994, p. 658–700, 835–839). Gross alpha and beta are analyzed using standard USEPA methodology, and the NWQL is fully certified under the USEPA Safe Drinking Water Act. NWQL performance for analysis of these radionuclides from 1993 to 1997 is shown in figures 7 and 8. A z-value was calculated to represent these results because sample concentrations vary widely.

Two different sample types are analyzed as part of the study--a cross-check sample and a mixed blind sample. Three times each year, the laboratory must successfully analyze a cross-check sample that contains one alpha emitter and one beta emitter. These samples serve as a quality-assurance check of method performance. The mixed blind sample is sent to the laboratory twice each year. Although generally prepared in reagent water, this sample type better reflects a naturally occurring environmental sample in that many radionuclides are present, which poses significant analytical challenges.

Over the last 5 years, the results of NWQL analyses have been well within the strict USEPA study control limits 94 percent of the time, even though mean radionuclide activities for the study have varied by almost a factor of 50. In fact, 93 percent of the NWQL results are within 2 standard deviations from the mean, indicating excellent method performance.

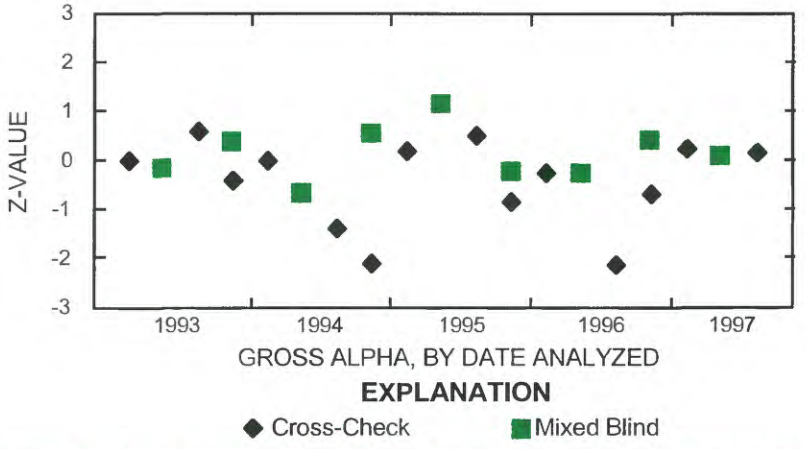


Figure 7. Results of National Water Quality Laboratory performance-evaluation studies for gross alpha from 1993 to 1997. These studies are administered by the U.S. Environmental Protection Agency.

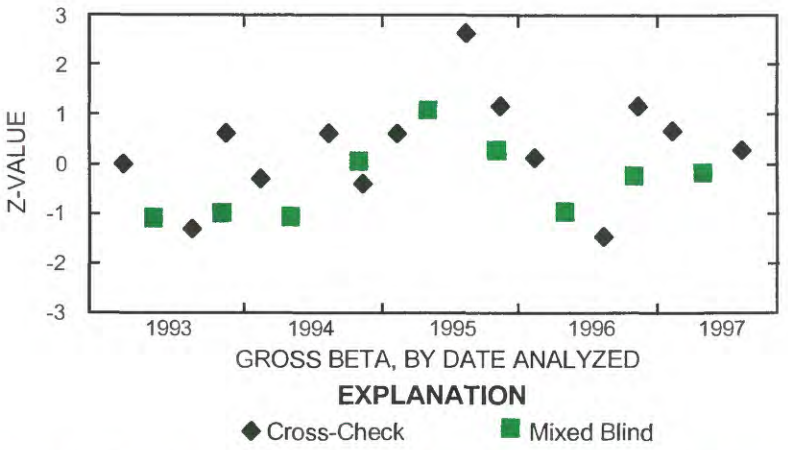


Figure 8. Results of National Water Quality Laboratory performance-evaluation studies for gross beta from 1993 to 1997. These studies are administered by the U.S. Environmental Protection Agency.

The NWQL has also taken part in the USEPA performance-evaluation studies for uranium since September 1994. In August 1997, USEPA approved the method that NWQL is using for analysis of uranium, and the laboratory is now fully certified for this radionuclide. Although not shown in this Fact Sheet, NWQL results for this radionuclide are also excellent. Greater than 90 percent of the uranium concentrations are within 2 standard deviations of the sample mean and are well within the acceptance limits.

SUMMARY

Participation in national and international performance-evaluation studies provides many benefits to the National Water Quality Laboratory and its customers. Results from such studies offer an independent check of credibility and capability. These studies also provide a means for laboratories to be uniformly evaluated. Consistent involvement in performance-evaluation studies provides laboratories the opportunity to improve analytical techniques. Through participation in these studies and other quality-assurance programs, the National Water Quality Laboratory has been able to improve its performance while serving as a reliable source of environmental analytical data.

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