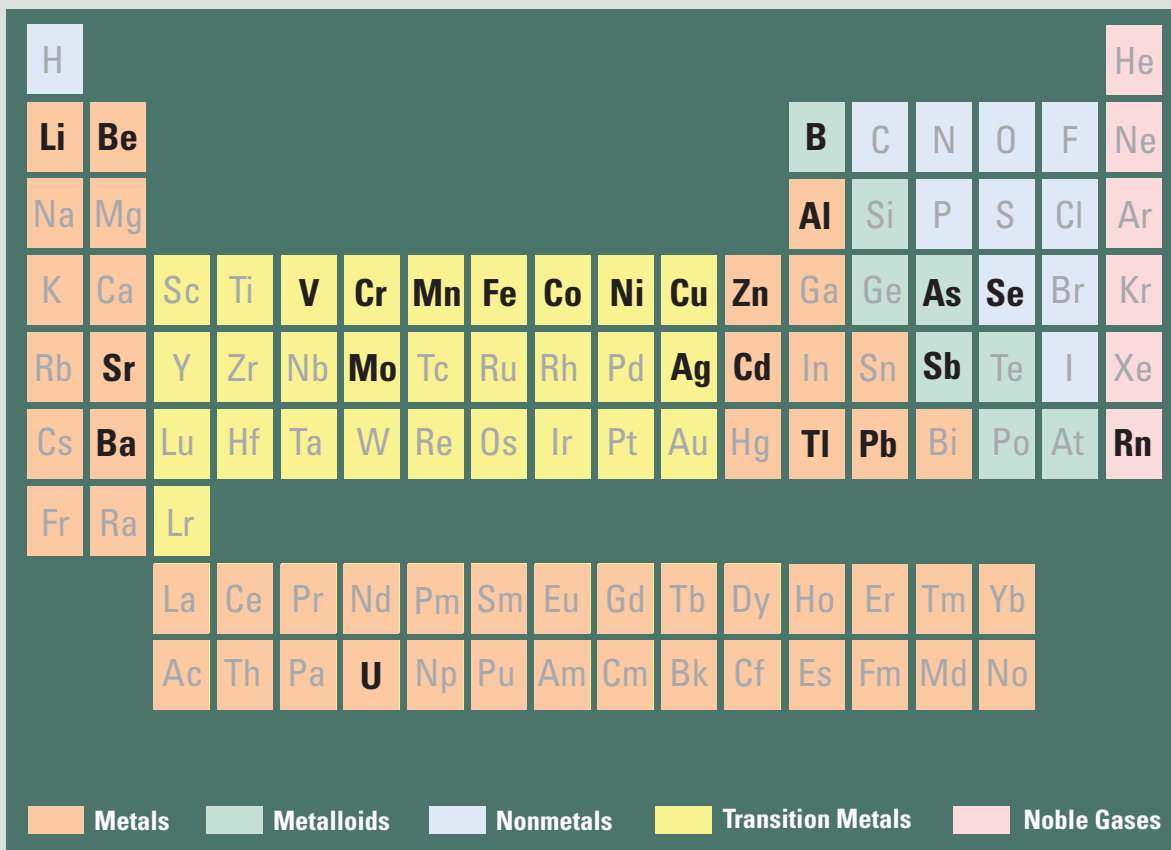


National Water-Quality Assessment Program

Review of Trace Element Blank and Replicate Data Collected in Ground and Surface Water for the National Water-Quality Assessment Program, 1991–2002



Scientific Investigations Report 2006–5093

Cover: Periodic table showing the trace elements, in bold, that are covered in this report. Periodic table adapted from the American Chemical Society's online periodic table, accessed on December 8, 2005, at http://www.chemistry.org/portal/a/c/s/1/acdisplay.html?DOC=sitertools%5Cperiodic_table.html#

Review of Trace Element Blank and Replicate Data Collected in Ground and Surface Water for the National Water-Quality Assessment Program, 1991–2002

by Lori E. Apodaca¹, David K. Mueller², and Michael T. Koterba³

Scientific Investigations Report 2006-5093

National Water-Quality Assessment Program

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Sacramento, California
2006

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Suggested reference:
Apodaca, L.E., Mueller, D.K., and Koterba, M.T., 2006, Review of trace element blank and replicate data collected in ground and surface water for the National Water-Quality Assessment Program, 1991–2002: U.S. Geological Survey Scientific Investigations Report 2006-5093, 32 p.

FOREWORD

The U.S. Geological Survey (USGS) is committed to providing the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the quality of the Nation's water resources is critical to assuring the long-term availability of water that is safe for drinking and recreation and suitable for industry, irrigation, and habitat for fish and wildlife. Population growth and increasing demands for multiple water uses make water availability, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa/>). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities.

From 1991-2001, the NAWQA Program completed interdisciplinary assessments in 51 of the Nation's major river basins and aquifer systems, referred to as Study Units (<http://water.usgs.gov/nawqa/studyu.html>). Baseline conditions were established for comparison to future assessments, and long-term monitoring was initiated in many of the basins. During the next decade, 42 of the 51 Study Units will be reassessed so that 10 years of comparable monitoring data will be available to determine trends at many of the Nation's streams and aquifers. The next 10 years of study also will fill in critical gaps in characterizing water-quality conditions, enhance understanding of factors that affect water quality, and establish links between sources of contaminants, the transport of those contaminants through the hydrologic system, and the potential effects of contaminants on humans and aquatic ecosystems.

The USGS aims to disseminate credible, timely, and relevant science information to inform practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Robert M. Hirsch

Associate Director for Water

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Contents

Abstract	1
Introduction	2
Purpose and Scope	2
Acknowledgments	2
Trace Element Data Collected	4
Procedures to Aggregate Blank and Replicate Data	4
Methods Used for Data Analysis	5
Methods to Determine Bias	5
Methods to Determine Variability	6
Trace Element Contamination Bias	6
Ground Water	9
Surface Water	9
Trace Element and Radon Sample Variability	15
Ground Water	15
Surface Water	22
Implications of Quality Control Results to Environmental Data	26
Potential Effects of Contamination Bias	26
Potential Effects of Sample Variability	28
Confidence Limit for an Individual Water-Quality Measurement or Multiple Measurements ...	28
Exceedance of a Water-Quality Standard	28
Two Water-Quality Measurements are Different	28
Summary	30
Glossary of Data-Quality Terms	31
References	31

Note: The data sets used for analysis in this report are posted on the Web site for this report (<http://pubs.water.usgs.gov/sir/2006-5093A>).

Figures

1. Locations of the 52 National Water-Quality Assessment Program study units that contributed the data analyzed in this report	3
2. Upper 95-percent confidence limits for contamination of aluminum, barium, boron, chromium, cobalt, copper, iron, manganese, nickel, strontium, and zinc that are based on data from ground-water field blanks	10
3. Upper 95-percent confidence limits for contamination of aluminum, barium, boron, copper, iron, manganese, strontium, and zinc that are based on data from surface-water field blanks	13
4. Ground-water data used to select low and high ranges of replicate concentrations for select trace elements and radon.....	17
5. Surface-water data used to select low and high ranges of replicate concentrations for select trace elements	23

Tables

1. Upper 95-percent confidence limit by percentiles for contamination in trace elements from ground-water field-blank data	7
2. Upper 95-percent confidence limit by percentiles for contamination in trace elements from surface-water field-blank data	8
3. Number of trace element ground-water and surface-water replicate sample sets and number of consistent detections within the replicate sets	15
4. Estimated sample variability at measured concentrations in ground-water trace element data	16
5. Estimated sample variability at measured concentrations in surface-water trace element data	25
6. Summary of trace-element environmental ground-water and surface-water data collected from 1991 to 2002.....	27
7. Estimated sample variability and confidence intervals around U.S. Environmental Protection Agency drinking-water standards for select trace elements in ground water and surface water.	29

Abbreviations

AL, action level
AMCL, alternative maximum contaminant level
CRL, common reporting level
GFAA, graphite-furnace atomic absorption
HA, health advisory
HGAA, hydride generation atomic absorption
IBSP, Inorganic Blind Sample Project
ICP-AES, inductively coupled plasma-atomic emission spectroscopy
ICP-MS, inductively coupled plasma-mass spectrometry
loess, local regression nonparametric smoothing technique
LRL, laboratory reporting level
MCL, Maximum Contaminant Level
MRL, method reporting level
NAWQA, National Water-Quality Assessment (U.S. Geological Survey) program
NWQL, National Water Quality Laboratory (U.S. Geological Survey)
pCi/L, picocuries per liter
QC, quality control
RSD, relative standard deviation
SD, standard deviation
SDWR, Secondary Drinking Water Regulations
UCL, upper confidence limit
USEPA, U.S. Environmental Protection Agency
USGS, U.S. Geological Survey
 $\mu\text{g/L}$, microgram per liter

Notes: Concentrations of chemical constituents in water are given in microgram per liter ($\mu\text{g/L}$).

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Review of Trace Element Blank and Replicate Data Collected in Ground and Surface Water for the National Water-Quality Assessment Program, 1991–2002

By Lori E. Apodaca, David K. Mueller, and Michael T. Koterba

Abstract

In the process of interpreting and analyzing trace element water-quality data for ground and surface water, it is important to determine the bias and variability that may be associated with these data. Trace element quality control samples (blanks and replicates) collected in the field for the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program from 1991 to 2002 were reviewed to determine the potential bias and variability that may be associated with the environmental samples. Bias in the data may be related to contamination from the field or laboratory during the collection, processing, shipping, or analysis of the samples. Sample variability can affect the interpretation of differences between individual measurements or mean concentrations. Trace element quality control data are available for 23 trace elements: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), silver (Ag), strontium (Sr), thallium (Tl), uranium (U), vanadium (V), and zinc (Zn). In addition, replicate data for radon (Rn) in ground water were reviewed. Statistical analyses were used to estimate the likelihood of contamination bias and sample variability that could occur in the environmental samples. The 95-percent upper confidence limit was calculated at select percentiles to assess the potential for trace element contamination. The 95-percent confidence intervals were calculated for sample variability.

The trace elements Sb, Be, and Tl in ground water and Sb, Be, Co, Mo, and U in surface water are unaffected by contamination. Limited quality control data (blanks) for Li and V in ground water and surface water do not allow for a good assessment on the potential contamination associated with these trace elements. Potential contamination was identified for Al, As, Ba, B, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Se, Ag, Sr, and Zn in ground water and surface water. Evidence of potential contamination was shown for Co, Mo, and U in ground water; potential contamination was shown for Tl in surface water. In comparing the potential contamination for these trace elements with the U.S. Environmental Protection Agency's (USEPA) drinking-water standards, the contamination for most of these trace elements is less than 10 percent of the drinking-water standard; therefore, contamination would have little or no effect when comparing trace element concentrations with the USEPA drinking-water standards. The exceptions are Al, Cd, and possibly Pb in ground water, and As and possibly Pb in surface water. Potential contamination identified for these trace elements is greater than 10 percent of the USEPA drinking-water standard, but affects only 5 percent or less of the As, Cd, and Pb samples. For most trace elements, the level of potential contamination is not large enough to significantly affect the measured concentration of the environmental sample. The exceptions may be Fe in ground water and Al in surface water, which have concentrations for at least 10 percent of the environmental samples that exceeded the USEPA drinking-water standards.

Sample variability for some of the trace elements could not be determined because there were either no detected concentrations, or there were less than 10 replicate sets with detected concentrations. These trace elements are Be, Ag, and Tl for ground water and Sb, Be, Cr, Co, Pb, Ag, and Tl for surface water. For most trace elements, sample variability was less than 10 percent, which would have little or no effect on the reported concentrations. The exceptions are Al, Cd, Cu, Pb, Rn (at concentrations less than about 700 picocuries per liter), Se, and Zn in ground water and Cu, Se, and Zn in surface water, all of which have sample variability ranging from 10 to 20 percent. Sample variability should be considered when evaluating the potential error associated with a sample measurement.

Collection of additional quality control samples for some of these trace elements to determine bias and variability is probably warranted particularly for those trace elements that the NAWQA Program did not begin sampling until 1998. Results obtained from the analysis of the quality control data can be applied to the interpretation of the environmental data collected from 1991 to 2002 and for water-quality data that are currently being collected as part of the NAWQA Program.

Introduction

The U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program was implemented in 1991 to improve the scientific and public understanding of water quality in the Nation's major river basins and ground-water systems. The goals of the NAWQA Program are to describe current water-quality conditions and trends in the Nation's rivers, streams, and ground water to understand the natural characteristics and human influences that affect water quality (Hirsch and others, 1988). In Cycle I (1991–2001), the first decade of extensive monitoring within 52 study units (*fig. 1*), work concentrated primarily on gathering comparable information on water quality in surface water and ground water.

To interpret trace element environmental water-quality data, information is needed to determine the bias and variability in the water-quality data that can result from sample collection, processing, shipping, and analysis. Sample bias and

variability can be evaluated by collecting quality control (QC) samples such as blank and replicate samples that are collected with the environmental samples. Bias is a systematic error and can be either positive or negative. An example of positive bias is contamination of the samples. Variability is a random error that affects the ability to reproduce an analysis.

Purpose and Scope

This report describes the results of the analysis of the trace element blank and replicate data collected with the environmental samples from 1991 to 2002 of the NAWQA Program. The QC data analysis is used to (1) describe the frequency and magnitude of trace element contamination using field blank data; (2) evaluate variability of the water-quality data using field replicate data; and (3) identify potential effects of bias and variability in interpreting the trace element data.

Trace elements reviewed in this report include aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), silver (Ag), strontium (Sr), thallium (Tl), uranium (U), vanadium (V), and, zinc (Zn). In addition, radon (Rn) replicate sample analyses in ground water were reviewed.

The results of the QC data analysis are compared with the U.S. Environmental Protection Agency's (USEPA) drinking-water standards to assess the potential effects of bias and variability on the environmental data (U.S. Environmental Protection Agency, 2004). This report does not address QC or trace element data that are contaminated or trace element data errors related to the coding of trace element data.

Acknowledgments

The authors would like to thank Leslie DeSimone and George Groschen for their technical reviews of this manuscript. Also, the work done by the Cycle I NAWQA study unit hydrologists and hydrologic technicians who collected the trace element water-quality data is greatly appreciated. Without their efforts, the analysis of the trace element QC data would not have been possible.

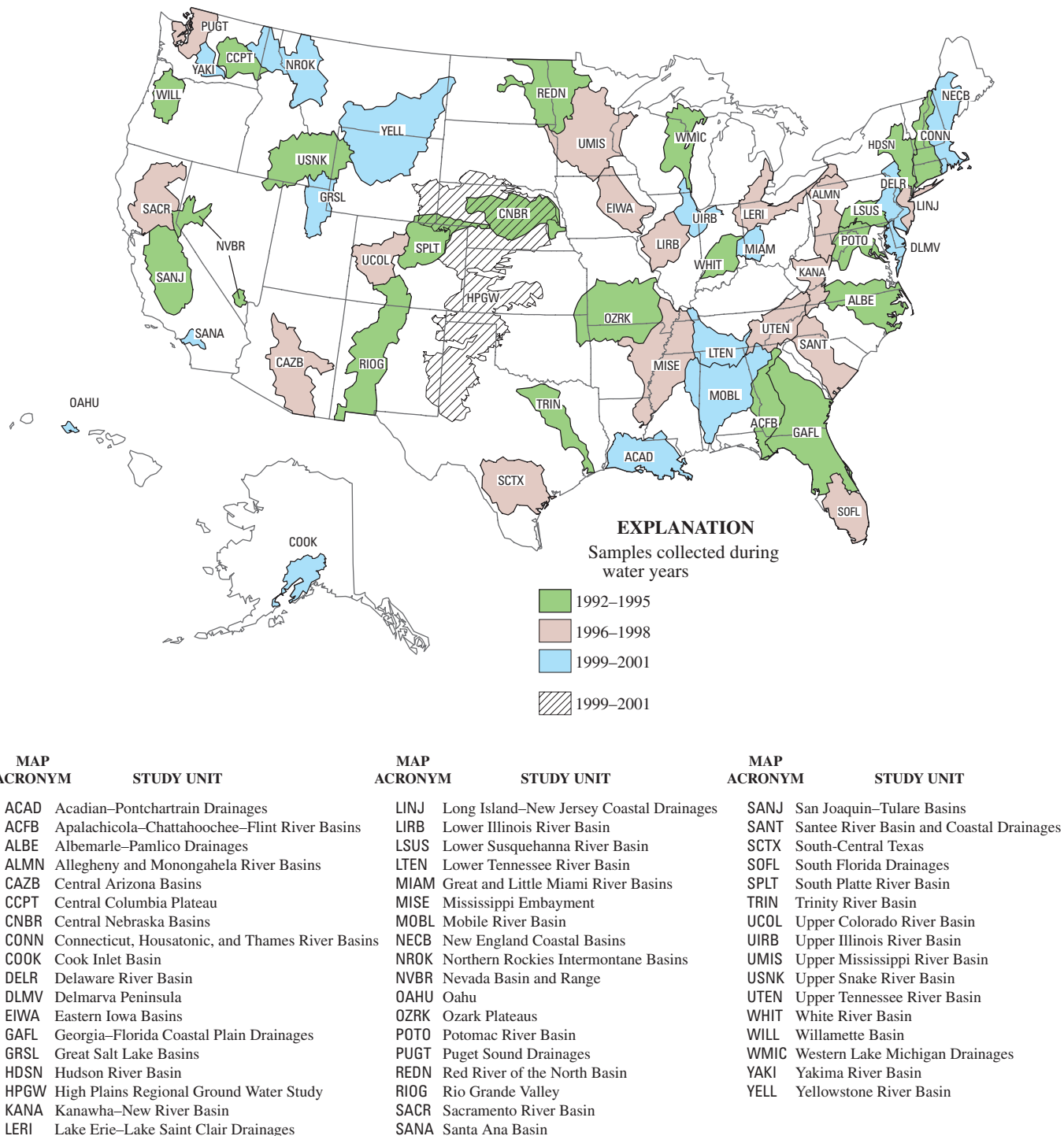


Figure 1. Locations of the 52 National Water-Quality Assessment Program study units that contributed the data analyzed in this report.

Trace Element Data Collected

For the 52 study units that were sampled in Cycle I (1992–2001), implementation of the study-unit investigations were phased so that the water-quality data were collected in about one-third of the study units at a time. During Cycle I of the NAWQA Program, sampling occurred over a period of 3 water years (water year is the period from October 1 through September 30 and identified by the year in which it ends) in each study unit. After sampling was completed during the three year period, sampling was implemented that involved water-quality sampling at a few select surface-water and ground-water sites. For the first group of 20 study units, sampling occurred mainly during water years 1993–95, but some limited sampling did occur in water year 1992, followed by sampling at selected sites during water years 1996–2001. The second group of 16 study units began sampling during water years 1996–1998, followed by sampling at selected sites during water years 1999–2001. The third group, consisting of 16 study units, completed sampling during water years 1999–2001. Four study units from the third group completed water-quality sampling in water year 2002. Data from these study units have been included in the analysis of the trace element QC data.

During Cycle I, trace element sampling initially was optional and focused mainly on ground water (1992/3–95). Surface-water sampling generally consisted of synoptic sampling to address local trace element issues. Ground-water samples were collected for Rn analysis by most study units during Cycle I. From 1996 to 1998, trace element sampling became a more integrated part of the NAWQA Program and was fully implemented into the NAWQA Program from 1999 to 2001.

The differences in the timing as to when trace elements were collected in Cycle I, in the media targeted for sampling, and in the laboratory methods used during Cycle I, have led to differences in the number of QC samples available for each trace element. From 1992 to 1993, about 15 percent of the water-quality samples that were collected consisted of QC samples (P. Patrick Leahy, U.S. Geological Survey, written commun., 1992 and 1993). QC sampling was fully integrated into the sampling design beginning in 1994 (Koterba and others, 1995; Mueller and others, 1997). QC sampling required that blanks and replicates be taken at regular intervals throughout a sampling effort.

Trace element environmental and QC samples were analyzed at the USGS's National Water Quality Laboratory (NWQL), Denver, Colorado. The trace elements discussed in this report typically were analyzed by two different analytical techniques: inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) (Garbarino, 1999). Additional

analytical techniques were used for As, Cr, and Se. As and Se were analyzed using graphite-furnace atomic absorption (GFAA), hydride generation atomic absorption (HGAA), and ICP-MS. Cr was analyzed using GFAA, and ICP-AES or ICP-MS analytical techniques. Review of the analytical data for As, Cr, and Se from the NWQL Inorganic Blind Sample Project (IBSP) indicates that these methods are comparable, with the relative error between the analytical value and the most probable value averaging less than 0.2 percent for the period when samples were collected during Cycle I for both methods (Ludtke and Woodworth, 1997).

Analysis of trace elements, prior to 1993, involved the use of analytical methods that were available at the NWQL. In 1993, a low-level (1 µg/L or less) trace element analytical schedule was developed for the NAWQA Program along with a low-level (0.5 µg/L or less) blank schedule (Garbarino and Taylor, 1996). B, Sr, and Tl were added to the NAWQA low-level trace element schedule in 1996; in addition, reporting levels decreased, thus, eliminating the need for the low-level blank schedule. In 1998, Li and V were added to the trace element schedule (Garbarino, 1999). Beginning in October 1999, the NWQL also provided semiquantified (E-remarked) values below the laboratory reporting level (LRL) for select trace elements (Childress and others, 1999). Rn was analyzed using scintillation vial counting throughout Cycle I. Fe and Mn were analyzed using the NAWQA Program's major-ions schedule; however, Mn concentrations from the trace element schedule were used in this report because the trace element analytical schedule had a lower method reporting level (MRL).

Procedures to Aggregate Blank and Replicate Data

The main objective in the aggregation of blank and replicate data for trace elements was to obtain a data set that could be used to assess bias and variability in the trace element environmental data. Because of differences in sample collection methods, when blanks and replicates were collected, and the emphasis on trace elements in ground water rather than on surface water, QC data for these two media are analyzed separately. For each medium, however, identical procedures are used to aggregate the QC blank data for each trace element in relation to a single reporting level, which is referred to in this report as a "common reporting level" (CRL). The use of a single common reporting level, however, can result in the loss of data, particularly for those trace elements with several MRLs that are below the selected reporting level. Therefore, for some of the trace elements, the blank data have also been censored and analyzed at the second most CRL.

The first CRL was selected as the most frequently used MRL in the environmental and blank samples from among those used for a particular trace element in Cycle I, except for Sr, where the MRL of the blank samples was used. This approach was used to obtain the maximum number of uncensored values at or above the CRL. In selecting the CRL for a particular trace element, the QC data for each trace element were processed independent of one other. Quantified (not E-remarked), semi-quantified (E-remarked), or less than (<) values below the CRL became a “<CRL” value for statistical purposes. Samples that are V-marked (samples identified as being contaminated) were not used in determining the CRL. If possible, a second CRL was selected that was often the next lowest common MRL. The second CRL is used to better define the potential contamination, but consists of a smaller sample size.

Water that was used for collecting the blank samples essentially was free of the analytes of interest; analyte concentrations in the blank water samples are documented by the NWQL prior to distribution to the NAWQA study units. To assess potential causes of bias in the environmental samples, all blank sample types collected during Cycle I were reviewed. These samples included source solution, equipment, and field blanks; however, the field blanks were the most useful in interpreting the bias associated with the environmental samples. Generally, no more than about a dozen suitable source-solution blanks or equipment blanks are available for a particular trace element in ground water or surface water.

The trace element replicate data set that is used in this report includes samples that are identified as being either environmental or replicate samples that have the same site and date. The type of replicate samples collected for ground water were most often identified as a “sequential” replicate (96 percent of the replicates collected). Sequential replicates are samples collected immediately following the environmental sample. For surface water, however, several types of replicate samples were collected that included concurrent, sequential, and split replicate samples. All replicate sample types in the surface-water samples were combined to increase the number of replicate samples available for a particular trace element, as most trace elements had limited data with detected values. Other reasons for combining the replicate data are that the variability in the sample data are most likely a result of laboratory processing and analysis. Mueller (1998) reviewed the standard deviation for nitrogen and phosphorus concentrations of split and other types of replicate samples and determined that variability could not be attributed to the type of replicate sample collected. In this report, replicate trace element data are not censored to a CRL.

All QC data used in this report were retrieved from the USGS's NAWQA Data Warehouse (<http://water.usgs.gov/nawqa/data>). Retrievals for blank data were conducted

in March 2002 and a later retrieval for replicate data was conducted in October 2003. The only difference between these two data retrievals is that there are replicate samples from study units that completed their Cycle I sampling in water year 2002. The data sets used for analysis in this report are posted on the Web site for this report (<http://pubs.water.usgs.gov/sir2006-5093/>). The glossary located in the back of this report defines QC terms that might be unfamiliar to some readers.

Methods Used for Data Analysis

Bias and variability associated with trace element water-quality data can be determined by statistical analysis of field blank and replicate samples. The trace element field blank data were censored to a CRL before analysis because of the different MRLs used and inconsistencies early in Cycle I as to the schedules used for analysis. Trace element replicate data were not given a CRL.

Methods to Determine Bias

A graphical approach (consisting of time series plots of contaminant concentrations) was initially used to determine whether blank contamination occurred above or below the CRL during a specified period in Cycle I. In addition, to assess the potential for trace element blank contamination at or above the selected CRL, a one-sided nonparametric 95-percent upper confidence limit (UCL) was calculated at select percentiles (50th, 75th, 85th, and 90th through 99th) for the trace element concentrations using the method of Hahn and Meeker (1991). Hahn and Meeker (1991) used a distribution-free UCL for a percentile, which is appropriate for skewed data. The method uses order statistics, which is based on ranking the data concentration from large to small, then uses a binomial probability to determine the UCL. The SAS statistical program (SAS Institute, Inc, 1990) was used to calculate the UCL at the selected percentiles. The UCL is used to determine the maximum contamination expected for a specified percentage of water samples. For example, the 95-percent UCL confidence limit for the 90th percentile indicates that, with 95-percent confidence, the specified amount of contamination would be exceeded in no more than 10 percent of the samples. The 95-percent confidence at the 90th percentile can also be described as the maximum contamination expected in 90 percent of the samples with only a 5-percent chance that the contamination has been underestimated. The amount of contamination identified in the blank samples relates to the environmental samples, which are collected, processed, shipped, and analyzed in the same manner as the blank samples.

Methods to Determine Variability

Information on the ground-water and surface-water replicate data was summarized by the number of replicate samples collected and the consistency of detections. Replicate variability can be determined only when both samples in a replicate pair have detections. Thus, replicate data sets with measured concentrations less than the MRL were excluded. In addition, replicate data sets with inconsistent detections (that is, where the trace element was detected in one sample but not in both) also were excluded. The reason for excluding these samples is that concentrations less than the MRL typically were rounded to a whole number, such that the calculation of the relative standard deviation (RSD) would be quite variable between replicate sets, even if the difference in concentration between the environmental and the replicate sample was relatively small. Also, only data that were reported to at least one decimal place were used in evaluating the variability between replicate sets for a particular trace element. Rn data, which are reported primarily as whole numbers, however, were not excluded in the replicate data analysis.

Sample variability of replicate samples is best characterized by different statistical measures over different concentration ranges. Variability over a large range of concentrations can be approximated by dividing the concentration range into segments where either the standard deviation (SD) or RSD is relatively constant (Anderson, 1987). Concentration ranges for the replicate sets were determined by plotting the mean sample concentration and the SD and RSD. The RSD or coefficient of variance, in percent, is defined as the SD divided by the mean concentration (\bar{C}) times 100:

$$\text{RSD} = [(\text{SD}/\bar{C}) \times 100]. \quad (1)$$

An approximate boundary between concentration ranges can be determined by the change in slope of a loess (local regression nonparametric smoothing technique) curve (S-Plus, 2002) through the center of the data. For low concentrations—those close to the MRL—the mean SD is approximately constant and therefore, is an appropriate measure of the sample variability. The mean SD generally increases with concentration; therefore, variability is most appropriately represented by the mean RSD for the upper range of concentrations. Because of the small number of replicate sets for some of the trace elements, a change in the slope of the loess curve was not observed; therefore, the mean RSD was used to evaluate the variability over the entire concentration range. Using the mean RSD over the entire range most likely overestimates the variability at high concentrations and underestimates the variability at low concentrations.

After the sample variability has been determined for the low and high concentration ranges, then confidence intervals can be determined for any one measurement such as an environmental sample. The confidence interval for an individual measurement is defined as:

$$[C_L, C_U] = C \pm Z_{(1-\alpha/2)} \times \sigma, \quad (2)$$

where

- C_L, C_U = the lower and upper limits of concentration for the 100(1 - α) percent confidence interval,
- C = individual measured concentration,
- α = probability that the confidence interval does not include the true concentration,
- Z = the ordinate of the normal curve (Z-value) that contains 100(1 - α) percent of the distribution, and
- σ = sampling variability for the measured concentration: low range σ = SD and high range $\sigma = C (\text{RSD}/100)$.

For multiple samples, the error associated with the mean concentration as a result of sampling variability is reduced, as indicated in the following equation:

$$[C_L, C_U] = \bar{C} \pm Z_{(1-\alpha/2)} \frac{\sigma}{\sqrt{n}}, \quad (3)$$

where

- n = the number of samples,
- \bar{C} = the mean concentration for these samples; and the

other variables are as previously defined above.

Trace Element Contamination Bias

The potential contamination for the 23 different trace elements was determined separately for ground-water (*table 1*) and surface-water (*table 2*) data. For most of the trace elements sampled in Cycle I, there is about one third to one-half as many surface-water blanks as compared with ground-water blanks.

In evaluating the QC data for each trace element, time series plots showed no evidence of contamination for specific time periods for any of the 23 trace elements. The distribution of the trace element concentrations greater than the CRL in blanks is more likely to be a result of changes in the sampling frequency or reporting level (number of significant decimal places) rather than by an overall increase or decrease in concentrations during Cycle I. This is similar to the results of Mueller and Titus (2005) who reviewed nutrient QC data collected by the NAWQA Program from water years 1992 to 2001. For example, systematic contamination among the study units is apparent for Al, B, Fe, and Zn (*tables 1* and *2*). For other trace elements, high concentrations in blanks were observed in only a few study units; no temporal pattern in contamination was observed, and so, these cases are likely not the result of systematic contamination.

Table 1. Upper 95-percent confidence limit by percentiles for contamination in trace elements from ground-water field-blank data.

[Bold faced values indicate contamination greater than the common reporting level. Al, aluminum; Ag, silver; As, arsenic; B, boron; Ba, barium; Be, beryllium; Bi, bismuth; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; Fe, iron; Pb, lead; Li, lithium; Mn, manganese; Mo, molybdenum; Ni, nickel; Sb, antimony; Se, selenium; Sr, strontium; Tl, thallium; U, uranium; USEPA, U.S. Environmental Protection Agency; V, vanadium; Zn, zinc; na, not applicable; µg/L, microgram per liter; <, less than; —, too few data to compute]

	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe	Pb	Li	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn
USEPA Drinking-Water Standard ¹	350–200	³⁶	³¹⁰	^{42,000}	³⁴	⁴⁶⁰⁰	³⁵	³¹⁰⁰	—	^{51,300}	²³⁰⁰	¹⁵	—	⁴³⁰⁰	⁴⁰	^{41,000}	³⁵⁰	⁴¹⁰⁰	^{4,000}	³²	³³⁰	—	^{42,000}
Common Reporting Level (µg/L)	1.0	1.0	1.0	1.0	1.0	4.0	1.0	1.0	1.0	1.0	3.0	1.0	0.3	1.0	1.0	1.0	1.0	1.0	1.0	0.1	0.1	1.0	1.0
Number of blanks	330	347	329	344	346	164	353	343	343	345	423	343	37	546	341	339	302	343	186	151	368	37	341
95-percent Upper Confidence Limit (µg/L)																							
Percentile																							
50th (median)	3.0	<1.0	<1.0	<1.0	<1.0	5.9	<1.0	<1.0	<1.0	<1.0	<3.0	<1.0	<0.3	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<0.1	<0.1	<1.0	<1.0
75th	4.0	<1.0	<1.0	<1.0	<1.0	9.2	<1.0	<1.0	<1.0	<1.0	5.0	<1.0	<0.3	<1.0	<1.0	<1.0	<1.0	<1.0	0.16	<0.1	<1.0	<1.0	3.0
85th	4.9	<1.0	<1.0	<1.0	<1.0	12	<1.0	<1.0	<1.0	1.0	8.0	<1.0	0.36	<1.0	<1.0	<1.0	<1.0	<1.0	0.3	<0.1	<1.0	<1.0	6.0
90th	6.0	<1.0	<1.0	<1.0	<1.0	13	<1.0	<1.0	<1.0	2.0	11	<1.0	0.78	<1.0	<1.0	<1.0	<1.0	<1.0	0.78	<0.1	<1.0	<1.0	8.0
91st	6.5	<1.0	<1.0	<1.0	<1.0	13	<1.0	<1.0	<1.0	2.1	12	<1.0	0.78	<1.0	<1.0	<1.0	<1.0	<1.0	0.78	<0.1	<1.0	<1.0	9.0
92nd	7.0	<1.0	<1.0	<1.0	<1.0	13	<1.0	<1.0	<1.0	3.0	15	<1.0	0.78	<1.0	<1.0	<1.0	<1.0	<1.0	0.78	<0.1	<1.0	<1.0	11
93rd	8.0	<1.0	<1.0	<1.0	<1.0	14	<1.0	<1.0	<1.0	3.0	20	<1.0	—	<1.0	<1.0	<1.0	<1.0	<1.0	1.6	<0.1	<1.0	<1.0	14
94th	8.3	<1.0	<1.0	<1.0	<1.0	15	<1.0	<1.0	<1.0	3.8	21	<1.0	—	<1.0	<1.0	<1.0	<1.0	<1.0	2.3	<0.1	<1.0	<1.0	14
95th	9.0	<1.0	<1.0	<1.0	<1.0	15	<1.0	<1.0	<1.0	4.0	29	<1.0	—	<1.0	<1.0	<1.0	<1.0	<1.0	3.0	<0.1	<1.0	<1.0	18
96th	10	<1.0	<1.0	<1.0	<1.0	19	<1.0	<1.0	<1.0	4.4	36	<1.0	—	<1.0	<1.0	<1.0	<1.0	<1.0	3.4	<0.1	<1.0	<1.0	21
97th	12	<1.0	<1.0	<1.0	<1.0	19	<1.0	<1.0	<1.0	5.3	42	<1.0	—	<1.0	<1.0	<1.0	<1.0	<1.0	6.1	<0.1	<1.0	<1.0	36
98th	14	<1.0	<1.0	<1.0	<1.0	22	<1.0	<1.0	<1.0	12	46	<1.0	—	<1.0	<1.0	<1.0	<1.0	<1.0	19	<0.1	<1.0	<1.0	38
99th	91	<1.0	1.0	<1.0	<1.0	—	<1.0	<1.0	<1.0	4.5	1.5	<1.0	—	<1.0	<1.0	<1.0	<1.0	<1.0	2.0	<0.1	<1.0	<1.0	68
Common Reporting Level (µg/L)	0.3	0.2	0.18	0.2	0.2	2	0.3	0.2	0.2	0.2	na	0.3	na	0.1	0.2	0.5	0.7	0.2	na	na	0.2	0.21	0.5
Number of blanks	147	152	9	147	152	142	153	144	152	154	na	152	na	190	152	149	40	148	na	na	na	153	4
95-percent Upper Confidence Limit (µg/L)																							
Percentile																							
50th (median)	2.9	<0.2	na	<0.2	<0.2	5.1	<0.3	<0.2	<0.2	0.24	na	<0.3	na	<0.1	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	0.92
75th	3.6	<0.2	na	0.27	<0.2	7.9	<0.3	0.27	<0.2	0.56	na	<0.3	na	0.15	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	2.1
85th	4.1	<0.2	na	0.47	<0.2	10	<0.3	0.33	<0.2	0.79	na	<0.3	na	0.25	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	3.5
90th	4.8	<0.2	na	0.6	<0.2	11	<0.3	0.5	<0.2	1.4	na	<0.3	na	0.35	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	6.8
91st	4.8	<0.2	na	0.77	<0.2	12	<0.3	0.54	0.22	1.8	na	<0.3	na	0.44	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	7
92nd	5	<0.2	na	1	<0.2	12	<0.3	0.68	0.36	1.9	na	<0.3	na	0.47	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	7.2
93rd	5.2	<0.2	na	1.3	<0.2	12	<0.3	0.72	0.37	2.2	na	<0.3	na	0.54	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	12
94th	5.6	<0.2	na	1.9	<0.2	12	<0.3	0.76	0.42	2.7	na	<0.3	na	0.61	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	18
95th	6.4	<0.2	na	3.6	<0.2	13	<0.3	0.83	0.82	3.9	na	<0.3	na	0.79	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	25
96th	6.5	<0.2	na	3.9	<0.2	13	<0.3	0.89	0.89	4.3	na	<0.3	na	0.86	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	38
97th	8.5	<0.2	na	5.2	<0.2	14	<0.3	1.1	1.4	13	na	<0.3	na	1.1	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	68
98th	—	<0.2	na	—	<0.2	—	<0.3	—	1.4	13	na	<0.3	na	1.2	<0.2	<0.5	<0.7	<0.2	na	na	<0.2	na	—
99th	—	—	na	—	—	—	—	—	—	—	na	—	na	—	—	—	—	—	—	na	—	na	—

¹U.S. Environmental Protection Agency, 2004.²Secondary Drinking Water Regulation (SDWR): is a non-enforceable Federal guideline to address cosmetic or aesthetic effects of drinking water.³Maximum Contaminant Level (MCL): the highest level of contaminant that is allowed in drinking water.⁴Health Advisory (HA): is an acceptable drinking-water level for a chemical substance that is based on health effects information. HAs are not legally enforceable, but are a standard that serves as a guidance to assist Federal, state, and local officials.⁵Action Level (AL): concentration of a contaminant that triggers treatment or other requirements that a water system must follow. For lead and copper, the action level is the level where 10 percent of the homes tested exceed the standard.

Table 2. Upper 95-percent confidence limit by percentiles for contamination in trace elements from surface-water field-blank data.

[Bold faced values indicate contamination greater than the common reporting level. Al, aluminum; Ag, silver; As, arsenic; B, boron; Ba, barium; Be, beryllium; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; Fe, iron; Pb, lead; Li, lithium; Mn, manganese; Mo, molybdenum; Ni, nickel; Sb, antimony; Se, selenium; Sr, strontium; Tl, thallium; U, uranium; USEPA, U.S. Environmental Protection Agency; V, vanadium; Zn, zinc; na, not applicable; µg/L, microgram per liter; <, less than —, too few data to compute]

	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe	Pb	Li	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	
USEPA Drinking-Water Standard ¹	250–200	36	310	32,000	34	4600	35	3100	—	31,300	3300	315	4300	440	4100	350	4100	4,000	32	330	—	330	—	42,000
Common Reporting Level (µg/L)	1.0	1.0	1.0	1.0	1.0	4.0	1.0	1.0	1.0	1.0	3.0	1.0	0.3	1.0	1.0	1.0	1.0	1.0	0.1	0.1	0.1	0.1	1.0	1.0
Number of blanks	119	130	86	124	138	55	139	125	126	127	831	129	9	875	130	124	119	142	57	54	127	10	124	
	95-percent Upper Confidence Limit (µg/L)																							
50th (median)	2.0	<1.0	<1.0	<1.0	<1.0	<4.0	<1.0	<1.0	<1.0	<1.0	<3.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<0.1	<1.0	<1.0	<1.0	<1.0
75th	4.0	<1.0	<1.0	<1.0	5.5	<1.0	<1.0	<1.0	<1.0	<1.0	3.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<0.1	<1.0	<1.0	<1.0	3.0
85th	5.0	<1.0	<1.0	<1.0	9.4	<1.0	<1.0	<1.0	<1.0	<1.0	5.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	0.39	<1.0	<1.0	<1.0	4.0
90th	7.0	<1.0	<1.0	<1.0	11	<1.0	<1.0	<1.0	<1.0	1.0	6.1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	0.65	<1.0	<1.0	<1.0	4.3
91st	7.0	<1.0	<1.0	<1.0	14	<1.0	<1.0	<1.0	<1.0	1.0	7.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	0.65	<1.0	<1.0	<1.0	6.0
92nd	10	<1.0	<1.0	<1.0	14	<1.0	<1.0	<1.0	<1.0	1.0	8.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	3.9	0.17	<1.0	<1.0	8.0
93rd	15	<1.0	<1.0	1.0	<1.0	14	<1.0	<1.0	<1.0	1.0	8.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	3.9	0.17	<1.0	<1.0	11
94th	34	<1.0	<1.0	1.1	<1.0	—	<1.0	<1.0	<1.0	1.0	10	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	3.9	0.17	<1.0	<1.0	11
95th	45	<1.0	1.25	1.1	<1.0	—	<1.0	<1.0	<1.0	2.0	10	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.0	—	<1.0	<1.0	13
96th	45	<1.0	1.25	2.0	<1.0	—	<1.0	<1.0	<1.0	2.3	20	1.8	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	2.0	—	<1.0	<1.0	13
97th	79	<1.0	—	3.0	<1.0	—	<1.0	<1.0	<1.0	2.7	32	6.3	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	3.0	—	<1.0	<1.0	13
98th	—	—	—	—	—	—	—	—	—	—	57	—	—	—	—	—	—	—	—	—	—	—	—	—
99th	—	—	—	—	—	—	—	—	—	—	75	—	—	—	—	—	—	—	—	—	—	—	—	—
Common Reporting Level (µg/L)	0.3	0.2	0.18	0.2	0.2	2	0.3	0.2	0.2	0.2	na	0.3	na	0.1	0.2	0.5	0.7	0.2	na	na	na	0.2	0.21	0.5
Number of blanks	46	57	6	46	52	44	55	41	51	51	na	52	na	84	51	50	11	46	na	na	na	55	5	48
	95-percent Upper Confidence Limit (µg/L)																							
50th (median)	0.36	<0.2	na	<0.2	<0.2	<2.0	<0.3	<0.2	<0.2	<0.2	na	<0.3	na	<0.1	<0.2	<0.5	na	<0.2	na	na	<0.2	na	<0.2	<0.5
75th	3.3	<0.2	na	<0.2	<0.2	3.5	<0.3	<0.2	<0.2	0.34	na	<0.3	na	<0.1	<0.2	<0.5	na	<0.2	na	na	<0.2	na	<0.2	1.1
85th	7.0	<0.2	na	1.22	<0.2	9.4	<0.3	0.21	<0.2	0.49	na	<0.3	na	0.12	<0.2	<0.5	na	<0.2	na	na	<0.2	na	<0.2	2.9
90th	15	<0.2	na	0.31	<0.2	11	0.42	0.34	<0.2	0.75	na	<0.3	na	0.15	<0.2	<0.5	na	<0.2	na	na	<0.2	na	<0.2	11
91st	34	<0.2	na	0.9	<0.2	11	0.42	0.34	<0.2	0.75	na	<0.3	na	0.15	<0.2	<0.5	na	<0.2	na	na	<0.2	na	<0.2	13
92nd	34	<0.2	na	0.9	<0.2	14	0.7	0.34	<0.2	2.3	na	<0.3	na	0.2	<0.2	<0.5	na	<0.2	na	na	<0.2	na	<0.2	13
93rd	34	<0.2	na	0.9	<0.2	14	0.7	—	<0.2	2.3	na	<0.3	na	0.47	<0.2	<0.5	na	<0.2	na	na	<0.2	na	<0.2	13
94th	—	<0.2	na	—	<0.2	14	0.7	—	<0.2	2.3	na	<0.3	na	0.42	<0.2	<0.5	na	<0.2	na	na	<0.2	na	<0.2	—
95th	—	—	na	—	—	—	—	—	—	—	na	—	na	0.92	<0.2	<0.5	na	—	na	na	<0.2	na	<0.2	—
96th	—	—	na	—	—	—	—	—	—	—	na	—	na	0.92	<0.2	<0.5	na	—	na	na	<0.2	na	<0.2	—
97th	—	—	na	—	—	—	—	—	—	—	na	—	na	—	—	—	na	—	na	na	<0.2	na	<0.2	—
98th	—	—	na	—	—	—	—	—	—	—	na	—	na	—	—	—	na	—	na	na	<0.2	na	<0.2	—
99th	—	—	na	—	—	—	—	—	—	—	na	—	na	—	—	—	na	—	na	na	<0.2	na	<0.2	—

¹U.S. Environmental Protection Agency, 2004.
²Secondary Drinking Water Regulation (SDWR): is a non-enforceable Federal guideline to address cosmetic or aesthetic effects of drinking water.
³Maximum Contaminant Level (MCL): the highest level of contaminant that is allowed in drinking water.
⁴Health Advisory (HA): is an acceptable drinking-water level for a chemical substance that is based on health effects information. HAs are not legally enforceable, but is a standard that serves as a guidance to assist Federal, state, and local officials.
⁵Action Level (AL): concentration of a contaminant that triggers treatment or other requirements that a water system must follow. For lead and copper, the action level is the level where 10 percent of the homes tested exceed the standard.

Ground Water

A UCL was calculated for trace element ground-water blank data collected during Cycle I. The 95-percent UCL was selected, and calculations were completed for the 50th, 75th, 85th, and 90th through 99th percentiles, where possible. In addition, calculations of the 95-percent UCL were determined at two CRLs if there was more than one MRL reported for a particular trace element. The use of the lower CRL more accurately defines the potential contamination. Using the lower CRL allows for a determination of the contamination at a value ranging from 0 to 1 µg/L instead of <1 µg/L, which can be important for trace elements at low concentrations.

In ground water, the potential contamination is estimated to be no greater than the MRLs for Sb, Be, Tl, and V at the selected CRLs (*table 1*). At the highest CRL, an additional 11 trace elements (As, Ba, Cd, Cr, Co, Pb, Mo, Ni, Se, Ag, and U) that were analyzed during Cycle I have an estimated contamination of less than the MRL for at least 90 percent of the samples (*table 1*). At the same CRL, Mn has potential contamination of less than the MRL for at least 85 percent of the samples; Cu and Li each have potential contamination of less than the MRL for at least 75 percent of the samples, and Fe and Sr have potential contamination of less than the MRL for at least 50 percent of the samples. The potential contamination for Pb at the UCL of the 99th percentile is likely related to one high value (7.0 µg/L). Similarly, the potential contamination for Cu at the UCL of the 85th percentile is high because of a measured value of 101 µg/L. These high values may be due to the sample being contaminated or being incorrectly coded as a blank sample. Al, B, and Zn, have potential contamination in at least 50 percent of all samples regardless of the MRL. Because of limited ground-water blank data for Li and V, additional data need to be collected to better assess the sample bias associated with these trace elements.

The lower CRL helps to provide a more accurate assessment of the potential contamination for 10 of the trace elements (Ba, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, and Se) sampled in Cycle I (*table 1*). For example, Ba at the higher CRL has a potential contamination of <1 µg/L for at least 85 percent of the samples. The estimate of <1 µg/L as the potential contamination is probably closer to 0.47 µg/L when calculating the 95-percent confidence limit at the lower CRL (*table 1*). The use of the lower CRL (lowering <1 µg/L to values ranging from <0.1 to <0.7 µg/L) helps to better quantify the potential contamination.

The 95-percent UCL has been plotted for Al, Ba, B, Cr, Co, Cu, Fe, Mn, Ni, Sr, and Zn field blank data to show the changes in the potential contamination for these trace elements at the selected CRLs (*figs. 2A, 2B, and 2C and table 1*). For five of the trace elements (Ba, Cr, Co, Mn, and Ni), a lower CRL also has been plotted. The lower CRL has not been plotted for Cu because of the likelihood that the estimated contamination is biased as a result of one high value. The use of the lower CRL provides a more accurate assessment of the potential contamination, particularly for those values below the higher CRL. The potential contamination varies depending on the trace element analyzed as shown in *figures 2A, 2B, and 2C*.

Surface Water

As with the ground-water blank data, the 95-percent UCL was selected, and calculations were completed for the 50th, 75th, 85th, and 90th through 99th percentiles (*table 2*). In addition, the 95-percent UCL was calculated for two CRLs, if more than one MRL was reported for a particular trace element.

For five of the trace elements (Sb, Be, Co, Mo, and U) in surface water, the potential contamination is estimated to be less than the MRL at the selected CRLs (*table 2*). As, Ba, Cd, Cr, Pb, Mn, Ni, Se, Ag, and Tl have potential contamination no greater than the MRL in 90 percent of the samples at the higher CRL. Similar to Pb in ground water, it appears that one sample that has a value of 6.3 µg/L in surface water is either contaminated or has been incorrectly coded as a blank sample. Also at the higher CRL, Cu has potential contamination of less than the MRL for at least 85 percent of the samples; Sr has potential contamination of less than the MRL for at least 75 percent of the samples; and B, Fe, and Zn have potential contamination of less than the MRL for at least 50 percent of the samples. Al has the potential for contamination in at least 50 percent of the samples, regardless of the MRL. Limited surface-water blank data for Li and V does not allow for an assessment on the potential contamination associated with the analysis of these trace elements in surface water.

The 95-percent UCL has been plotted for Al, Ba, B, Cu, Fe, Mn, Sr, and Zn for surface-water blank data at the selected CRLs (*figs. 3A and 3B and table 2*). In addition, the lower CRL has been plotted for Ba and Mn. As shown in *figures 3A and 3B*, the potential contamination varies depending on the trace element analyzed.

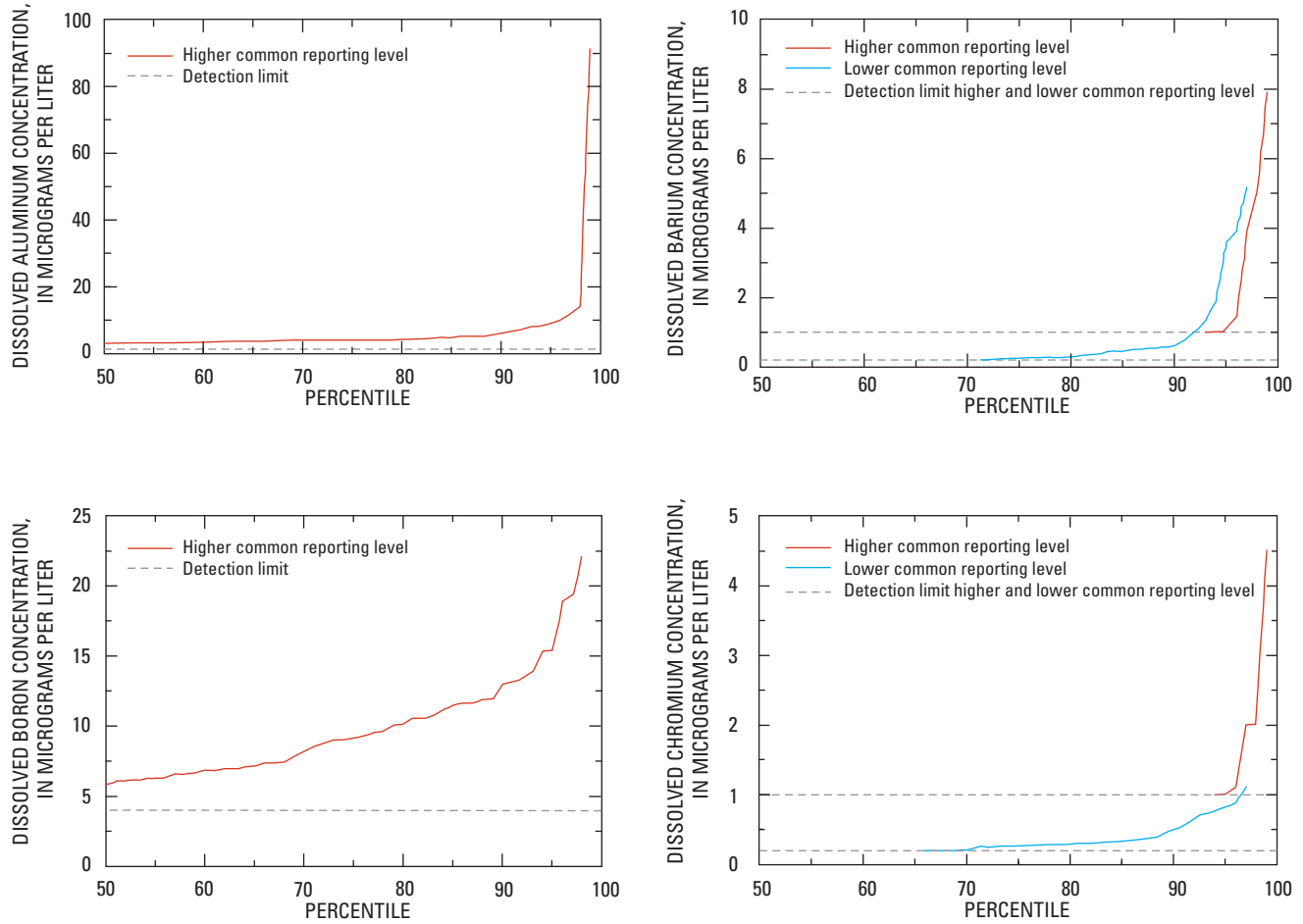


Figure 2A. Upper 95-percent confidence limits for contamination of aluminum, barium, boron, chromium, cobalt, copper, iron, manganese, nickel, strontium, and zinc that are based on data from ground-water field blanks.

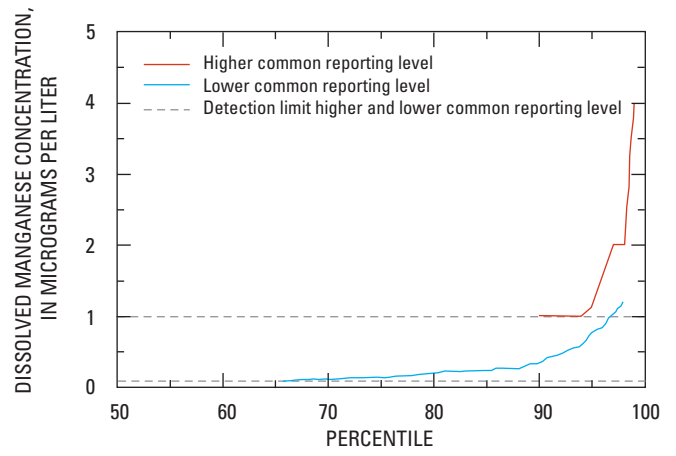
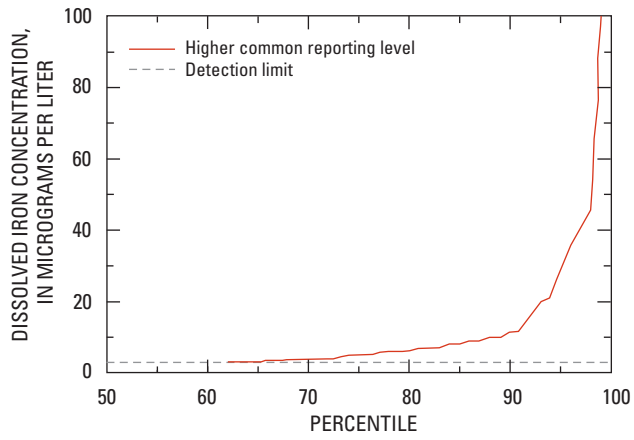
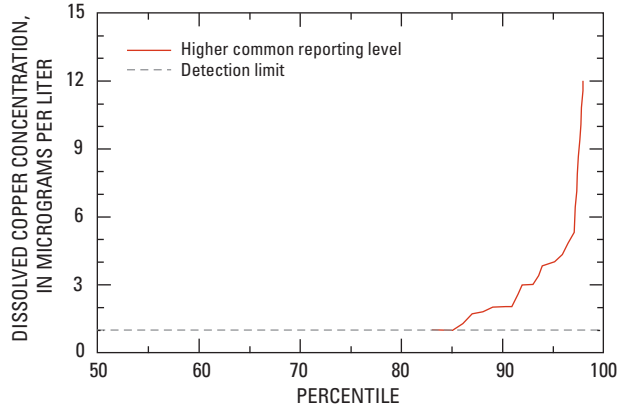
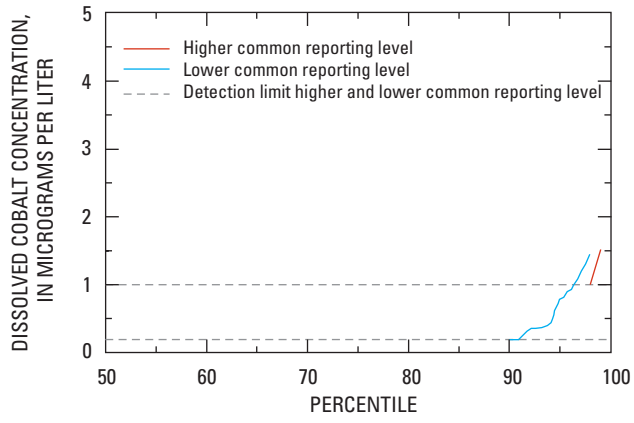


Figure 2B. Continued.

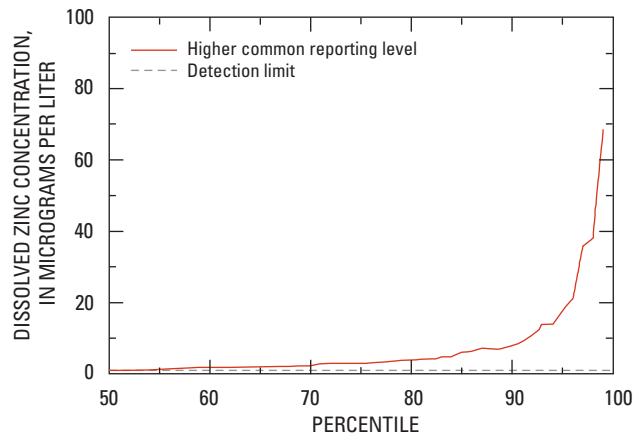
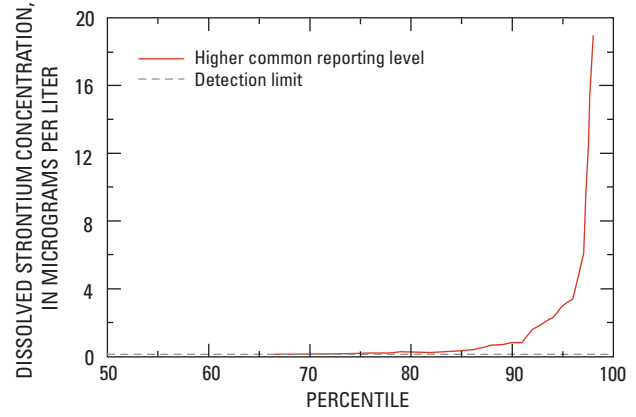
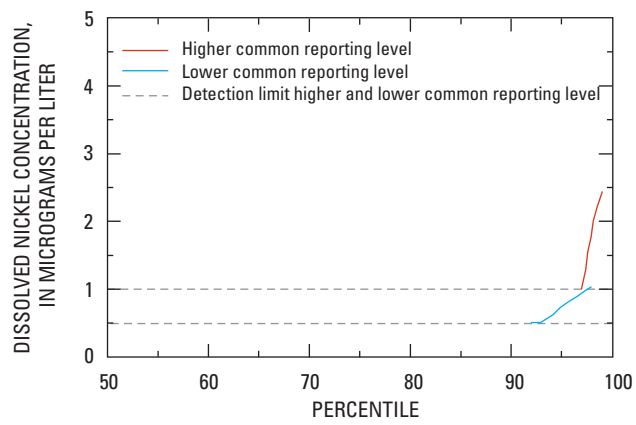


Figure 2C. Continued.

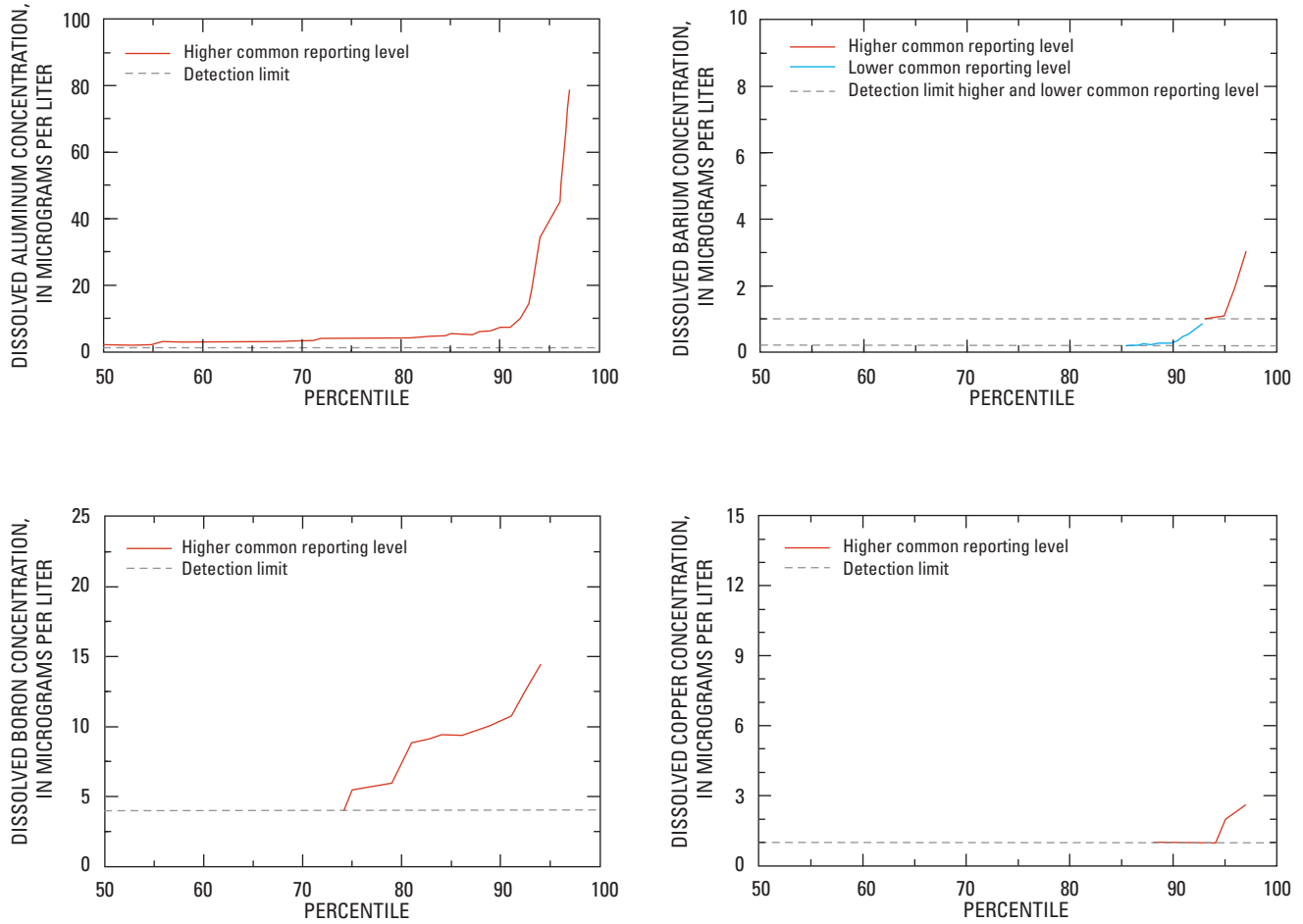


Figure 3A. Upper 95-percent confidence limits for contamination of aluminum, barium, boron, copper, iron, manganese, strontium, and zinc that are based on data from surface-water field blanks.

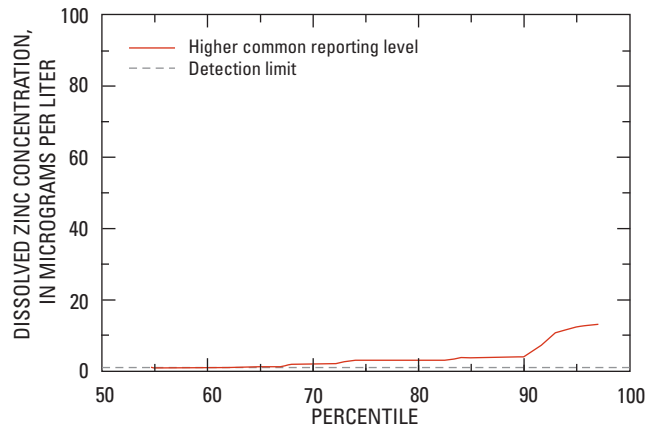
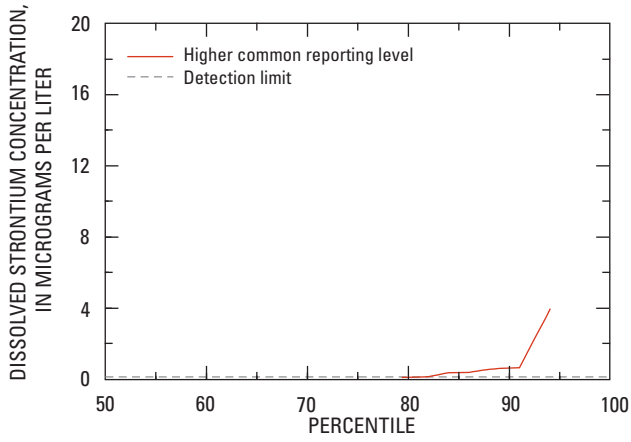
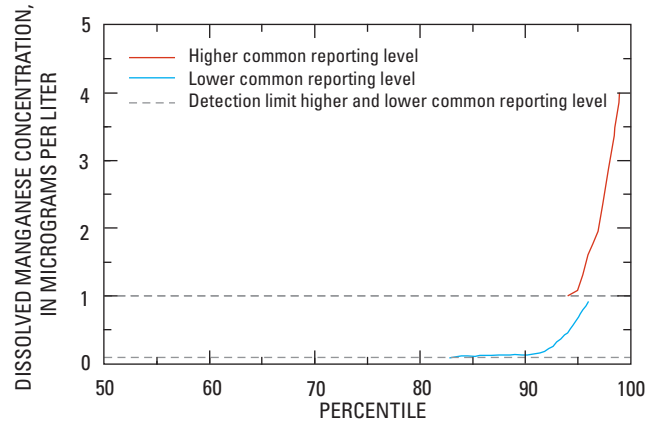
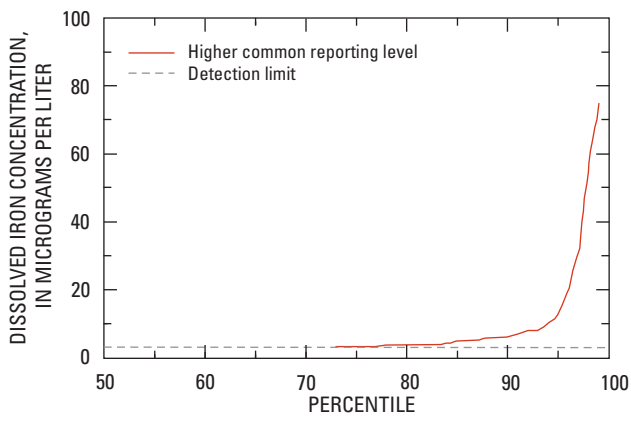


Figure 3B. Continued.

Trace Element and Radon Sample Variability

Field replicate data can be used to assess the overall variability that can affect the environmental samples. Information on the variability is important in determining the reproducibility of individual measurements, the likelihood that a measured value exceeds a standard, and the probability that two measured values are different. The replicate data are reviewed separately for ground water and surface water because environmental sample data will likely be aggregated and analyzed by ground-water or surface-water data. The numbers of replicate sets for each trace element and the number of consistent detections in the replicate sets for ground water and surface water are listed in *table 3*.

Ground Water

Sample variability can be estimated by calculating the SD and RSD of the replicate data sets and plotting these values with the mean concentrations for the trace elements and for Rn

determined for samples collected in Cycle I. The only trace element in ground water without any quantified concentrations in the replicate data sets is Ag; therefore, sampling variability cannot be determined for this trace element. The mean RSD was used to estimate the sample variability for Al, Sb, As, Ba, Be, Cd, Cu, Pb, Li, Mn, Mo, Se, Sr, Tl, and Zn (*table 4*). The reason for using this approach is that there is no consistency in the SD or RSD when plotted against the range of mean concentrations in the replicate data sets (see plots of Al and Cu; *figs. 4A, 4B, 4C, 4D, and 4E*). Using the mean RSD for estimating the sample variability for Be and Tl most likely is an overestimate because of the limited number of replicate data sets. Ideally, it is best to estimate the variability of the trace element detections for a range of concentrations over which the measure of variability is constant or relatively constant. Sample variability for B, Cr, Co, Fe, Ni, U, V, and Rn in ground water was determined for the low concentration range by using the SD and for the high concentration range by using the RSD (*table 4 and figs. 4A, 4B, 4C, 4D, and 4E*).

Table 3. Number of trace element ground-water and surface-water replicate sample sets and number of consistent detections within the replicate sets.

[—, no data]

Analytes	Number of replicate sample sets collected	Consistent detections (analyzed)	Number of replicate sample sets collected	Consistent detections (analyzed)
	Ground water		Surface water	
Aluminum	278	147	154	127
Antimony	350	41	113	8
Arsenic	369	202	125	60
Barium	276	272	119	119
Beryllium	348	7	118	1
Boron	143	128	95	83
Cadmium	275	28	123	16
Chromium	272	149	120	33
Cobalt	276	85	119	9
Copper	276	149	126	91
Iron	564	302	543	453
Lead	348	55	129	11
Lithium	108	99	45	25
Manganese	700	453	295	258
Molybdenum	348	206	130	77
Nickel	276	157	121	70
Radon	343	336	—	—
Selenium	350	112	156	58
Silver	345	0	123	1
Strontium	143	143	74	74
Thallium	102	8	13	1
Uranium	388	198	116	64
Vanadium	111	64	45	15
Zinc	276	180	126	85

Table 4. Estimated sample variability at measured concentrations in ground-water trace element data.

[pCi/L, picocuries per liter; RSD, relative standard deviation; SD, standard deviation; µg/L, microgram per liter; —, no data]

Analytes	Consistent detections		Consistent detections minus whole values		Low concentrations			High concentrations			Mean SD all ranges (µg/L or pCi/L)	Mean RSD all ranges (percent)	Mean concentration replicate sets		
	detections	values	Range (µg/L or pCi/L)	Number of replicate sets	Mean SD (µg/L or pCi/L)	Range (µg/L or pCi/L)	Number of replicate sets	Mean RSD (percent)	Minimum (µg/L or pCi/L)	Median (µg/L or pCi/L)			Maximum (µg/L or pCi/L)		
Aluminum	147	123	—	—	—	—	—	—	0.98	11.8	1.09	3.93	467		
Antimony	41	41	—	—	—	—	—	—	0.01	9.42	0.03	0.06	0.75		
Arsenic	202	125	—	—	—	—	—	—	0.33	7.62	0.16	1.92	108		
Barium	272	240	—	—	—	—	—	—	1.54	2.02	1.13	51.7	20,300		
Beryllium	7	7	—	—	—	—	—	—	0.06	6.23	0.05	0.12	7.71		
Boron	128	124	4.5–72.8	87	1.79	72.8–1,780	37	3.5	6.21	5.86	4.58	38.4	1,780		
Cadmium	28	28	—	—	—	—	—	—	0.15	13.1	0.02	0.08	4.18		
Chromium	149	120	0.51–2.39	63	0.19	2.39–30.2	57	9.6	0.36	11.5	0.51	2.37	30.2		
Cobalt	85	84	0.01–1.63	70	0.01	1.63–71.2	14	5.96	0.44	7.37	0.01	0.2	71.2		
Copper	149	138	—	—	—	—	—	—	0.69	10.3	0.15	1.96	403		
Iron	302	116	3.64–61.7	55	2.75	61.7–6,830	61	2.62	15.8	8.97	3.64	88.9	6,830		
Lead	55	48	—	—	—	—	—	—	0.23	12.5	0.04	0.39	9.12		
Lithium	99	99	—	—	—	—	—	—	1.24	7.06	0.35	3.88	164		
manganese	453	229	—	—	—	—	—	—	3.8	3.28	0.15	36.8	28,300		
molybdenum	206	152	—	—	—	—	—	—	0.14	3.51	0.16	2.84	188		
Nickel	157	131	0.03–1.20	36	0.08	1.20–52.3	95	9.01	0.26	11.2	0.03	1.96	52.3		
Radon (pCi/L)	336	336	44.5–697	240	19.9	697–211,000	96	4.13	49	5.85	44.5	435	211,000		
Selenium	112	89	—	—	—	—	—	—	0.4	10.3	0.26	1.9	41.1		
Silver	0	0	—	—	—	—	—	—	—	—	—	—	—		
Strontium	143	134	—	—	—	—	—	—	41.7	2.35	15.4	243	6,910		
Thallium	8	8	—	—	—	—	—	—	0.01	18.3	0.03	0.08	0.13		
Uranium	198	155	0.01–13.3	128	0.07	13.3–97.1	27	0.98	0.11	2.46	0.01	2.6	97.1		
Vanadium	64	64	0.12–1.77	23	0.16	1.77–171	41	10.9	1.17	15.2	0.12	2.35	171		
Zinc	180	156	—	—	—	—	—	—	2.78	11.8	1.03	7.25	5,190		

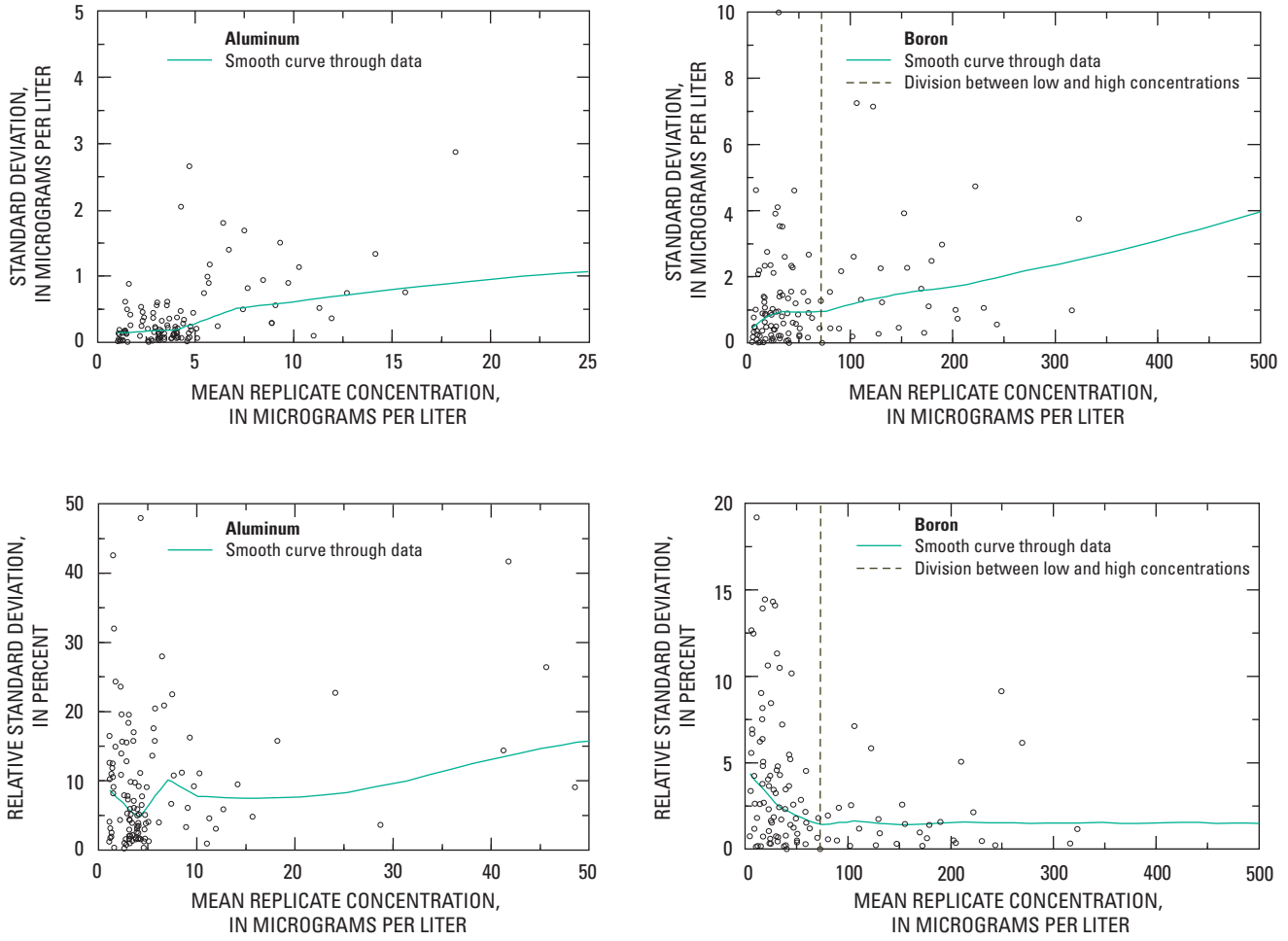


Figure 4A. Ground-water data used to select low and high ranges of replicate concentrations for select trace elements and radon.

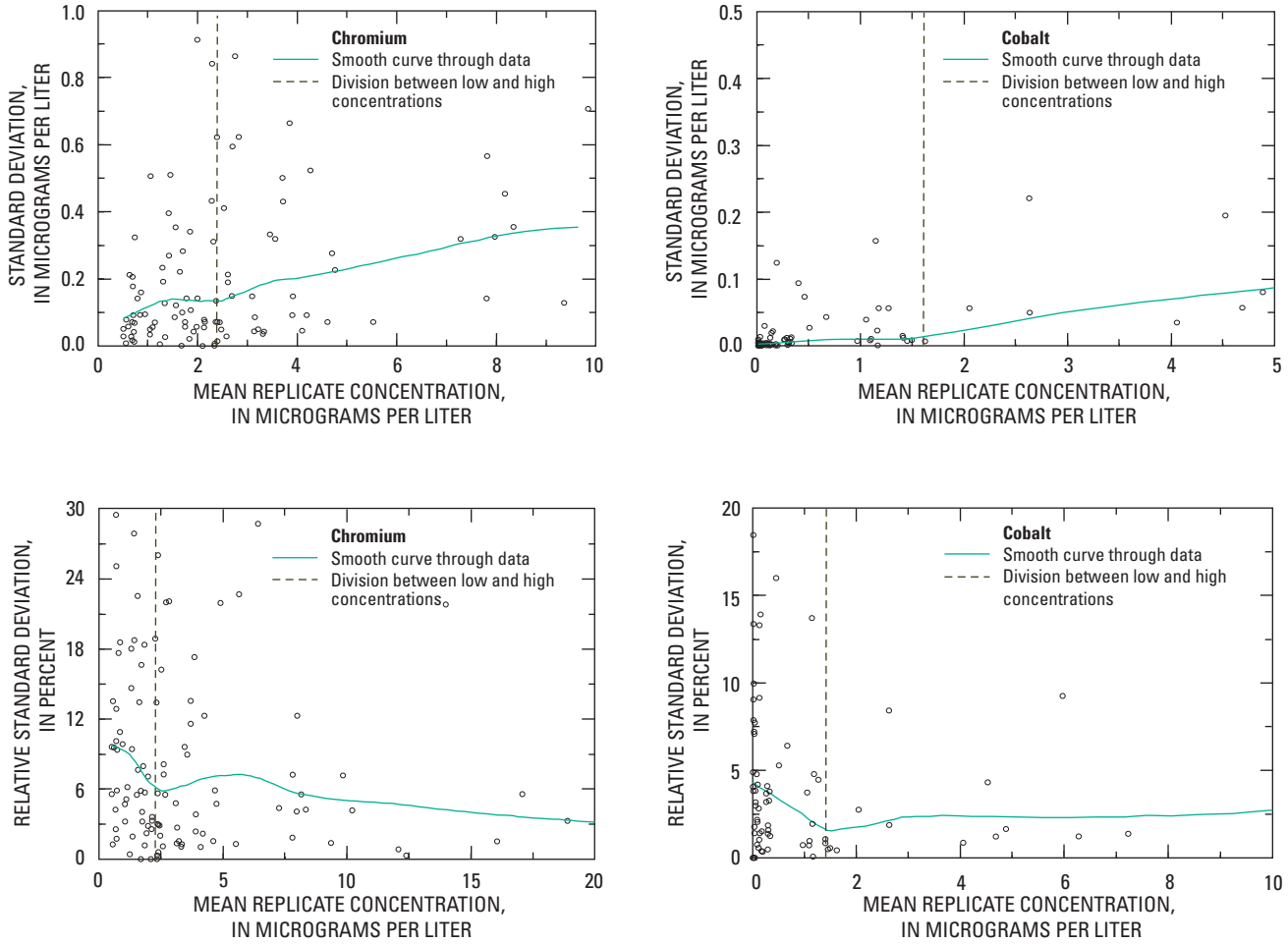


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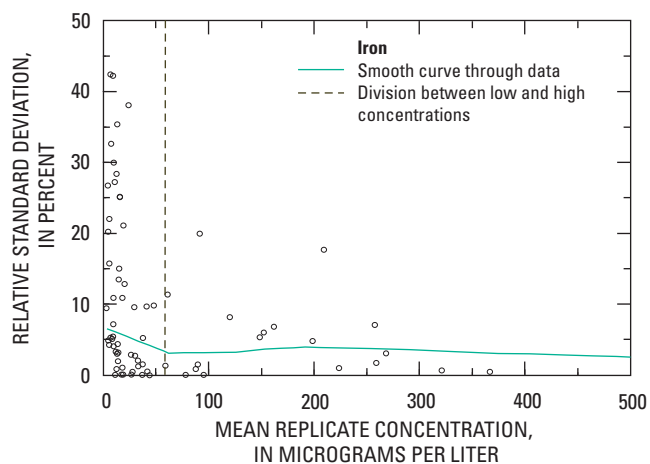
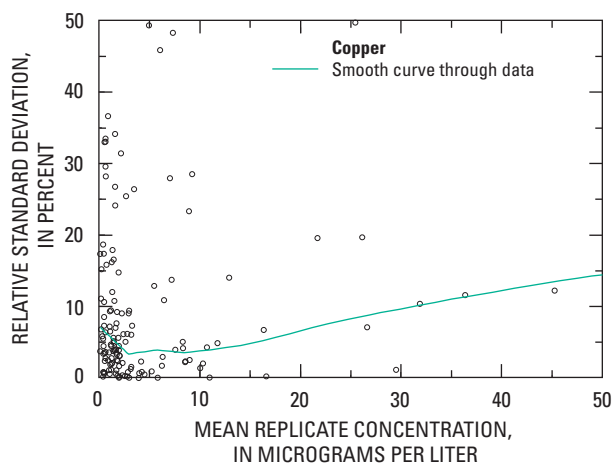
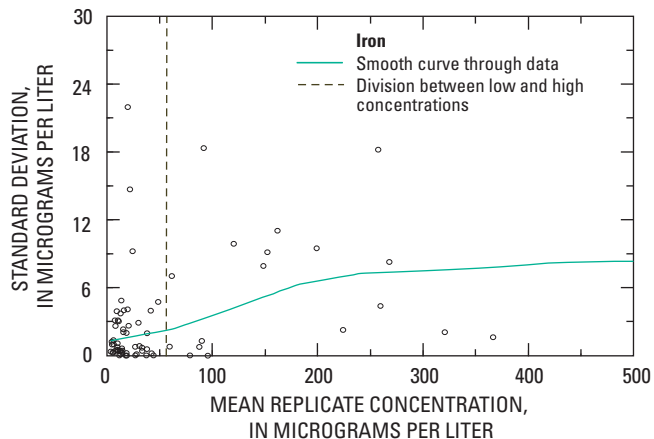
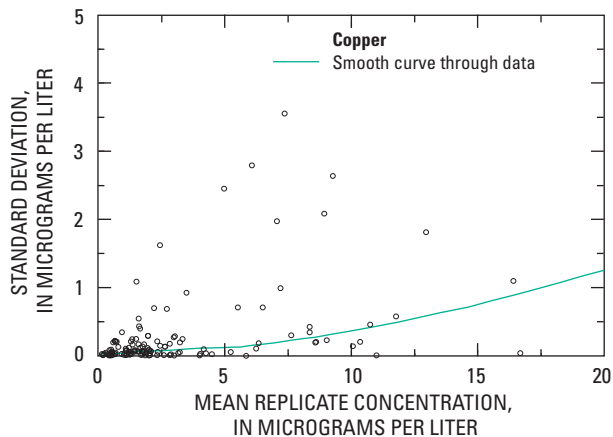


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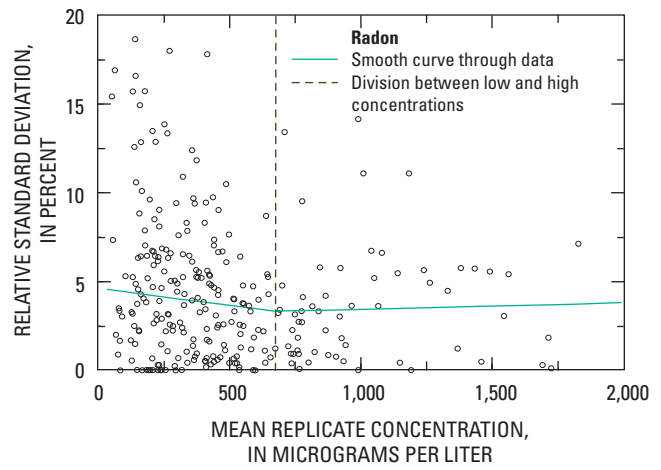
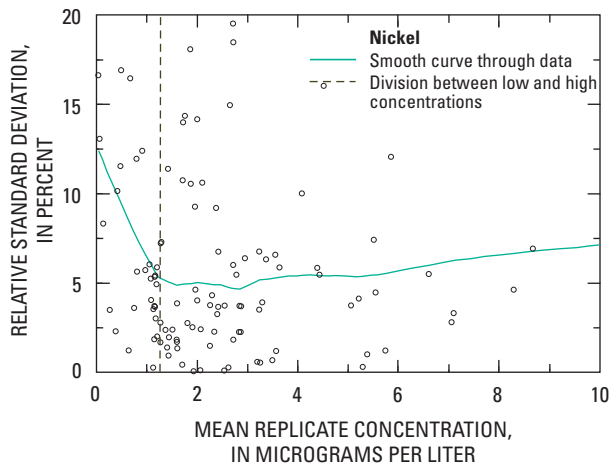
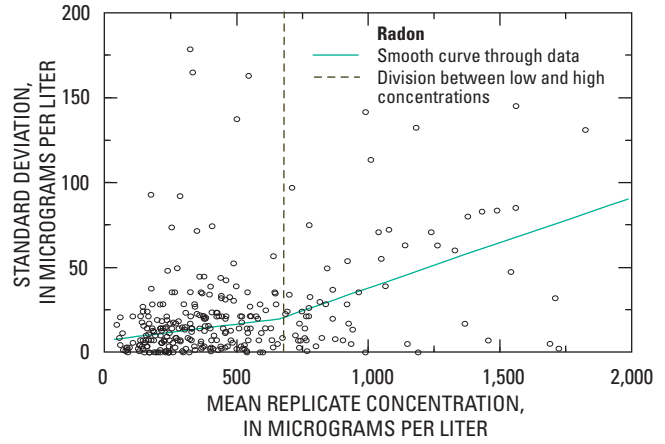
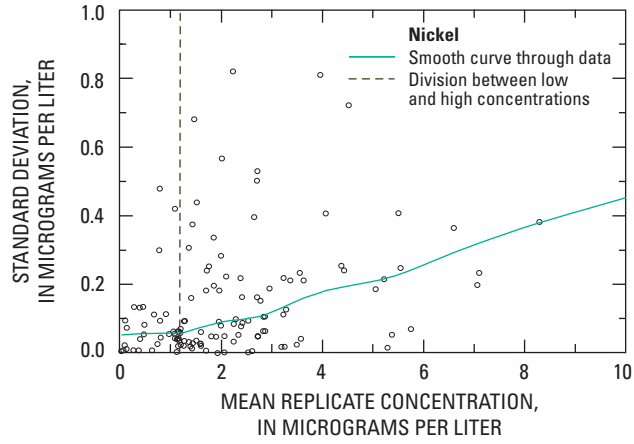


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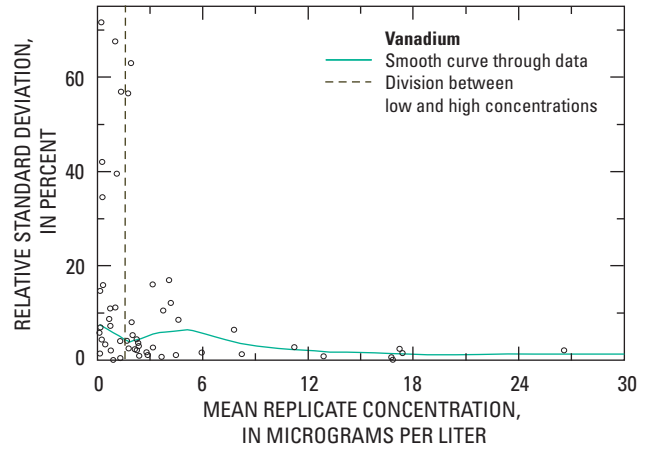
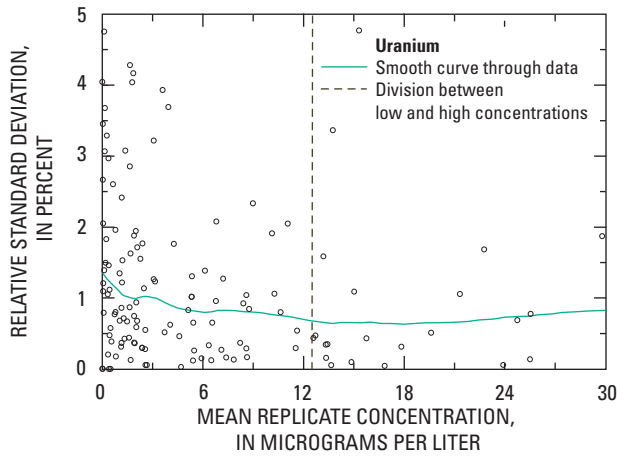
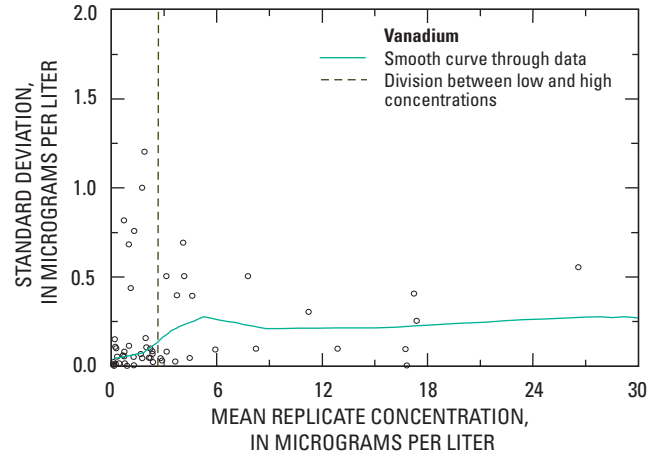
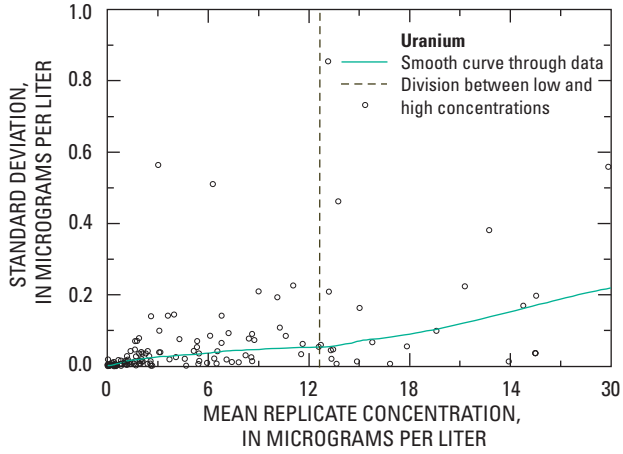


Figure 4E. Continued.

Confidence intervals for each trace element can be calculated using the estimated sample variability (*table 4*) and the appropriate statistic (Z) from a table of normal deviates. For a 95-percent confidence interval, the value of $\alpha = 0.05$ and the value of $Z_{(1-\alpha/2)} = 1.96$. As shown previously, it is possible to calculate the confidence limits of an individual measurement using equation 2 and the mean of multiple measurements using equation 3. For example, if U has a measured concentration of 2.5 $\mu\text{g/L}$ and an estimated sample variability for the concentration range of 0.07 $\mu\text{g/L}$ (*table 4*), then the 95-percent confidence interval can be calculated using equation 2.

$$[C_L, C_U] = 2.5 \pm 1.96 \times 0.07. \quad (4)$$

The inherent error associated with this measurement is ± 0.14 $\mu\text{g/L}$ or ± 5.49 percent of the measured concentration.

For a higher U concentration, such as 30 $\mu\text{g/L}$, the 95-percent confidence interval can be calculated using the same equation, but using the sample variability of 0.98 percent for the higher concentration.

$$[C_L, C_U] = 30 \pm 1.96 \left(30 \times \frac{0.98}{100} \right). \quad (5)$$

The inherent error associated with this measurement would be ± 0.57 $\mu\text{g/L}$ or ± 1.93 percent of the measured concentration. The confidence interval is relatively smaller for the larger concentration range.

In addition, a 95-percent confidence interval for a mean value of 2.5 $\mu\text{g/L}$ obtained from 10 measurements would have a smaller confidence interval than for an individual measurement, and can be calculated using equation 3:

$$[C_L, C_U] = 2.5 \pm 1.96 \times \frac{0.07}{\sqrt{10}}. \quad (6)$$

The error for 10 measurements would be ± 0.04 or ± 1.74 percent of the measured value. The sample variability for a mean of 10 measurements is less than it is for an individual measurement.

Surface Water

In surface water as with ground water, the sample variability can be determined by plotting the SD or RSD and the mean of the replicate data sets (*figs. 5A, 5B, and 5C and table 5*); however, only the mean RSD could be used to determine the variability for 11 of the trace elements (As, Ba, Cd, Li, Mo, Ni, Se, Sr, U, V, and Zn) because there is not a range in the data where either the SD or RSD are reasonably constant for the concentrations measured in the replicates sets (*table 5*). Using the mean of the RSD over the entire range of concentrations most likely overestimates the variability at high concentrations and underestimates variability at the low concentrations. Determination of the sample variability for Sb, Be, Cr, Co, Pb, and Tl, all of which have less than 10 replicate sets, overestimates the sample variability. Therefore, an accurate assessment of the sample variability cannot be made for these trace elements. In addition, as with ground water, the sample variability cannot be determined for Ag. For five trace elements (Al, B, Cu, Fe, and Mn) in surface water, the variability was determined for the low concentration range by SD and the high concentration range by RSD (*table 5 and figs. 5A, 5B, and 5C*).

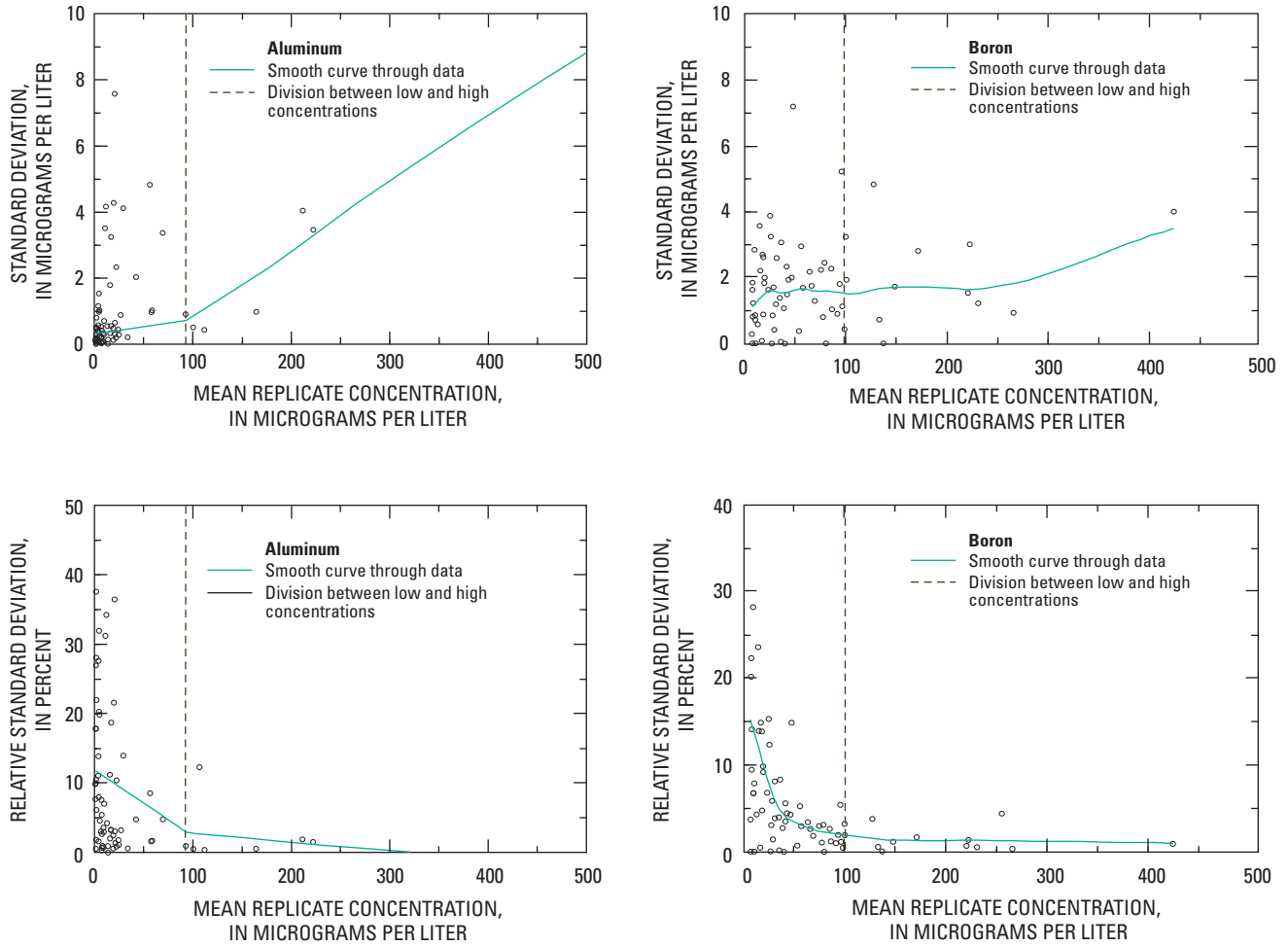


Figure 5A. Surface-water data used to select low and high ranges of replicate concentrations for select trace elements.

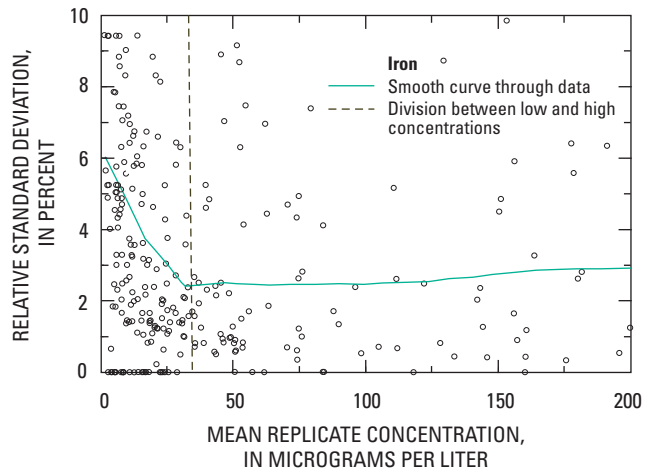
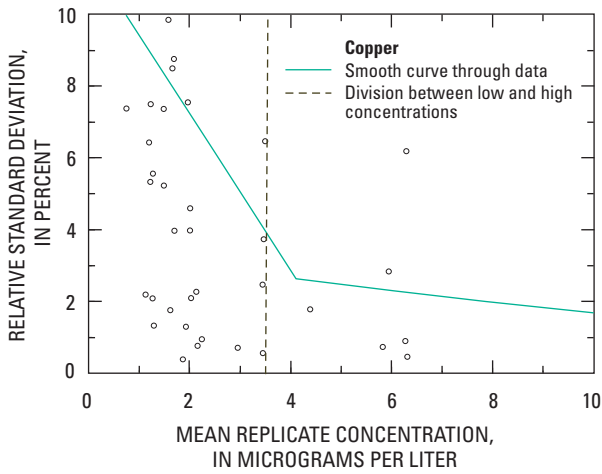
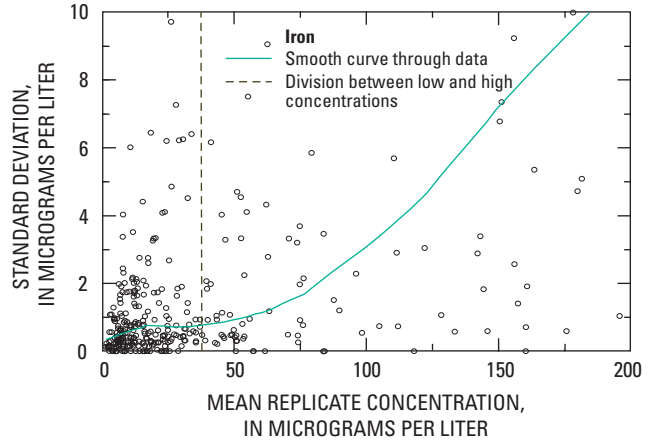
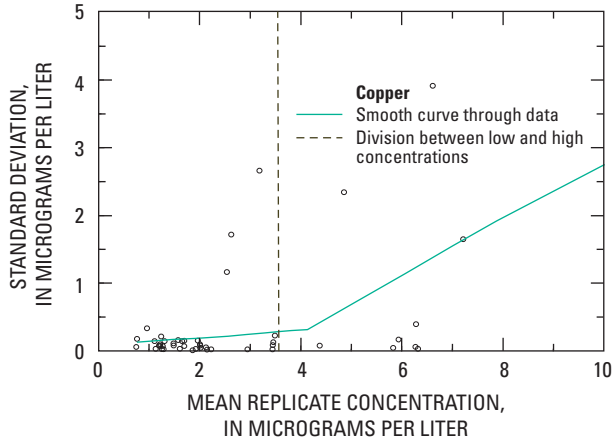


Figure 5B. Continued.

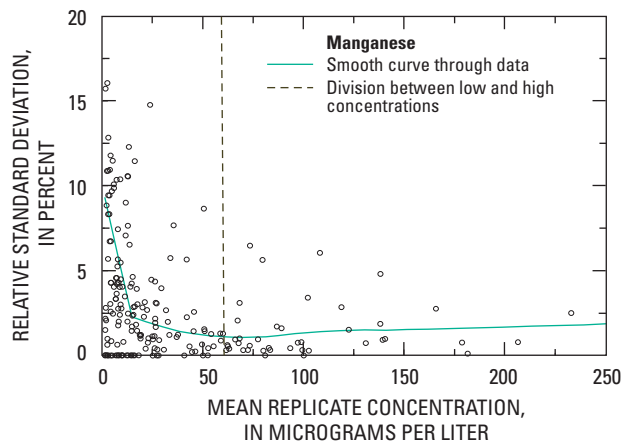
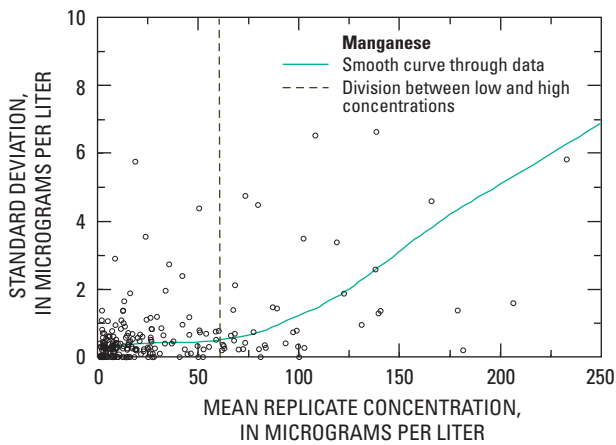


Figure 5C. Continued.

Table 5. Estimated sample variability at measured concentrations in surface-water trace element data.

[RSD, relative standard deviation; SD, standard deviation; µg/L, microgram per liter; —, no data]

Analytes	Consistent detections		Consistent detections minus whole values	Low concentrations			High concentrations			Mean SD all ranges (µg/L)	Mean RSD all ranges (percent)	Mean concentration replicate sets		
	127	8		Range (µg/L)	Number of replicate sets	Mean SD (µg/L)	Range (µg/L)	Number of replicate sets	Mean RSD (percent)			Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
				1.10–101	61	1.02	101–9,160	9	2.83					
Aluminum	127	8	70	1.10–101	61	1.02	101–9,160	9	2.83	4.89	8.7	1.1	13.3	9,160
Antimony	8	8	8	—	—	—	—	—	—	0.01	1.94	0.05	0.12	11.4
Arsenic	60	33	33	—	—	—	—	—	—	0.22	4.67	0.54	4.54	41.4
Barium	119	56	56	—	—	—	—	—	—	0.66	1.38	3.53	31.5	232
Beryllium	1	1	1	—	—	—	—	—	—	0.07	6.15	—	1.15	—
Boron	83	69	69	7.67–128	58	1.91	128–424	11	1.4	2.06	6.65	7.67	41.9	424
Cadmium	16	11	11	—	—	—	—	—	—	0.05	1.56	0.1	2.8	8.81
Chromium	33	7	7	—	—	—	—	—	—	0.06	4.8	0.6	1.6	3.95
Cobalt	9	8	8	—	—	—	—	—	—	0.06	3.17	0.05	1.02	15.7
Copper	91	48	48	0.75–4.39	37	0.23	4.39–336	11	13.1	0.42	11.6	0.75	2.01	336
Iron	453	381	381	1.42–33.3	235	1.07	33.3–5,730	146	5.53	4.81	7.23	1.42	23.2	5,730
Lead	11	9	9	—	—	—	—	—	—	0.06	3.51	0.08	1.7	20.1
Lithium	25	22	22	—	—	—	—	—	—	0.52	2.21	0.73	19	85
Manganese	258	226	226	1.44–61.9	173	0.58	61.9–3,030	53	2.76	1.34	4.97	1.44	17.6	3,030
Molybdenum	77	29	29	—	—	—	—	—	—	0.05	1.76	0.84	2.66	11.8
Nickel	70	31	31	—	—	—	—	—	—	0.23	8.17	0.26	1.97	11.8
Selenium	58	33	33	—	—	—	—	—	—	0.34	10.2	0.24	1.96	20.5
Silver	1	0	0	—	—	—	—	—	—	—	—	—	—	—
Strontium	74	51	51	—	—	—	—	—	—	4.18	1.2	24.3	110	2,200
Thallium	1	1	1	—	—	—	—	—	—	0.03	31.1	—	0.09	—
Uranium	64	28	28	—	—	—	—	—	—	0.17	1.51	0.18	7.41	50.2
Vanadium	15	14	14	—	—	—	—	—	—	0.34	4.5	1.46	5.7	31.4
Zinc	85	37	37	—	—	—	—	—	—	4.36	18.6	1.27	7.44	4,220

Implications of Quality Control Results to Environmental Data

Review of the QC data (blanks and replicates) is important when evaluating the effects of bias and variability associated with the environmental samples. Field blanks were collected in a manner similar to the collection of the environmental samples and, therefore, will reflect contamination bias associated with the environmental samples. Information on contamination can provide a more complete interpretation of the environmental data. Variability is important in determining the reproducibility of an individual measurement, the exceedance of a water-quality standard, or whether two measurements are different. Both of these variables are important when determining whether a water-quality standard has been exceeded.

Potential Effects of Contamination Bias

Calculation of the 95-percent UCL provides a measure of the uncertainty in the field blank contamination that can be used in evaluating the need to consider contamination in the analysis and interpretation of the trace element environmental data (*tables 1 and 2*). No evidence of contamination was identified for Sb, Be, Tl, and V in ground water and for Sb, Be, Co, Mo, and U in surface water; all concentrations were below the selected CRLs. For Li and V in ground water and surface water, additional data are needed to make an assessment of the potential contamination associated with these trace elements. For the other trace elements in ground water and surface water, evidence of contamination was identified, and this information can be used in evaluating the possible exceedances of the USEPA's drinking-water standards. Overall, if the potential contamination is less than 10 percent of the measured concentration, the effects of contamination on the measured value can be determined to be not significant (Mueller and Titus, 2005).

Contamination will likely not affect the measured concentrations for trace elements with USEPA drinking-water standards greater than 1,000 $\mu\text{g/L}$, such as Ba (2,000 $\mu\text{g/L}$, Maximum Contaminant Level [MCL]), Cu (1,300 $\mu\text{g/L}$, action level [AL]), Sr (4,000 $\mu\text{g/L}$, health advisory [HA]), or Zn (2,000 $\mu\text{g/L}$, HA) (U.S. Environmental Protection Agency, 2004). The potential contamination for these trace elements generally accounts for less than 1 percent of the drinking-water standard and is never more than 10 percent. Contamination is unlikely to cause problems with identifying exceedances of the USEPA drinking-water standards for these trace elements.

The trace elements As, Cd, Cr, Se, Tl, and U all have USEPA MCL drinking-water standards that range from 2 to 100 $\mu\text{g/L}$. In ground water, the maximum contamination identified for As, Cr, Se, Tl, and U is less than 10 percent of the USEPA's drinking-water standard for each trace element. The trace element Cd, however, which has a USEPA MCL of

5 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 2004), has a potential contamination of 1 $\mu\text{g/L}$ in 2 percent of the samples or 0.42 $\mu\text{g/L}$ in 3 percent of the samples. The contamination can account for up to 20 percent of the reported Cd concentration. In this case, contamination may affect the interpretation of some of the Cd data with respect to the USEPA drinking-water standard. For surface water, the maximum contamination identified for Cd, Cr, Se, and Tl is less than 10 percent of the USEPA drinking-water standard for each trace element. The maximum potential contamination observed for As in surface water is 1.25 $\mu\text{g/L}$ for at least 5 percent of the environmental samples. Contamination in about 5 percent of the surface-water samples may account for about 13 percent of the concentration.

For the trace elements B, Pb, Mn, Mo, Ni, and Ag, the USEPA drinking-water standards are either HA levels (B, 600 $\mu\text{g/L}$; Mn, 300 $\mu\text{g/L}$; Mo, 40 $\mu\text{g/L}$; Ni, 100 $\mu\text{g/L}$; and Ag, 100 $\mu\text{g/L}$) or an AL (Pb, 15 $\mu\text{g/L}$) (U.S. Environmental Protection Agency, 2004). For B, Mn, Mo, and Ni, the potential contamination is less than 5 percent of their USEPA drinking-water standard and will likely have little effect on the interpretation of the data with respect to this standard. The trace element Pb has a potential contamination in ground water and surface water that is greater than 10 percent of the USEPA drinking-water standard, but only in 3 percent or fewer of the blank samples.

The trace elements Al (50 to 200 $\mu\text{g/L}$) and Fe (300 $\mu\text{g/L}$) have USEPA Secondary Drinking Water Regulations (SDWR), which are non-enforceable Federal guidelines to address cosmetic and aesthetic effects of drinking water (U.S. Environmental Protection Agency, 2004). The potential contamination associated with Al at the 90th percentile in ground water and surface water is slightly greater than 10 percent of the lower end of the USEPA drinking-water standard. For Fe, the potential contamination in about 4 percent of the ground-water and surface-water samples is about 10 percent of the USEPA drinking-water standard.

The blank data for both ground water (*table 1*) and surface water (*table 2*) indicate that the maximum potential contamination for at least 95 percent of the samples is unlikely to be the cause of exceedances of the USEPA drinking-water standards for most of the trace element environmental data collected in Cycle I. Any issues related to contamination would likely affect only a small number of samples. In addition, the number of environmental samples that exceed the USEPA drinking-water standard (*table 6*) is typically less than 10 percent of the samples, and for about two-thirds of those trace elements, the potential contamination is less than 1 percent. Concentrations of Fe in ground water are exceptions, exceeding the SDWR for more than 20 percent of samples (*table 6*). Also, concentrations of Al in surface water exceed the lower end of the USEPA drinking-water standard in greater than 10 percent of the samples, and the contamination identified could affect the measured concentrations that are close to the lower end of the USEPA drinking-water standard.

Table 6. Summary of trace-element environmental ground-water and surface-water data collected from 1991 to 2002.

[Ag, silver; As, arsenic; B, boron; Ba, barium; Be, beryllium; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; Fe, iron; Pb, lead; Li, lithium; mg/L, milligram per liter; Mn, manganese; Mo, molybdenum; Ni, nickel; Sb, antimony; Se, selenium; Sr, strontium; Tl, thallium; U, uranium; USEPA, U.S. Environmental Protection Agency; V, vanadium; Zn, zinc; µg/L, microgram per liter; <, less than; —, no data]

	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe	Pb	Pb	Li	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	
USEPA Drinking-Water Standard ¹	250-200	36	310	32,000	34	600	35	31,000	—	51,300	3300	515	515	—	4300	40	4100	350	4100	4,000	32	330	—	42,000	
Common Reporting Level (mg/L)	1.0	1.0	1.0	1.0	1.0	4.0	1.0	1.0	1.0	1.0	3.0	1.0	1.0	0.3	1.0	1.0	1.0	1.0	1.0	0.1	0.1	1.0	1.0	1.0	
Ground Water																									
Number of samples	2,927	3,016	3,308	3,129	3,032	1,120	3,132	3,144	3,033	3,182	4,066	3,128	895	5,036	3,070	3,083	3,063	2,995	1,310	542	3,548	835	3,092		
Median	<1.0	<1.0	<1.0	54.3	<1.0	37.5	<1.0	1.1	<1.0	1.05	14	<1.0	6.74	7	<1.0	1.1	<1.0	<1.0	270	<0.1	<0.1	<1.0	1.4	4.89	
Maximum	1,450	6.3	550	5,050	18	3,380	16	148	684	2,040	81,000	479	1,230	28,200	4,730	666	93.5	8	44,000	0.72	553	190	3,290		
Number equal to or greater than the USEPA drinking-water standard	92	1	250	3	5	38	8	1	—	1	1,000	6	—	595	47	7	6	0	56	0	142	—	1		
Percent exceeding the USEPA drinking-water standard	3.14	0.03	7.56	0.1	0.16	3.39	0.25	0.03	—	0.03	24.7	0.19	—	11.8	1.53	0.23	0.2	0	4.27	0	4	—	0.03		
Surface Water																									
Number of samples	3,171	2,471	2,441	3,445	3,030	1,853	3,612	3,158	2,468	3,473	4,929	3,388	665	2,170	2,773	3,250	3,094	3,329	1,881	103	2,565	387	3,101		
Median	13.0	<1.0	<1.0	35	<1.0	54.3	<1.0	<1.0	<1.0	1.4	23.3	<1.0	13.9	7.77	<1.0	<1.0	<1.0	<1.0	140	<0.1	<0.1	<1.0	1.74	4	
Maximum	20,600	16.9	284	410	11	4,200	18.2	89	53.2	871	54,100	39	230	1,460	157	216	150	8	3,490	2.22	74	54.8	4,450		
Number equal to or greater than the USEPA drinking-water standard	492	15	126	0	1	61	88	0	—	0	227	9	—	23	8	3	13	0	0	1	27	—	52		
Percent exceeding the USEPA drinking-water standard	15.5	0.61	5.16	0	0.03	3.29	2.44	0	—	0	4.61	0.2	—	1.06	0.29	0.09	0.42	0	0	0.97	1.05	—	1.68		

¹U.S. Environmental Protection Agency, 2004.

²Secondary Drinking Water Regulation (SDWR): is a non-enforceable Federal guideline to address cosmetic or aesthetic effects of drinking water.

³Maximum Contaminant Level (MCL): the highest level of contaminant that is allowed in drinking water.

⁴Health Advisory (HA): is an acceptable drinking-water level for a chemical substance that is based on health effects information. HAs are not legally enforceable, but is a standard that serves as a guidance to assist Federal, state, and local officials.

⁵Action Level (AL): concentration of a contaminant that triggers treatment or other requirements that a water system must follow. For lead and copper, the action level is the level where 10 percent of the homes tested exceed the standard.

Potential Effects of Sample Variability

The sample variability determined for the trace elements analyzed in Cycle I can be used to (1) evaluate the confidence interval for an individual water-quality measurement or multiple measurements, (2) help determine whether a water-quality standard has been exceeded, and (3) help determine whether two water-quality measurements are different. These uses are explained in more detail below. Confidence intervals for trace elements and Rn (ground-water samples only) sampled in Cycle I that have USEPA drinking-water standards are calculated in *table 7* for the particular standard. The variability associated with each of these trace elements and Rn, as determined for ground water and surface water, are indicated in *tables 5* and *6*, respectively.

Confidence Limit for an Individual Water-Quality Measurement or Multiple Measurements

The influence of potential contamination on an individual water-quality measurement can be illustrated for selected concentrations of As. The trace element As has an MCL of 10 µg/L and a variability of 7.62 percent for ground water and 4.67 percent for surface water (*table 7*). The 95-percent confidence interval for As at a concentration of 10 µg/L ranges from 8.51 to 11.5 µg/L in ground water and from 9.08 to 10.9 µg/L in surface water. The potential error in the measurement from sample variability is ±1.49 µg/L in ground water or ±0.92 µg/L in surface water, which is a relative error of 14.9 percent for ground water and 9.2 percent for surface water. Although the relative error may be considered high, the absolute error is small (<1.5 µg/L). *Table 7* lists the variability for the other trace elements in ground water and surface water and for Rn in ground water. The potential errors associated with the sample variability will depend on the trace element analyzed.

The sample variability is less for a mean of ten measurements, and the confidence interval is smaller than it is for an individual water-quality measurement (*table 7*). For example, the 95-percent confidence interval for As in ground water at a concentration of 10 µg/L ranges from 9.54 to 10.5 µg/L, whereas the confidence interval ranges from 8.51 to 11.5 µg/L for an individual measurement. The relative error for 10 measurements is 4.7 percent compared with 14.9 percent for an individual measurement.

Exceedance of a Water-Quality Standard

Measured trace element concentrations are often compared with USEPA drinking-water standards to determine whether these standards have been exceeded. The variability

calculated for a particular trace element can be used to determine how much greater an individual measurement must be to assure that the water-quality sample has exceeded a standard. An upper confidence limit can be used to determine if the standard has been exceeded at a specified level of certainty. For example, for Cd that has an MCL of 5 µg/L, it is necessary to consider the sample variability in determining whether the standard has been exceeded. The 95-percent UCL can be calculated using equation 2 such that $\alpha = 0.05$ and $Z_{(1-\alpha/2)} = 1.645$ (Hahn and Meeker, 1991). For example, if the Cd concentration in ground water is 4.2 µg/L, then the UCL = $4.2 + [1.645 \times (4.2 \times 0.13)] = 5.1$ µg/L. If the Cd concentration in ground water is 4.1 µg/L, then the UCL = $4.1 + [1.645 \times (4.1 \times 0.13)] = 4.98$ µg/L. For Cd at a concentration of 4.1 µg/L or less, there is a 95-percent confidence that the standard has not been exceeded.

If there is bias associated with the analytical methods, then the upper confidence limit is not very useful in determining whether a water-quality standard has been exceeded. Therefore, a correction for bias would need to be applied before determining whether a water-quality standard has been exceeded.

Two Water-Quality Measurements are Different

The confidence intervals calculated from the replicate sample variability can be used to determine if two measurements (or means) are different. For example, if there is an overlap between the confidence intervals of two samples, then the measurements cannot be considered significantly different. If the confidence intervals do not overlap, then the differences in the measurements are significantly different.

For example, if Cd in ground water had a concentration of 5.0 µg/L, then the 95-percent confidence interval can be calculated using equation 2 for $Z_{(1-\alpha/2)} = 1.96$, which gives a confidence interval of 3.72–6.28 µg/L. A concentration of Cd at 6 µg/L would have a confidence interval of 4.46–7.54 µg/L. The confidence intervals for Cd concentrations between 5.0 and 6.0 µg/L overlap, and so, the two measurements cannot be considered significantly different. A concentration of 2.97 µg/L, however, would have a confidence interval of 2.16–3.64 µg/L and would be significantly different from a concentration of 5.0 µg/L. For other trace elements where the confidence intervals are much smaller, the change in concentration of a few tenths of a microgram per liter may indicate that the measurements were significantly different.

Table 7. Estimated sample variability and confidence intervals around U.S. Environmental Protection Agency drinking-water standards for select trace elements in ground water and surface water.

[pCi/L, picocuries per liter; RSD, relative standard deviation; USEPA, U.S. Environmental Protection Agency; µg/L, microgram per liter; —, no data]

Analytes	USEPA drinking-water standard ¹ (µg/L or pCi/L)	Estimated sample variability (percent, µg/L or pCi/L)		95-percent confidence interval for concentrations at the USEPA drinking-water standards (µg/L)			
		Ground water	Surface Water	Individual measurements		Mean of 10 measurements	
				Ground water	Surface water	Ground water	Surface water
Aluminum ²	³ 50–200	11.8	1.02 µg/L	38.4–61.6	48.0–52.0	46.3–53.7	49.4–50.6
Antimony	⁴ 6	9.42	—	4.89–7.11	—	5.65–6.35	—
Arsenic	⁴ 10	7.62	4.67	8.51–11.5	9.08–10.9	9.53–10.5	9.71–10.3
Barium	⁴ 2,000	2.02	1.38	1,920–2,080	1,950–2,050	1,980–2,030	1,980–2,020
Beryllium	⁴ 4	—	—	—	—	—	—
Boron ²	⁵ 600	3.50	1.40	559–641	584–616	587–613	595–605
Cadmium	⁴ 5	13.1	1.56	3.72–6.28	4.85–5.15	4.59–5.41	4.95–5.05
Chromium ²	⁴ 100	9.60	—	81.2–119	—	99.1–106	—
Cobalt ²	—	—	—	—	—	—	—
Copper ²	⁶ 1,300	10.3	13.1	1,040–1,560	966–1,630	1,220–1,380	1,190–1,410
Iron ²	³ 300	2.62	5.53	285–315	267–333	295–305	290–310
Lead	⁶ 15	12.5	—	11.3–18.7	—	13.8–16.2	—
Lithium	—	—	—	—	—	—	—
Manganese ²	⁵ 300	3.28	0.58 µg/L	281–319	299–301	294–306	300
Molybdenum	⁵ 40	3.51	1.76	37.3–42.8	38.6–41.4	39.1–40.9	39.6–40.4
Nickel ²	100	0.08 µg/L	8.17	99.8–100	84.0–116	100	95.0–105
Radon	⁴ 300 pCi/L	19.9 pCi/L	—	261–449	—	288–412	—
Radon	⁷ 4,000 pCi/L	4.13	—	3,680–4,320	—	3,900–4,100	—
Selenium	⁴ 50	10.3	10.2	39.9–60.1	40.0–60.0	46.8–53.2	46.8–53.2
Silver	⁵ 100	—	—	—	—	—	—
Strontium	⁵ 4,000	2.35	1.20	4,820–4,180	4,910–4,090	3,940–4,060	3,970–4,030
Thallium	⁴ 2	—	—	—	—	—	—
Uranium ²	⁴ 30	0.98	1.51	29.4–30.6	29.1–30.9	29.8–30.2	29.7–30.3
Vanadium ²	—	—	—	—	—	—	—
Zinc	⁵ 2,000	11.8	18.6	1,550–2,450	1,270–2,730	1,860–2,140	1,770–2,230

¹U.S. Environmental Protection Agency, 2004.

²See table 4 or 5 for variability of both low and high concentrations. For comparison with USEPA drinking-water standards the mean relative standard deviation (RSD) was used with the exceptions of nickel (Ni) and radon (Rn) in ground water and aluminum (Al) and manganese (Mn) in surface water where the standard deviation (SD) was used.

³Secondary Drinking Water Regulation (SDWR): is a non-enforceable Federal guideline to address cosmetic or aesthetic effects of drinking water.

⁴Maximum Contaminant Level (MCL): the highest level of contaminant that is allowed in drinking water.

⁵Health Advisory (HA): is an acceptable drinking-water level for a chemical substance that is based on health effects information. HAs are not legally enforceable, but is a standard that serves as a guidance to assist Federal, state, and local officials.

⁶Action Level (AL): concentration of a contaminant that triggers treatment or other requirements that a water system must follow. For lead and copper, the action level is the level where 10 percent of the homes tested exceed the standard.

⁷Alternative Maximum Contaminant Level (AMCL): Used for those states that create Multimedia Mitigation programs to address radon in indoor air.

Summary

Trace element field blank and replicate data collected for the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program during 1991–2002 were used to assess the bias and variability associated with trace element environmental concentrations in ground water and surface water. Field blanks are quality control (QC) samples that are used to measure the contamination that may be associated with the environmental water-quality samples. Field replicate QC samples can help evaluate the confidence interval for an individual water-quality measurement, determine whether a water-quality standard has been exceeded, and also determine whether two water-quality measurements are different. Trace element QC data are available for 23 trace elements: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), silver (Ag), strontium (Sr), thallium (Tl), uranium (U), vanadium (V), and zinc (Zn). In addition, replicate data for Rn in ground water were reviewed. Statistical analyses were used to estimate the likelihood of contamination bias and sample variability that would occur in the environmental samples. The 95-percent upper confidence limit (UCL) was calculated at select percentiles to assess the potential for trace element contamination. The 95-percent confidence intervals were calculated for sample variability.

Analysis of blank data indicates bias resulting from contamination is negligible for Sb, Be, and Tl in ground water and negligible for Sb, Be, Co, Mo, and U in surface water. Limited QC data for Li and V in ground water and surface water do not allow for a good assessment on the potential contamination associated with these trace elements.

Potential contamination was identified for Al, As, Ba, B, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Se, Ag, Sr, and Zn in ground water and surface water. Evidence of potential contamination was shown for Co, Mo, and U in ground water, and potential contamination was shown for Tl in surface water. When comparing the potential contamination of these trace elements with the U.S. Environmental Protection Agency's (USEPA) drinking-water standards, the contamination for most of these trace elements would have little or no effect on the trace element concentrations with respect to the USEPA drinking-water standards. Potential contamination associated with Al at the 90th percentile in ground water and surface water is slightly greater than 10 percent at the lower end of the USEPA drinking-water standard. Potential contamination for As in ground water is less than 10 percent of the USEPA drinking-water standard, but in surface-water contamination, contamination may account for 13 percent of the concentration at the 95th percentile. The trace element Cd has a potential contamination within about 20 percent of the USEPA drinking-water

standard at the 98th percentile in ground water and is less than the common reporting level (CRL) in surface water. The potential contamination identified for Pb may be biased high because of the presence of one sample in ground water and one sample in surface water that may either be contaminated or have been misidentified as QC blanks.

For most trace elements, there is no significant effect from contamination on the measured concentrations of the environmental samples in comparison to USEPA drinking-water standards. Median concentrations of the environmental samples for many trace elements in ground water and surface water during Cycle I are at or near the CRL. The number of environmental samples that exceed the USEPA drinking-water standards is typically less than 10 percent of the samples, and for about two-thirds of those trace element samples, exceedances are less than 1 percent. The exceptions may be Fe in ground water and Al in surface water, which have concentrations for at least 10 percent of the environmental samples that exceed the USEPA drinking-water standards. For these trace elements, it is possible that samples with concentrations close to the USEPA drinking-water standard would be affected by contamination.

In ground water and surface water, sample variability for Ag could not be determined because there were no detections in the replicate sets. For Be and Tl in ground water, the sample variability is overestimated because these trace elements have less than 10 replicate sets with detected concentrations. In addition for surface water, the sample variability is overestimated for Sb, Be, Cr, Co, Pb, and Tl, all of which have less than 10 replicate sets. Therefore, the sample variability for these trace elements cannot be determined. Depending on the trace element, sample variability can be small (less than 10 percent), which would have little or no effect on the reported concentration. For ground water, the trace elements with sample variability less than 10 percent are Sb, As, Ba, B, Cr, Fe, Mn, Mo, Ni, Sr, U, and Rn (at concentrations greater than 700 picocuries per liter) and for surface water, the trace elements with sample variability less than 10 percent are Al, As, Ba, B, Cd, Fe, Mn, Mo, Ni, Sr, and U. The other trace elements (ground water: Al, Cd, Cu, Se, Rn [at concentrations less than 700 picocuries per liter] and Zn; and surface water: Cu, Se, and Zn) have higher sample variability, but the variability is less than 20 percent. Also, the uncertainty in the mean concentration of multiple samples as a result of sample variability would be less than it is for an individual measurement. Sample variability needs to be considered when evaluating the potential error associated with a measurement.

Analysis of the trace element QC data collected from 1991 to 2002 can be used in the interpretation of the environmental water-quality data collected by the 52 NAWQA study units in Cycle I and in subsequent years. Additional QC data may be needed to obtain a better estimate on the bias and variability for some of the trace elements with limited data.

Glossary of Data-Quality Terms

Blank sample A sample prepared from water that is free of the analyte(s) of interest for determining contamination.

Concurrent replicates A set of samples that are collected at the same time and location.

Equipment blank Blank water that is passed through the entire sampling equipment system collected in a controlled environment, such as a laboratory, and subjected to identical collection, processing, preservation, and laboratory handling as used for environmental samples.

Field blank Blank water that is passed through the entire sampling equipment system onsite and subjected to identical collection, processing, preservation, transportation, and storage procedures and laboratory handling as used for environmental samples.

Replicates A set of samples that are collected close in time and space and in a manner so that the samples are thought to be identical in composition.

Sequential replicates A set of samples that are collected consecutively, generally one after the other.

Source-solution blank A sample of blank water taken directly from the source container without exposure to any sampling equipment.

Split replicates A single sample that is divided into two or more equal subsamples.

Water year A continuous 12-month period selected to present data relative to hydrologic or meteorological phenomena during which a complete annual hydrologic cycle normally occurs. The water year used by the U.S. Geological Survey runs from October 1 through September 30 and is designated by the year in which it ends.

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