A product of the California Groundwater Ambient Monitoring and Assessment Program

Prepared in cooperation with the California State Water Resources Control Board

Updated Study Reporting Levels (SRLs) for Trace-Element Data Collected for the California Groundwater Ambient Monitoring and Assessment (GAMA) Program Priority Basin Project, October 2009–October 2018

Scientific Investigations Report 2020–5034

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

Cover: A GAMA field crew member collecting a field blank, photograph taken by George L. Bennett V, July 2019.

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Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
	Volume	
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
	Mass	
microgram (µg)	$3.527e^{-8}$	ounce, avoirdupois (oz)

Supplemental Information

Concentrations of chemical constituents in water are given in micrograms per liter (µg/L).

Abbreviations

AL-US	U.S. Environmental Protenction Agency Action Level
BD-90/90	90th percentile concentrations calculated using the binomial probability distribution for greater than 90 percent confidence
GAMA	Groundwater Ambient Monitoring and Assessment Program
IBW	inorganic blank water
LEP	laboratory evaluation process
NAWQA	National Water-Quality Assessment Program (USGS)
NWQL	National Water Quality Lab
OWQ	Office of Water Quality
PBP	Priority Basin Project
QA	quality-assurance
QC	quality-control
QSB	Quality Systems Branch
SRL	study reporting level
SWRCB	California State Water Resources Control Board
USGS	U.S. Geological Survey

Updated Study Reporting Levels (SRLs) for Trace-Element Data Collected for the California Groundwater Ambient Monitoring and Assessment (GAMA) Program Priority Basin Project, October 2009–October 2018

By George L. Bennett V

Abstract

Groundwater samples have been collected in California as part of statewide investigations of groundwater quality conducted by the U.S. Geological Survey for the Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project (PBP) since 2004. The GAMA-PBP is being conducted in cooperation with the California State Water Resources Control Board to assess and monitor the quality of groundwater resources used for public and domestic drinking-water supply and to improve public knowledge of groundwater quality in California. Quality-control samples (including but not limited to field, equipment, and source-solution blanks) were collected to evaluate and quantify the quality of the groundwater sample results.

The GAMA-PBP previously determined study reporting levels (SRLs) for trace-element results based primarily on field blanks collected in California from May 2004 through March 2013. SRLs are raised reporting levels used to reduce the likelihood of reporting false detections attributable to contamination bias. The purpose of this report is to identify any changes in the pattern or magnitude of concentrations or detections in field blanks since the last evaluation that would require changing or ending the use of SRLs implemented in October 2009. Constituents analyzed were aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, hexavalent chromium, cobalt, copper, iron, lead, lithium, manganese, molybdenum, nickel, selenium, silver, strontium, thallium, uranium, vanadium, and zinc.

For this review, data from 167 field blanks collected from October 2009 through October 2018 by the GAMA-PBP for trace elements were compiled. Based on a consistent pattern of decreasing cobalt and manganese concentrations in field blanks from 2009 to 2013, the GAMA-PBP decided to reevaluate all trace-element SRLs, effectively setting an end date for previously defined SRLs. Beginning October 2013, SRLs would be determined from field-blank data collected through October 2018. The detection frequency and upper limit of potential contamination bias (BD-90/90) were determined from field blanks for each trace element. The BD-90/90, that is, the upper 90-percent confidence limit of the 90th percentile concentration of potential extrinsic contamination, was calculated by assuming the binomial probability distribution. These results were compared to each constituent's detection limit to determine whether an SRL was necessary to minimize the potential for detections in the groundwater samples, attributed principally to contamination bias. Results of the evaluation were used to set SRLs for trace-element data collected by the GAMA-PBP between October 2013 and October 2018. Trace elements prescribed an SRL based on this review were hexavalent chromium, cobalt, copper, lead, and zinc. This review also resulted in the removal of SRLs from iron, manganese, molybdenum, and nickel. Although an SRL for hexavalent chromium could not be evaluated in the earlier reviews because the data were not collected regularly until 2015, one was established herein as 0.34 micrograms per liter (µg/L). The SRL for cobalt, as previously implemented, had been to reject all results; it was changed to 0.16 µg/L following a reduction in cobalt field-blank detection frequency resulting from mitigation steps, starting in 2014, aimed at reducing contamination bias introduced by high-capacity capsule filters used during sample collection. The SRL for copper did not change, and the SRL for lead changed very little based on this review. Lastly, the SRL for zinc was lowered from 6.2 µg/L to 3.9 µg/L.

Introduction

To assess the quality of ambient groundwater in aquifers used for public and domestic drinking-water supply and to establish a baseline groundwater-quality monitoring program on a statewide scale, the California State Water Resources Control Board (SWRCB), in cooperation with the U.S. Geological Survey (USGS), implemented the Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project (PBP).

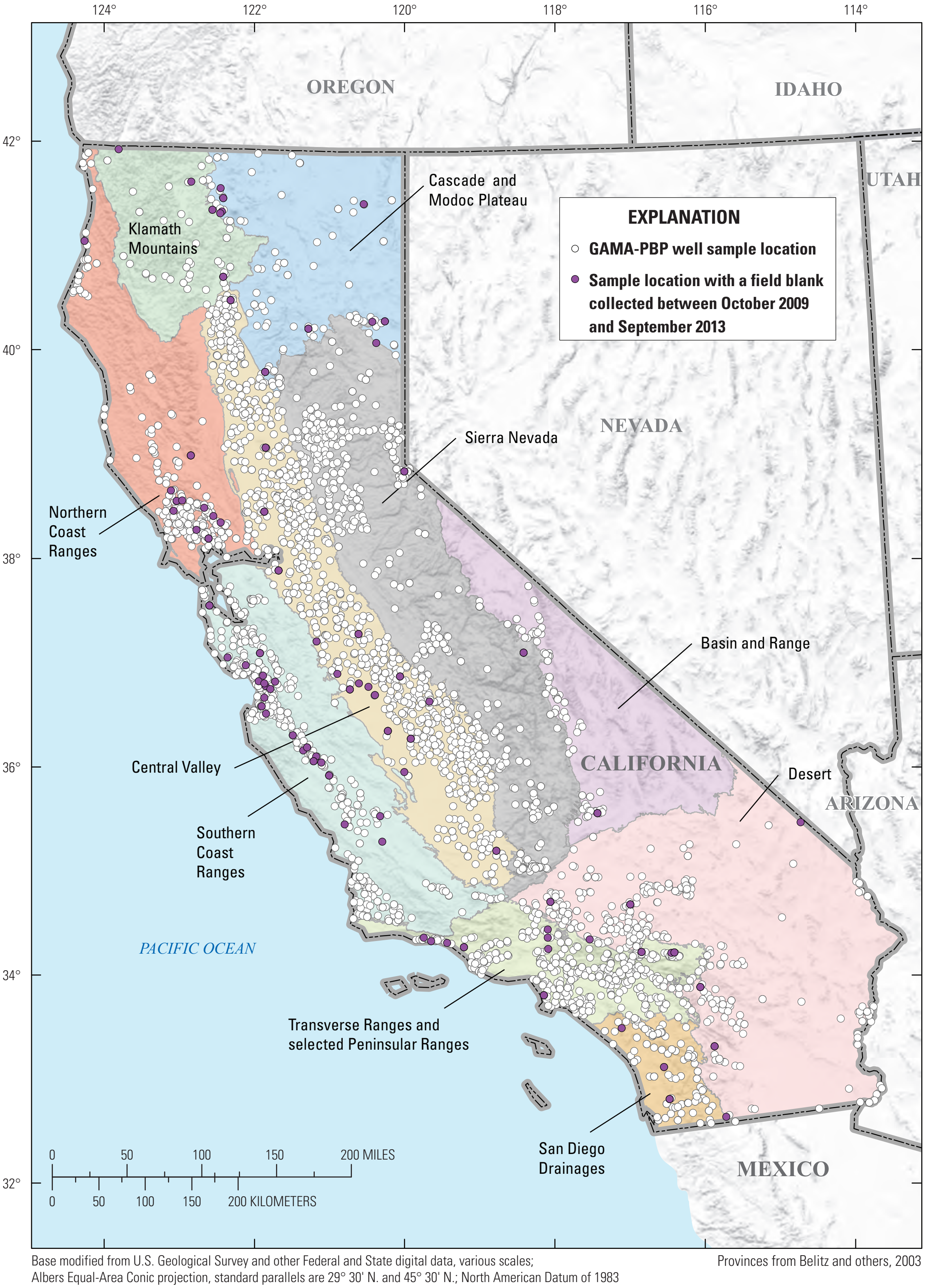
The GAMA-PBP follows a rigorous quality-assurance (QA) plan based on modified versions of protocols defined by the USGS National Water-Quality Assessment (NAWQA) Program (Koterba and others, 1995) and the National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated). Specific modifications are detailed in Bennett and Fram (2014) and Shelton and Fram (2017). Quality-control (QC) samples were collected at about 10 percent of the wells to evaluate potential contamination, as well as bias and variability of the data that may have resulted from sample collection, processing, storage, transportation, and laboratory analysis. The QC samples included field, source-solution, and equipment blanks, replicates, and matrix spikes. This report focuses on results from field, source-solution, and equipment blanks. A field blank is a QC sample collected in the field in the same manner as the environmental sample that exposes it to all aspects of sample collection while using bottled water certified to be free of the target analytes. A source-solution blank is collected in the field using a freshly opened bottle of blank water (source solution) that is poured directly into the sample bottles and sent to the lab to confirm the source solution is free of the target analytes. An equipment blank is a sample collected in a clean environment using just the portable pump used in the field to collect field blanks. This allows for the assessment of contamination of samples by the portable pump and the effectiveness of the pump cleaning procedures.

Groundwater samples collected for the GAMA-PBP were analyzed for a suite of constituents, including trace elements. Trace elements occur naturally and help define water characteristics and quality. Trace-element occurrence and concentration can also be affected by anthropogenic influences. The primary laboratory used to analyze most of the samples is the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado. Since 2015, Weck Laboratories, Inc. (hereinafter referred to as Weck), in City of Industry, California, was contracted to analyze samples for hexavalent chromium (Cr[VI]) for the GAMA-PBP. Between October 2009 and September 2013, 90 trace-element field blanks were collected by the GAMA-PBP (fig. 1). Trace-element field blanks were also collected from 77 sites between October 2013 and October 2018 (fig. 2). Of those 77 sites, 51 had Cr(VI) field blanks collected at them.

This QC evaluation examines blanks collected for trace element and Cr(VI) analysis and is focused on controlling the risk of reporting false positives. The GAMA-PBP uses laboratories that have very-low method detection limits (parts per billion), and previous QC evaluations of field blanks by the GAMA-PBP identified low-level contamination of select trace elements and established study unit reporting levels (SRLs) for those constituents (Olsen and others, 2010; Davis and others, 2014). This report, like Olsen and others (2010) and Davis and others (2014), establishes SRLs in order to reduce false positives. Established SRLs are far less than any regulatory or non-regulatory benchmark for drinking water and have little effect on the interpretation of trace-element results where the focus is generally on detections with concentrations greater than one-half of the benchmark concentrations used to provide context to the results.

Purpose and Scope

This report describes the evaluation of data derived from 167 trace-element field blanks and 19 source-solution blanks collected along with groundwater samples from October 2009 through October 2018 by the GAMA-PBP. Data from 51 field and 7 source-solution blanks for Cr(VI) were also included in the evaluation. Additionally, data from 8 blanks collected to test the portable pumps used to collect blanks in the field (equipment blanks) were also compiled and analyzed. Only 5 of the equipment blanks included analyses of Cr(VI). Using a simplified version of the methodology developed and detailed in Olsen and others (2010) and revisited in Davis and others (2014), this evaluation determined when trace-element contamination bias in field blanks changed and updates the SRLs most recently defined by Davis and others (2014) based on the available blank results. The updated SRLs were set to minimize potential contamination bias in groundwater-quality results while maintaining consistent and accurate reporting levels for comparison and interpretation of data over extended periods of time. Trace-element field blanks collected by the GAMA-PBP during the previous evaluation of Davis and others (2014) were included as a basis of comparison for more recent field blanks presented in this report.



Base modified from U.S. Geological Survey and other Federal and State digital data, various scales;
Albers Equal-Area Conic projection, standard parallels are 29° 30′ N. and 45° 30′ N.; North American Datum of 1983

Provinces from Belitz and others, 2003

Figure 1. Hydrologic provinces, locations of wells sampled for the Groundwater Ambient Monitoring and Assessment Priority Basin Project (GAMA-PBP) Aquifer Assessments 2004–18, and sample locations of trace-element field blanks between October 2009 and September 2013.

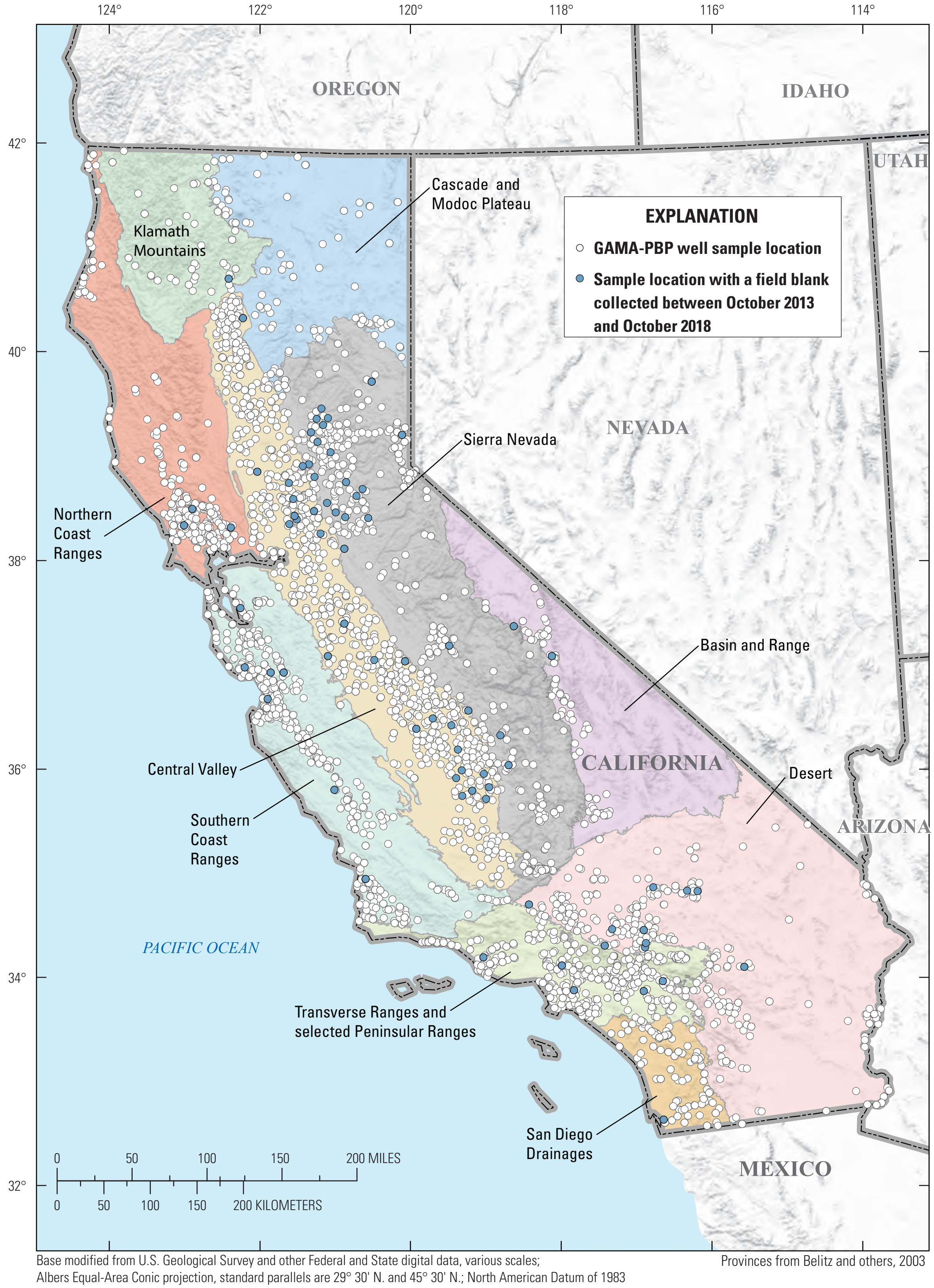


Figure 2. Hydrologic provinces, locations of wells sampled for the Groundwater Ambient Monitoring and Assessment Priority Basin Project (GAMA-PBP) Aquifer Assessments 2004–18, and sample locations of trace-element field blanks between October 2013 and October 2018.

Methods

This investigation used specific methods to collect groundwater and associated QC samples, analyze these samples and report the results, compile the field QC data, and evaluate the combined data to characterize any potential bias that could affect the groundwater sample results. These methods are described below.

Methods for Collecting Samples for Trace Element and Hexavalent Chromium Analysis

Environmental sample collection for trace-element analysis (NWQL) and Cr(VI) analysis (Weck) followed modified protocols developed by the NAWQA Program (Koterba and others, 1995) and the USGS National Field Manual (U.S. Geological Survey, variously dated; Bennett and Fram, 2014; Shelton and Fram, 2017). The protocols were developed to ensure that the samples are representative of the aquifer being sampled and that they are handled consistently from site to site thereby minimizing the potential for contamination. A thorough description of the entire process is provided in Davis and others (2014).

Field blanks were collected at about 10 percent of GAMA-PBP sites in order to determine if contamination of the samples is occurring that could be attributed to the equipment or procedures used in the field or at the laboratory. Field blanks for trace elements and Cr(VI) were collected using a portable diaphragm pump. Inorganic blank water (IBW) was pumped through the fittings of the pump, spigot, and sample line. Certified IBW was obtained from the NWQL. Teflon tubing was used at the pump inlet and outlet to connect to the sample-collection equipment. Field blanks were collected at well or spring sites by pumping at least 4 to 8 liters (L) of IBW through the clean sample-collection equipment to simulate the well-purging step before collecting the sample. Following this purge, IBW was pumped through the equipment to be collected as blank samples, following the same protocols as were used for the groundwater samples, including filtration and preservation. For this assessment and that of Davis and others (2014), it was assumed that the portable pump equipment used to pump IBW through the sample equipment was not a significant source of contamination when cleaned regularly. Eight blanks were collected to test this assumption; for these, the IBW contacted only the pump equipment (equipment blanks).

Source-solution blanks were collected whenever a new lot of IBW was shipped from the NWQL to verify that the IBW used for the field blanks was free of analytes of interest. Source-solution blanks were collected by pouring IBW directly into sample containers that were then preserved, stored, and shipped in the same manner as the groundwater samples. Source-solution blanks were used to supplement analyses that had been performed at the NWQL in certifying the quality of the IBW.

Laboratory Quality Control and Certification

The NWQL (D.L. Stevenson, U.S. Geological Survey, written commun., 2013) and Weck follow thorough QA plans, and both labs conduct laboratory QC, including laboratory method blanks, continuing calibration verification checks, reagent spikes, certified standard reference materials, and external blind proficiency samples. The NWQL maintains certification by the National Environmental Laboratory Accreditation Program (NELAP) and other certifications (U.S. Geological Survey, 2019a), and Weck maintains certification with the California Department of Public Health, Environmental Laboratory Accreditation Program (ELAP), and other certifications (Weck Laboratories, Inc., 2019).

The Quality Systems Branch (QSB) within the USGS Water Mission Area (formerly the Branch of Quality Systems [BQS] within the Office of Water Quality) maintains independent oversight of QA at the NWQL and coordinates blind testing of blanks and reference samples through the Inorganic Blind Sample Project (U.S. Geological Survey, 2019b). The GAMA-PBP prepares an annual Laboratory Evaluation Process (LEP) for USGS and non-USGS laboratories including Weck. The LEPs present a compilation and review of the in-house QC results provided by the laboratory. LEPs are designed to ensure projects are continuously working with laboratories to ensure data-quality objectives defined by each project are being met.

Data Analysis Methods for Evaluating Bias

Four tools were used to evaluate the trace-element field-blank data: (1) time-series plots, (2) detection frequencies, (3) 90th percentile concentrations calculated by using the binomial probability distribution for greater than 90 percent confidence, referred to as the “BD-90/90 concentration” by Olsen and others (2010) and Davis and others (2014), and (4) the Wilcoxon rank-sum test, a non-parametric statistical method used to compare two independent groups of data to determine if there are significant differences between the groups (Helsel and Hirsch, 2002). These tools were used to identify any changes in the frequency and concentrations of detections in field blanks so that SRLs could be revised, if necessary.

Time-series plots facilitate visual identification of trends or temporal components in the data, which might correspond to changes in the conditions under which the field blanks or groundwater samples were collected. Time-series plots of blank results were prepared for all constituents (figs. 3–8).

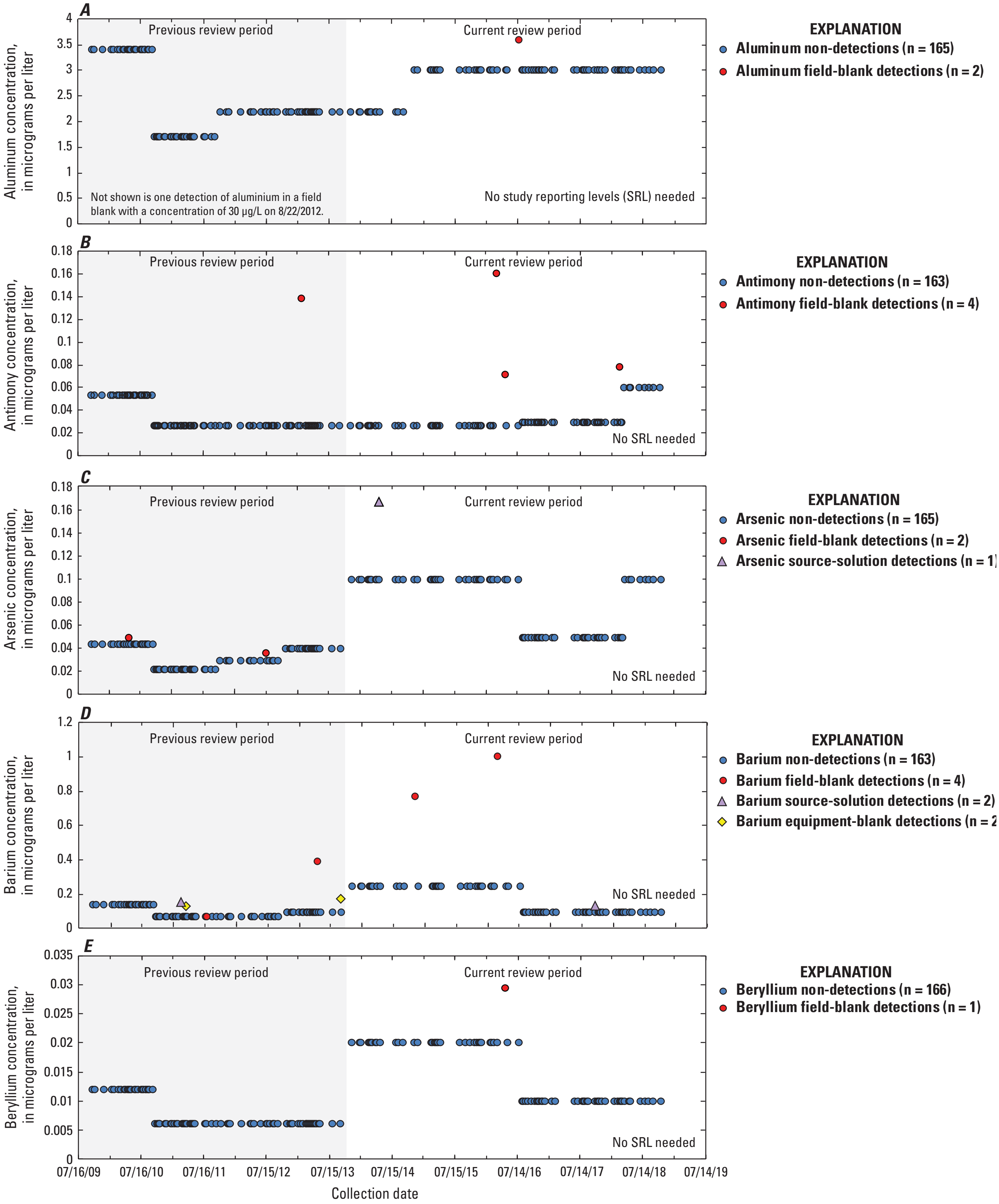


Figure 3. Trace-element concentrations in field, source-solution, and equipment blanks (when detected) and study reporting levels (SRLs) for constituents detected in fewer than 5 percent of the field blanks collected from October 2013 through October 2018, Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project: *A*, aluminum; *B*, antimony; *C*, arsenic; *D*, barium; *E*, beryllium; *F*, boron; *G*, cadmium; *H*, chromium; *I*, iron; *J*, lithium; *K*, manganese; *L*, molybdenum; *M*, nickel; *N*, selenium; *O*, silver; *P*, strontium; *Q*, thallium; *R*, uranium; and *S*, vanadium. [µg/L, microgram per liter]

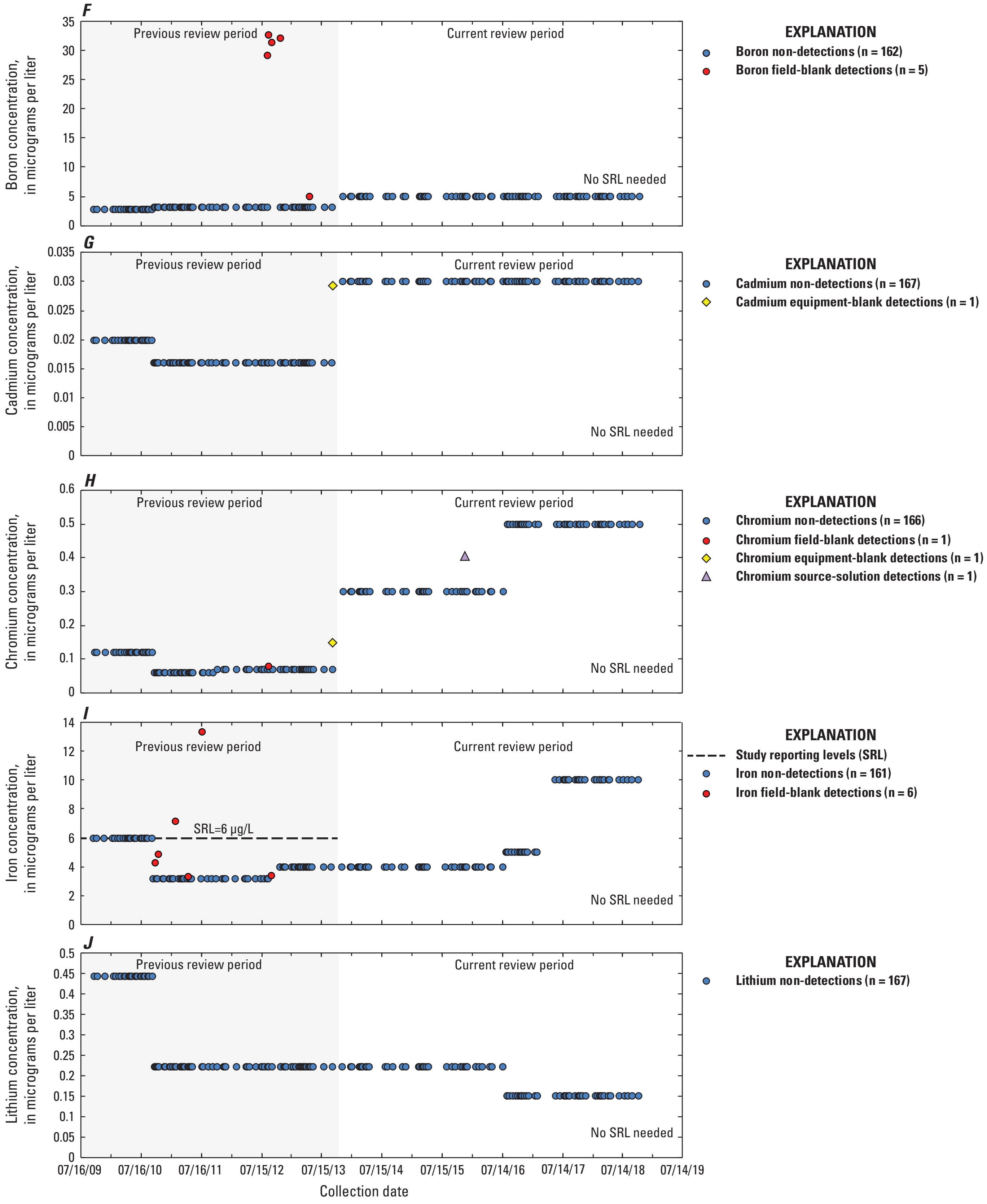


Figure 3. —Continued

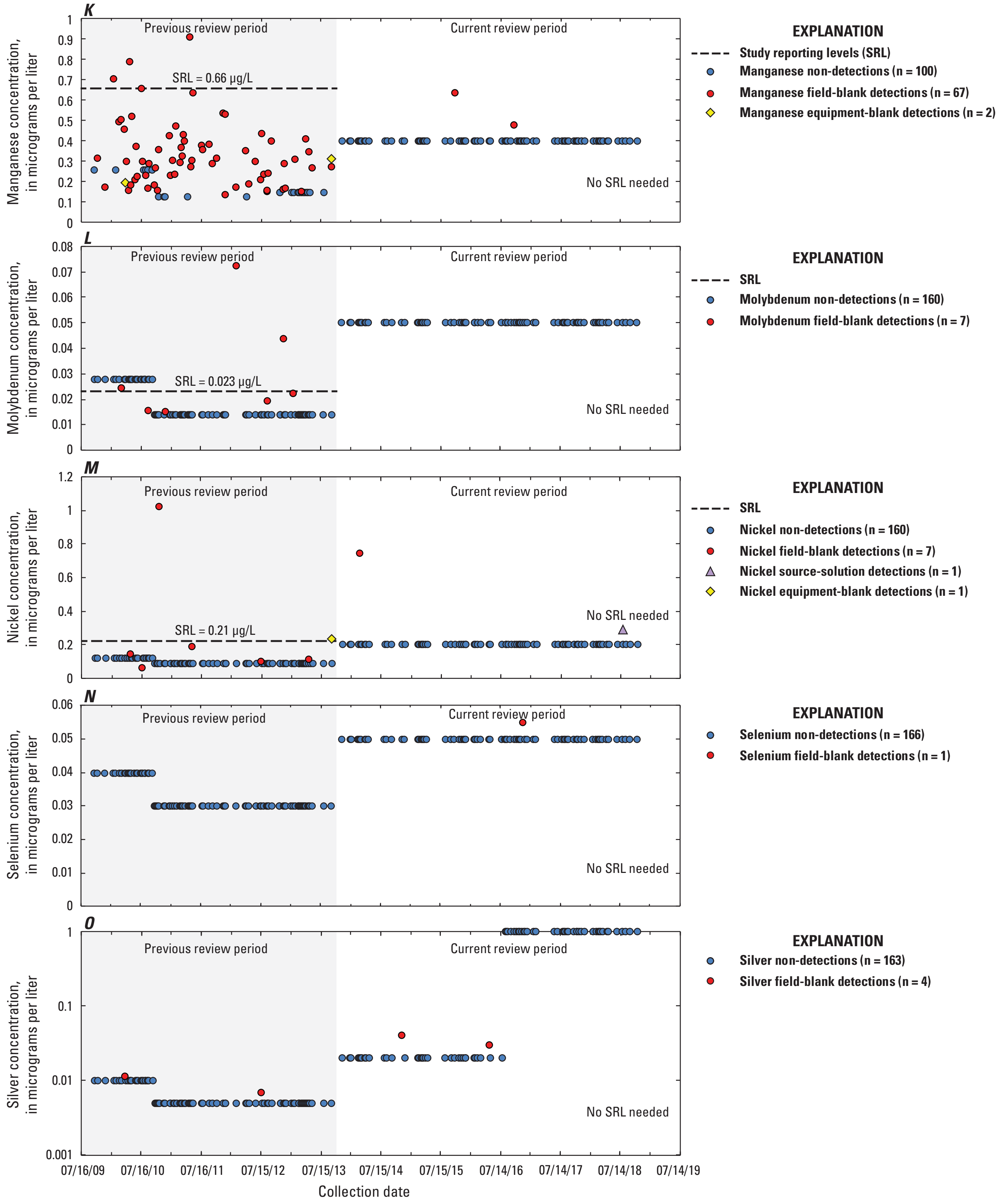


Figure 3. —Continued

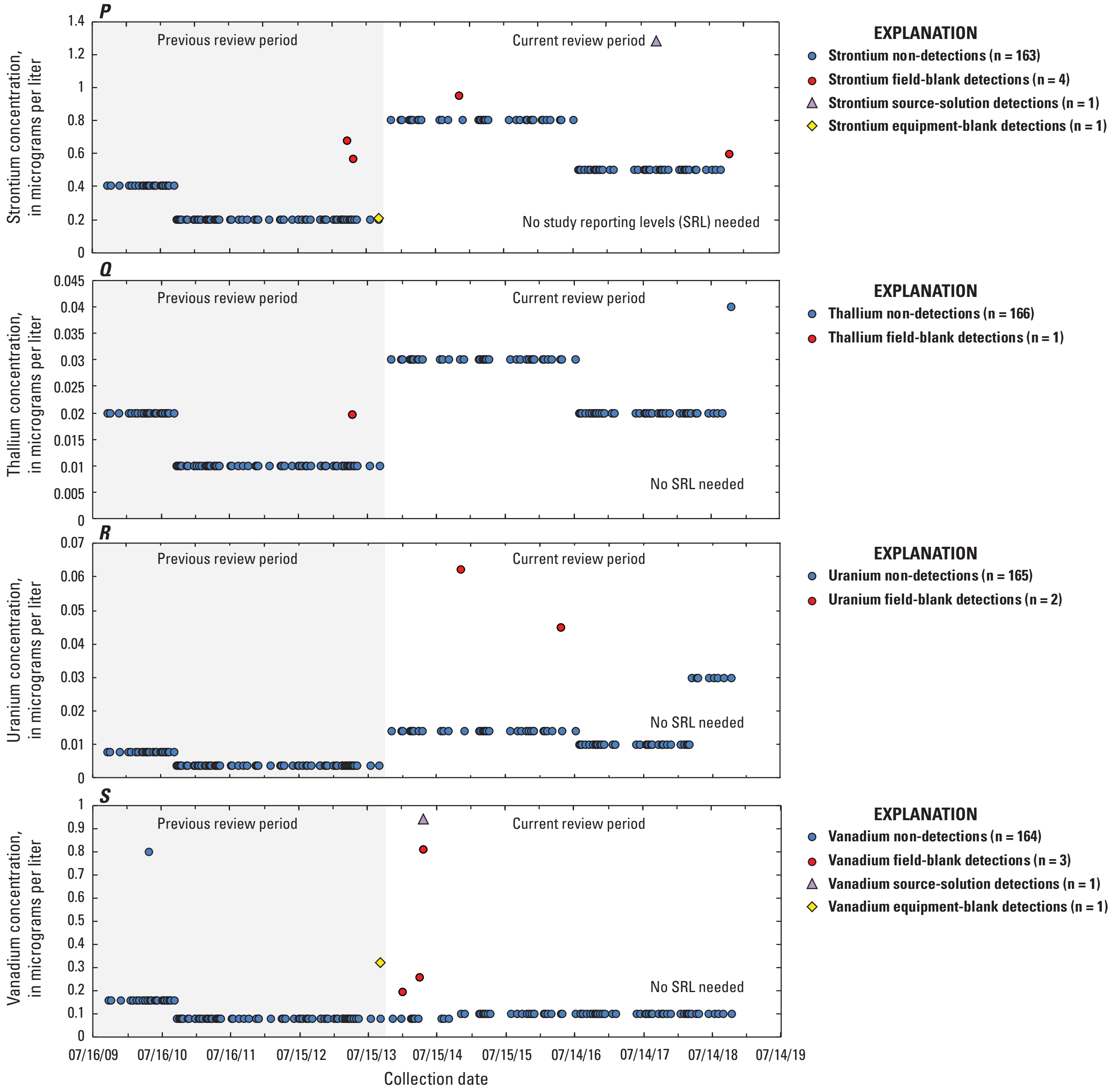


Figure 3. —Continued

Non-detections were plotted at their respective detection limit concentrations by using a different symbol than was used for the detections. Detections in source-solution and equipment blanks were plotted to aid in identifying instances of potential contamination in the source solution (IBW) used for the field blanks. Blanks collected between October 2009 and October 2018 were included in the time series plots, which cover the entirety of the Davis and others (2014) review period and the current SRL review periods. The collection of Cr(VI) samples didn't begin until September 2015, therefore the time-series available to be plotted is shorter than other trace elements (fig. 4).

Detection frequencies in field blanks, calculated for each trace element by dividing the number of detections by the total number of field blanks, are an easy way to identify potential contamination bias. Trace-element detection frequencies in field blanks from Davis and others, 2014, and from the current review are shown in table 1. For the time period used to evaluate recent contamination bias (hereinafter referred to as the "current review period") and update SRLs—October 2013 through October 2018—77 field blanks were analyzed for each of the trace elements, except for Cr(VI), which had 51. For 77 ranked values, the 4th highest value statistically defines the BD-90/90 concentration. Thus, the detection frequency in a population of 77 field blanks must be less than 5.1 percent (no more than 3 detections) for the BD-90/90 concentration to be a non-detection. Therefore, a detection frequency of 5 percent was used as a threshold for identifying trace elements (including Cr[VI]) requiring additional scrutiny and possible establishment or modification of an SRL.

BD-90/90 concentrations were calculated by using the binomial probability distribution from the method reported by Hahn and Meeker (1991). This approach was used to determine the upper 90-percent confidence limit for the 90th percentile of potential extrinsic contamination for each trace element. Calculations were made by using the BINOMDIST function in Excel for Office 365 (Microsoft Corporation, Redmond, Washington), which takes the form

$$CL = BINOMDIST(number\_s,\ trials,\ probability\_s,\ cumulative) \tag{1}$$

where

CL is the confidence limit for the specified rank and for the percentile of interest;

number_s is the number of successes in trials, in this case, the specified rank minus 1;

trials is the number of trials, in this case, the number of field blanks;

probability_s the probability of success on each trial, in this case, 0.90 for the 90th percentile; and

cumulative is a logical value that determines the form of the function, in this case TRUE, such that BINOMDIST returns the cumulative distribution function, which assumes that there are at most (cumulatively) *number_s* successes.

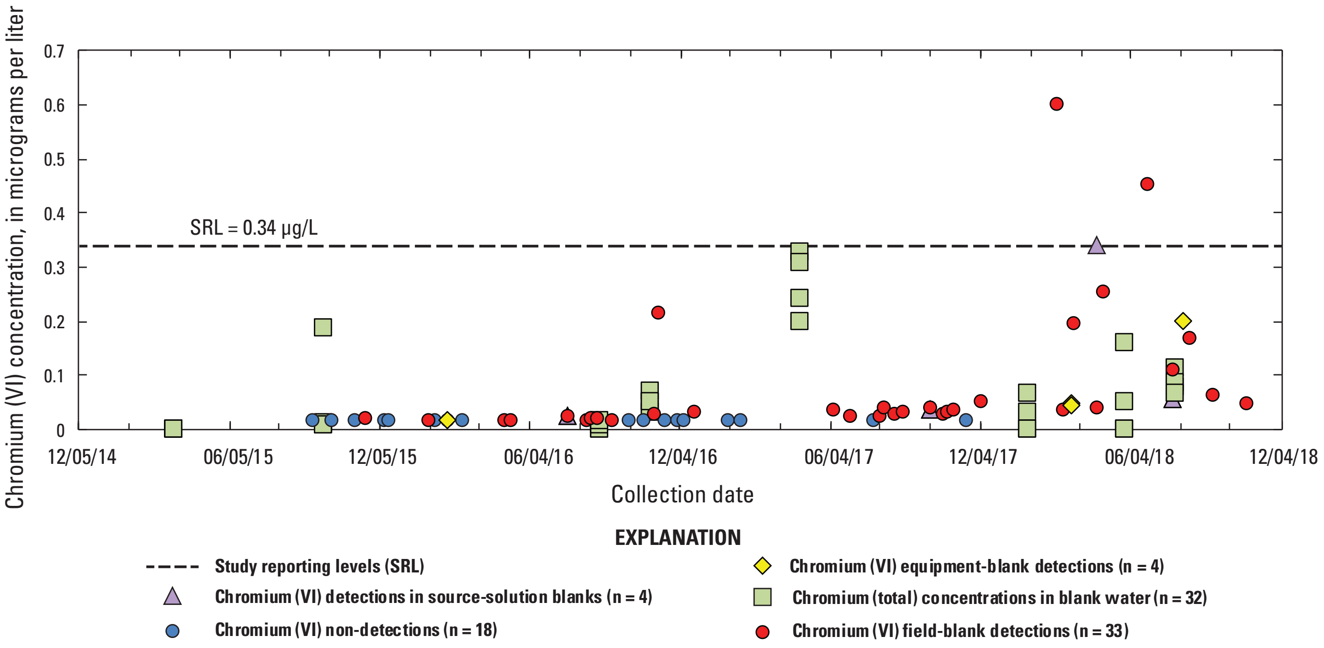


Figure 4. Chromium (VI) concentrations in field, source-solution, and equipment blanks collected September 2015 through October 2018 and analyzed at Weck Laboratories, Inc., total chromium concentrations in blank water tests conducted at the National Water Quality Laboratory plotted in time series, and study reporting level (SRL), Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project.

Table 1. Detection frequencies for trace elements in field blanks collected for the U.S. Geological Survey (USGS) Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project between October 2009 and March 2013, and between October 2013 and October 2018.

[<, less than; >, greater than; na, not applicable]

Constituent	Detection frequency in field blanks (percent)	
	October 2009–March 2013 (n = 69)[1]	October 2013–October 2018 (n = 77)
Detected in <5 percent of field blanks (2013–18)		
Aluminium	1.4	1.3
Antimony	1.4	3.9
Arsenic	1.4	0
Barium	2.9	2.6
Beryllium	0	1.3
Boron	na[2]	0
Cadmium	0	0
Chromium	1.4	0
Iron	7.2	0
Lithium	0	0
Manganese	73	2.6
Molybdenum	8.7	0
Nickel	5.8	1.3
Selenium	0	1.3
Silver	1.4	2.6
Strontium	0	2.6
Thallium	0	0
Uranium	0	2.6
Vanadium	0	3.9
Detected in >5 percent of field blanks (2013–18)		
Hexavalent chromium	na	[3]65
Cobalt	99	42
Copper	36	44
Lead	57	30
Zinc	36	32

[1] As reported in Davis and others (2014) for samples collected using the short sampling lines.

[2] Detections of boron in field blanks during this review period were attributed to contaminated blank water.

[3] Detection frequency calculated from 51 field blanks with hexavalent chromium analysis from Weck Laboratories, Inc., during the current review period.

The BD-90/90 concentrations represent the upper threshold of potential contamination bias of trace-element results. For trace elements that had BD-90/90 concentrations above their respective detection limit, the chance that a groundwater concentration less than the respective BD-90/90 concentration was significantly affected by extrinsic contamination was greater than 10 percent. For these trace elements, the likely source(s) of contamination was determined, and an SRL was set equal to the BD-90/90 concentration. A statistically robust BD-90/90 is calculated with enough data points to reduce sensitivity to outliers. Having from 52 to 64 samples results in the 3rd highest value in the dataset being set as the BD-90/90, while for 65–77 it is the 4th highest value, for 78–99 it is the 5th highest value, and for 100–102 it is the 6th highest value. The GAMA-PBP considers 52 or more samples to be an ideal number of blank results for determination of an SRL.

In Olsen and others (2010) and Davis and others (2014), the evaluation of field blanks was supplemented by evaluation of internal and third-party laboratory QC data collected by the NWQL and the USGS Quality Systems Branch (QSB). They calculated the range of concentrations, mean concentration, and standard deviation for laboratory-blank analyses and compared them with the detection limit for each trace element. This was done to evaluate random error that could affect the analytical method results and to evaluate systematic errors that can create positive or negative deviations in results from the target value (Davis and others, 2014). Analysis of laboratory QC data collected by NWQL and QSB were not included in the reevaluation of SRLs in this report. In the previous reports, the potential biases (positive or negative) observed in the laboratory QC data affected the ultimate decision to implement an SRL or at what level the SRL was set for only three of the trace elements: iron, molybdenum, and nickel. For the other trace elements, the laboratory QC results indicated which required some caution when interpreting results near the detection limit. For instance, Davis and others (2014) list aluminum, arsenic, barium, chromium, silver, strontium, and vanadium as having laboratory QC data suggesting either variability based on laboratory blank results or bias based on QSB blind blanks that might cause concerns. Ultimately, for these constituents an SRL was not determined to be necessary based on field-blank results (Davis and others, 2014).

Certificates of analysis for the IBW used for the field, source-solution, and equipment blanks and certificates of analysis for the capsule filters used for the field blanks and the groundwater samples were reviewed to determine whether any bias could be attributed to the IBW or the capsule filters.

Groundwater detections at concentrations less than an SRL are considered to have an unacceptably high likelihood of positive bias, and therefore, should be reported as less than the SRL. This is contrary to the way detections less than the SRL were reported in Olsen and others (2010) and Davis and others (2014). In those reports, detections were reported as less than or equal to the reported value. The idea was that users of the data would know the magnitude of each detected concentration and that the true concentration could be less than or equal to the detected concentration. This report rejects that guidance and follows traditional laboratory reporting practices with respect to established detection limits. Detections less then the established SRL will be reported as less than the SRL.

Results

The dataset used for the evaluation of SRLs and the examination of potential contamination bias included all field, source-solution, and equipment blanks collected for the GAMA-PBP from October 2009 through October 2018. This dataset was compiled and is presented in Bennett (2020). Associated environmental groundwater samples and other ancillary data, including sample notes, blank-water lot numbers, and filter lot numbers for the blanks collected by the GAMA-PBP were also compiled to help interpret the QC data. The dataset includes 167 field and 19 source-solution blanks and their associated groundwater sample results plus an additional 8 equipment blanks.

After reviewing the time-series plots, a notable shift in the contamination bias (decreasing blank concentrations and detection frequency) for cobalt (fig. 5) and manganese (fig. 3*K*) was observed. Concentrations of each generally decreased from about 2011 to 2013, and detections of manganese in blanks became much more infrequent starting late in 2013. Part of the reduction of manganese detections in blanks is likely related to the fact that the detection limit for manganese was raised from 0.1 to 0.4 µg/L beginning October 2013. Detection limit updates are generally implemented by the NWQL and occur at the beginning of a new fiscal year (October). The shift in cobalt and manganese patterns and the timing of new reporting levels being implemented by the NWQL were used to mark an obvious point from which to begin a reevaluation of SRLs by the GAMA-PBP. The previously defined SRLs may be overly conservative if trends in contamination bias are declining over time and periodically should be reevaluated to ensure they are still relevant.

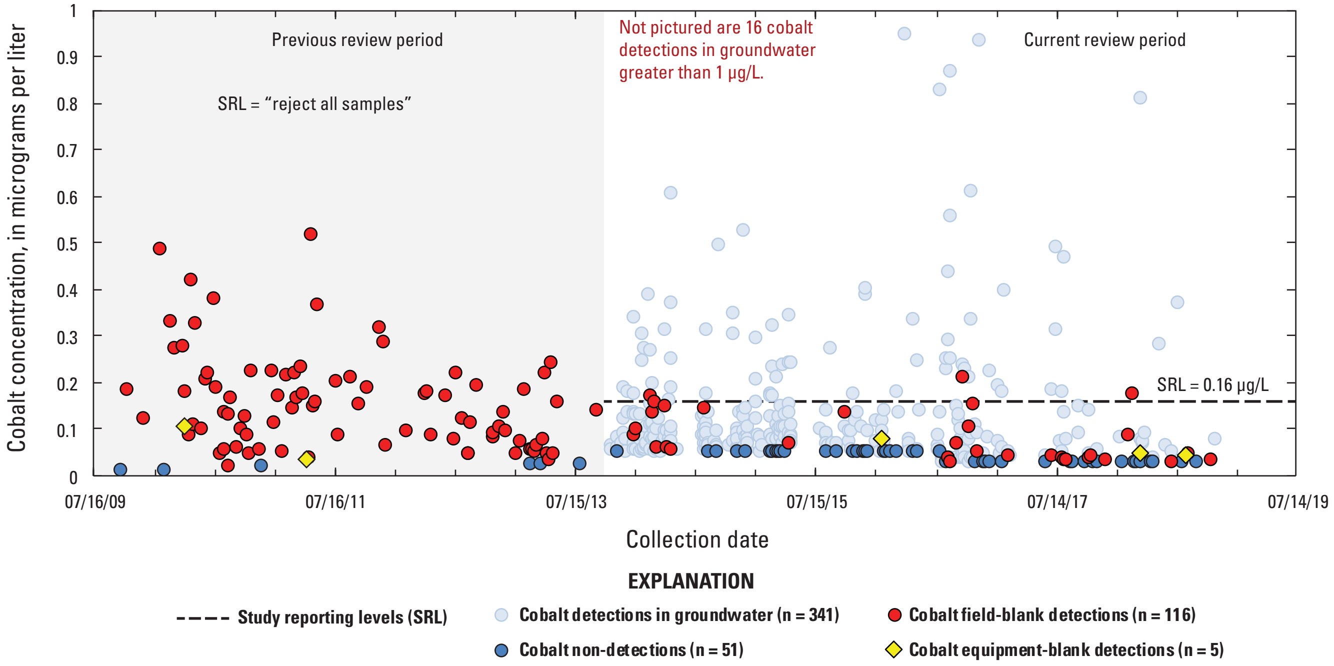


Figure 5. Cobalt concentrations in field, source-solution, and equipment blanks collected October 2009 through October 2018 plotted in time series, study reporting level (SRL), and cobalt concentrations in groundwater samples collected between October 2013 and October 2018, Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project. [µg/L, microgram per liter]

Results of the reevaluation of contamination bias between October 2013 and October 2018 for each trace element were categorized into two groups: (1) trace elements detected in less than 5 percent of field blanks and (2) trace elements detected in greater than 5 percent of the field blanks (table 1). Detection frequencies for each trace element in field blanks collected by the GAMA-PBP between October 2009 and March 2013, the period reviewed by Davis and others (2014), are tabulated in table 1 for comparison with those from the current review period. Time-series plots of the field, source-solution, and equipment blank results for each trace element (and groundwater detections for cobalt), along with the SRLs from October 2009 to October 2018, are displayed in figures 3*A*–*S* and 4–8. SRLs for trace elements based on results from the first two assessments (Olsen and others, 2010 and Davis and others, 2014) and the SRLs based on results from the current review period are compiled in table 2.

Trace Elements Detected in Fewer Than 5 Percent of Field Blanks

Of the 24 trace elements analyzed (including Cr[VI]) for samples collected from October 2013 to October 2018 for the GAMA-PBP, 8 were not detected in any of the field blanks: arsenic, boron, cadmium, chromium, iron, lithium, molybdenum, and thallium (table 1). Eleven trace elements—aluminum, antimony, barium, beryllium, manganese, nickel, selenium, silver, strontium, uranium, and vanadium—had detection frequencies of less than 5 percent (table 1). For a trace element detected in less than 5 percent of the 77 field blanks collected between October 2013 and October 2018, the BD-90/90 value was a non-detection (lower than the trace-element detection limit); therefore, no SRLs were defined for the 19 trace elements detected in less than 5 percent of the field blanks.

Aluminum (Al)

From October 2013 through October 2018, 1 of 77 field blanks (1.3 percent) collected for aluminum had a detection (fig. 3*A*; table 1). The detection limit for aluminum changed from 2.2 µg/L to 3 µg/L beginning October 2014. The one detection of aluminum in the field blanks was 3.6 µg/L. There were no detections of aluminum in the 19 source-solution or 8 equipment blanks collected October 2009–October 2018 (fig. 3*A*). Based on the field blanks collected during the current review period, the SRL for aluminum was not updated from the previous SRL of “none” (table 2).

Antimony (Sb)

From October 2013 through October 2018, 3 of the 77 field blanks (3.9 percent) collected for antimony had a detection (fig. 3*B*; table 1). The three detections ranged in concentration from 0.07 µg/L to 0.16 µg/L. There were no detections of antimony in 19 source-solution or 8 equipment blanks collected October 2009–October 2018. There were changes in the detection limit for antimony from 0.027 µg/L to 0.03 µg/L beginning August 2016 and from 0.03 µg/L to 0.06 µg/L beginning March 2018. Based on the field blanks collected during the current review period, the SRL for antimony was not updated from the previous SRL of “none” (table 2).

Arsenic (As)

From October 2013 through October 2018, none of the 77 field blanks collected for arsenic had a detection (fig. 3*C*; table 1). Arsenic was detected in one source-solution blank collected in 2014 at a concentration of 0.17 µg/L and none of the equipment blanks (fig. 3*C*). There was a change in the detection limit for arsenic from 0.1 µg/L to 0.05 µg/L beginning September 2016. The detection limit changed back to 0.1 µg/L beginning March 2018. From October 2009 through March 2013, arsenic was only detected twice in field blanks with both detections having concentrations less than the current 0.1 µg/L detection limit (Davis and others, 2014). Arsenic was detected in one source-solution blank collected in 2014 at a concentration of 0.14 µg/L and none of the equipment blanks (fig. 3*C*). Based on the field blanks collected during the current review period, the SRL for arsenic was not updated from the previous SRL of “none” (table 2).

Barium (Ba)

From October 2013 through October 2018, barium was detected in 2 of 77 field blanks (2.6 percent) with concentrations of 0.77 µg/L and 1.01 µg/L (fig. 3*D*; table 1). From October 2009 through March 2013, 2 of the 69 field blanks (2.9 percent) collected for barium had detections (Davis and others, 2014). The detection limit for barium changed from 0.25 µg/L to 0.1 µg/L in August 2016; however, both blank detections occurred before the detection limit was lowered. Barium was detected in two source-solution blanks, once in 2011 and again in 2017, at low concentrations close to the detection limit (fig. 3*D*). Barium was detected in two equipment blanks during the previous review periods at low concentrations. Based on the field blanks collected during the current review period, the SRL for barium was not updated from the previous SRL of “none” (table 2).

Table 2. Parameter codes, analytical methods, benchmark type and value, range of detection limits, and study reporting levels (SRLs) for trace element data collected for the U.S. Geological Survey (USGS) Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project, May 2004–September 2009, October 2009–September 2013, and updated SRLs starting October 2013.

[The five-digit parameter code is used to uniquely identify a specific constituent or property. **Analytical method abbreviations**: cICP-MS, collision/reaction cell inductively coupled plasma-mass spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; ICP-AES, inductively coupled plasma-atomic emission spectrometry; IC-UV-Vis, ion chromatography with post-column derivatization and UV-visable spectroscopic detection. **Benchmark types**: ***Regulatory health-based benchmarks***: AL-US, EPA action level; HAL-US, EPA lifetime health advisory level; MCL-CA, SWRCB-DDW maximum contaminant level; MCL-US, EPA maximum contaminant level. ***Non-regulatory health-based benchmarks***: HBSL, USGS Health Based Screening Level; RL-CA, SWRCB-DDW response level. ***Non-regulatory aesthetic-based benchmarks***: SMCL-CA, SWRCB-DDW secondary maximum contaminant level. **Abbreviations**: µg/L, microgram per liter; EPA, Environmental Protection Agency; na, not available; SWRCB-DDW, California State Water Resources Control Board Division of Drinking Water.]

Constituent	Parameter code	Analytical method	Benchmark type	Benchmark value (µg/L)	Range of detection limits (µg/L)	SRLs		
						May 2004–September 2009 (µg/L)[1]	October 2009–September 2013 (µg/L)[2]	Starting October 2013 (µg/L)[3]
Aluminium	01106	cICP-MS	MCL-CA	1,000	3.4–6.0	1.6	None	None
Antomony	01095	cICP-MS	MCL-US	6	0.04–0.12	None	None	None
Arsenic	01000	cICP-MS	MCL-US	10	0.04–0.20	None	None	None
Barium	01005	cICP-MS	MCL-CA	1,000	0.14–0.50	0.36	None	None
Beryllium	01010	cICP-MS	MCL-US	4	0.01–0.04	None	None	None
Boron	01020	ICP-MS	HAL-US	6,000	2.8–10	None	None	None
Cadmium	01025	cICP-MS	MCL-US	5	0.02–0.06	None	None	None
Chromium	01030	cICP-MS	MCL-CA	50	0.12–1.0	0.42	None	None
Hexavalent chromium	01032	IC-UV-Vis	HBSL	20	[4]0.0044–0.015	Not calculated	Not calculated	0.34
Cobalt	01035	cICP-MS	na	na	0.01–0.10	None	Report all results as “reviewed and rejected.”	0.16
Copper	01040	cICP-MS	AL-US	1,300	0.4–1.6	1.7	2.1	2.1
Iron	01046	ICP-AES	SMCL-CA	300	4–20	6	6	None
Lead	01049	cICP-MS	AL-US	15	0.03–0.08	0.65	0.82	0.83
Lithium	01130	ICP-MS	na	na	0.3–1.0	None	None	None
Manganese	01056	cICP-MS	SMCL-CA	50	0.2–0.8	0.2	0.66	None
Molybdenum	01060	cICP-MS	HAL-US	40	0.02–0.10	None	0.023	None
Nickel	01065	cICP-MS	MCL-CA	100	0.12–0.40	0.36	0.21	None
Selenium	01145	cICP-MS	MCL-US	50	0.04–0.10	None	None	None
Silver	01075	cICP-MS	MCL-US	100	0.008–2	None	None	None
Strontium	01080	ICP-MS	HAL-US	4,000	0.4–1.6	0.99	None	None
Thallium	01057	ICP-MS	MCL-US	2	0.02–0.08	None	None	None
Uranium	22703	cICP-MS	MCL-US	30	0.006–0.06	None	None	None
Vanadium	01085	cICP-MS	RL-CA	500	0.16–0.20	0.1	None	None
Zinc	01090	cICP-MS	SMCL-CA	5,000	2–4	4.8	6.2	3.9

[1] SRL defined by Olsen and others, 2010.

[2] SRL defined by Davis and others, 2014.

[3] SRL calculated using the 90th percentile concentration of potential extrinsic contamination calculated by using the binomial probability distribution for greater than 90 percent confidence (BD-90/90).

[4] Detection limit ranges reported for hexavalent chromium determination using IC-UV-Vis (EPA method 218.7).

Beryllium (Be)

From October 2013 through October 2018, 1 of the 77 field blanks (1.3 percent) collected for beryllium had a detection at a concentration of 0.03 µg/L (fig. 3*E*; table 1). Beryllium was not detected in any of the 19 source-solution or 8 equipment blanks collected October 2009–October 2018 (fig. 3*E*). The detection limit for beryllium changed from 0.02 µg/L to 0.1 µg/L in August 2016. Based on the field blanks collected during the current review period, the SRL for beryllium was not updated from the previous SRL of "none" (table 2).

Boron (B)

From October 2013 through October 2018, none of the 77 field blanks collected had a detection of boron (fig. 3*F*; table 1). Boron had been detected in five blanks during the previous review (fig. 3*F*). The lot number of IBW used to collect the field blanks having detections of boron in 2012 greater than 25 µg/L (fig. 3*F*) was reported to have boron at concentrations up to 30 µg/L (Davis and others, 2014). Boron was not detected in any of the 19 source-solution or 8 equipment blanks collected October 2009–October 2018 (fig. 3*F*). The detection limit for boron during the current review period remained constant at 5 µg/L. Based on the field blanks collected during the current review period, the SRL for boron was not updated from the previous SRL of "none" (table 2).

Cadmium (Cd)

From October 2013 through October 2018, none of the 77 field blanks collected had a detection of cadmium (fig. 3*G*; table 1). Cadmium was not detected in any of the 19 source-solution blanks and only 1 of 8 equipment blanks (0.029 µg/L) collected October 2009–October 2018 (fig. 3*G*). The detection limit for cadmium during the current review period remained constant at 0.03 µg/L. Based on the field blanks collected during the current review period, the SRL for cadmium was not updated from the previous SRL of "none" (table 2).

Chromium (Cr)

From October 2013 through October 2018, none of the 77 field blanks collected had a detection of chromium (fig. 3*H*; table 1). Chromium was detected in 1 of 19 source-solution blanks (0.4 µg/L) and 1 of 8 equipment blanks (0.15 µg/L) collected October 2009–October 2018 (fig. 3*H*). The detection limit for chromium during the current review period changed from 0.3 µg/L to 0.5 µg/L in August 2016. Based on the field blanks collected during the current review period, the SRL for chromium was not updated from the previous SRL of "none" (table 2).

Iron (Fe)

From October 2013 through October 2018, none of the 77 field blanks collected had a detection of iron (fig. 3*I*; table 1). Iron was not detected in any of the 19 source-solution blanks or 8 equipment blanks collected from October 2009 to October 2018 (fig. 3*I*). Iron was detected in 7.2 percent of blanks analyzed during the previous review by Davis and others (2014), and they established an SRL for iron of 6 µg/L (table 2, fig. 3*I*). The detection limit for iron increased twice during the current review period, changing from 4 µg/L to 5 µg/L in August 2016 and from 5 µg/L to 10 µg/L in June 2017. Based on the current detection limit of 10 µg/L and field-blank data during the current review period, the SRL for iron has been updated from the previous SRL of 6 µg/L to "none" (table 2).

Lithium (Li)

From October 2013 through October 2018, none of the 77 field blanks collected had a detection of lithium (fig. 3*J*; table 1). Lithium was not detected in any of the 19 source-solution or 8 equipment blanks collected from October 2009 to October 2018 (fig. 3*J*). The detection limit for lithium was lowered from 0.22 µg/L to 0.15 µg/L in August of 2015. Based on the field blanks collected during the current review period, the SRL for lithium was not updated from the previous SRL of "none" (table 2).

Manganese (Mn)

Between October 2009 and September 2013, manganese was detected in 65 of 90 field blanks (73 percent) with concentrations ranging from 0.14 to 0.91 µg/L (fig 3*K;* table 1). The median manganese concentration in field blanks during this time was 0.3 µg/L. Based on the blank results, an SRL for manganese of 0.66 µg/L was established by Davis and others (2014; table 2). The occurrence of manganese in field blanks during this time coincides with the observation of contamination bias of cobalt and manganese samples attributed to the high-capacity capsule filters used during sample collection from October 1, 2008, to about September 30, 2014 (U.S. Geological Survey, 2016). Nationally, manganese was being detected in approximately 33 percent of field blanks (U.S. Geological Survey, 2016).

Recommendations from the USGS Office of Water Quality (OWQ) to address low-level detections of manganese in field blanks collected using high-capacity capsule filters have been to increase the deionized water rinse volume, track filter lot numbers, review certificates of analysis for detections of analytes of interest, and to evaluate environmental concentrations with respect to blank data. Filter lot numbers and the results of quality-control tests conducted by the NWQL on the high-capacity capsule filters used for the collection of trace elements between late 2012 and early 2019 are shown in table 3. It has been noted that despite the prescribed increase in field rinsing, the contamination has not always been mitigated (U.S. Geological Survey, 2016).

From October 2013 through October 2018, 2 of the 77 field blanks collected had a detection of manganese (fig. 3*K*; table 1). Manganese was not detected in any of the 19 source-solution blanks collected October 2009–October 2018 but was detected in 2 equipment blanks collected during the previous review period (fig. 3*K*). In October 2013, the detection limit for manganese was raised from 0.15 µg/L to 0.4 µg/L, and the number of manganese detections in field blanks dropped significantly. Based on the field blanks collected during the current review period, the SRL for manganese was updated from the previous SRL of 0.66 µg/L to “none” (table 2).

Molybdenum (Mo)

From October 2013 through October 2018, none of the 77 field blanks collected had a detection of molybdenum (fig. 3*L*; table 1). Molybdenum was not detected in any of the 19 source-solution or 8 equipment blanks collected from October 2009 to October 2018. The detection limit for molybdenum was raised beginning October 2013 from 0.014 µg/L to 0.05 µg/L, which may account for the decrease in blank detection starting in October 2013. Davis and others (2014) had established an SRL for molybdenum of 0.023 µg/L; however, based on the field blanks collected during the current review period, the SRL for molybdenum was updated to “none” (table 2).

Table 3. Concentrations of cobalt and manganese in high-capacity filters tested by the U.S. Geological Survey National Water Quality Laboratory (NWQL) for use in the collection of trace-element blanks—December 2012–March 2019.

[mm/dd/yyyy, month/day/year; µg/L, microgram per liter; na, not available; nd, not detected]

Manufacturer lot number	Certificate date (mm/dd/yyyy)	Cobalt concentration[1] (µg/L)				Manganese concentration[1] (µg/L)			
		Laboratory reporting level	Reported concentration[2]	Minimum	Maximum	Laboratory reporting level	Reported concentration[2]	Minimum	Maximum
FW7427	12/03/2012	0.023	0.0016	na	na	0.15	0.0071	na	na
FZ8372	03/08/2013	0.023	0.011	0.0041	0.015	0.15	0.029	0.019	0.036
FZ0324	02/25/2014	0.05	0.0034	nd	0.0018	0.4	0.021	0.012	0.016
FZ1395	04/29/2014	0.05	0.0034	0.0023	0.0044	0.4	0.021	0.018	0.033
FZ1557	05/28/2014	0.05	0.0024	0.0001	0.0082	0.4	0.062	0.023	0.18
FZ2194	11/11/2014	0.05	0.0046	0.0019	0.0077	0.4	0.024	0.011	0.048
FZ4118	04/20/2015	0.05	0.0055	0.0008	0.012	0.4	0.021	0.01	0.025
FZ4362	10/26/2015	0.05	0.0022	0.0003	0.0066	0.4	nd	nd	0.0054
FZ8418	04/22/2016	0.05	0.0022	0.0003	0.0066	0.4	nd	nd	0.0054
FC0692	01/05/2017	0.03	nd	nd	nd	0.4	0.011	nd	0.02
FC2587	05/25/2017	0.03	0.002	0.0014	0.0027	0.4	nd	nd	0.0058
FC4706	11/14/2017	0.03	0.007	na	na	0.4	0.014	na	na
FC7580	04/19/2018	0.03	0.0048	0.0023	0.0077	0.04	0.022	0.0066	0.088
FE1643	03/01/2019	0.03	0.0048	0.0023	0.0077	0.4	0.022	0.0066	0.088

[1] Reported concentrations are uncensored instrument readings provided by NWQL. Values are not significantly different from “zero” and should be interpreted to be “non-detections.”

[2] Ten capsule filters are tested from each new lot, as well as a capsule filter from a previously approved lot for a control, which is not included in the reported data. The “reported concentration” is the average result of the 10 new lot filters.

Nickel (Ni)

From October 2013 through October 2018, 1 of the 77 field blanks (1.3 percent) collected had a detection of nickel (fig. 3*M*; table 1). Nickel was detected in 1 of 19 source-solution and 1 of 8 equipment blanks collected from October 2009 to October 2018 (fig. 3*M*). Beginning October 2013, the detection limit for nickel was raised from 0.09 µg/L to 0.2 µg/L. Davis and others (2014) had established an SRL for nickel of 0.21 µg/L; however, based on the field blanks collected during the current review period, the SRL for nickel was updated to “none” (table 2).

Selenium (Se)

From October 2013 through October 2018, 1 of the 77 field blanks (1.3 percent) collected had a detection of selenium (fig. 3*N*; table 1). This was the only detection of selenium in field blanks going back to October 2009 (fig. 3*N*). Selenium was not detected in any of the 19 source-solution or 8 equipment blanks collected October 2009–October 2018 (fig. 3*N*). Beginning in October 2013, the NWQL detection limit for selenium was raised from 0.03 µg/L to 0.05 µg/L. Based on the field blanks collected during the current review period, the SRL for selenium was not updated from the previous SRL of “none” (table 2).

Silver (Ag)

From October 2013 through October 2018, 2 of the 77 field blanks (2.6 percent) collected had a detection of silver (fig. 3*O*; table 1). Silver was also detected in two field blanks between October 2009 and September 2013 (fig. 3*O*). Silver was not detected in any of the 19 source-solution or 8 equipment blanks collected October 2009–October 2018 (fig. 3*O*). Beginning in October 2013, the detection limit for silver was raised from 0.005 µg/L to 0.02 µg/L, and it was raised again in August 2016 from 0.02 µg/L to 1 µg/L. Based on the field blanks collected during the current review period, the SRL for silver was not updated from the previous SRL of “none” (table 2).

Strontium (Sr)

From October 2013 through October 2018, 2 of the 77 field blanks (2.6 percent) collected had a detection of strontium (fig. 3*P*; table 1). Strontium was also detected in two field blanks between October 2009 and September 2013 (fig. 3*P*). Strontium was detected in 1 of the 19 source-solution blanks at a concentration of 1.3 µg/L, a higher concentration than any of the field blanks but far less than concentrations typically observed in groundwater. The median concentration of strontium in groundwater samples collected contemporaneously with the field blanks in the current review period was 282 µg/L. Beginning in October 2013, the detection limit for strontium was raised from 0.2 µg/L to 0.8 µg/L and was later lowered in August 2016 from 0.8 µg/L to 0.5 µg/L. Based on the field blanks collected during the current review period, the SRL for strontium was not updated from the previous SRL of “none” (table 2).

Thallium (Tl)

From October 2013 through October 2018, none of the 77 field blanks collected had a detection of thallium (fig. 3*Q*; table 1). Thallium was not detected in any of the 19 source-solution or 8 equipment blanks collected October 2009–October 2018 (fig. 3*Q*). Beginning in October 2013, the detection limit for thallium was raised from 0.01 µg/L to 0.03 µg/L and was later lowered in August 2016 from 0.03 µg/L to 0.02 µg/L. In October 2018, the detection limit was raised to 0.04 µg/L. Based on the field blanks collected during the current review period, the SRL for thallium was not updated from the previous SRL of “none” (table 2).

Uranium (U)

From October 2013 through October 2018, 2 of the 77 field blanks (2.6 percent) collected had a detection of uranium (fig. 3*R*; table 1). Concentrations of uranium in the two blanks were 0.062 and 0.045 µg/L. Uranium was not detected in any of the 19 source-solution or 8 equipment blanks collected October 2009–October 2018 (fig. 3*R*). The detection limit for uranium changed twice during the current review period. Beginning in October 2013, the detection limit for uranium was 0.014 µg/L. In August 2016, it was lowered to 0.01 µg/L, and it was raised in March 2018 to 0.03 µg/L. Based on the field blanks collected during the current review period, the SRL for uranium was not updated from the previous SRL of “none” (table 2).

Vanadium (V)

From October 2013 through October 2018, 3 of the 77 field blanks (3.9 percent) collected had a detection of vanadium (fig. 3*S*; table 1). Concentrations of vanadium in the three blanks were 0.19, 0.26, and 0.81 µg/L, and all occurred relatively early in 2014. Vanadium was detected in 1 of the 19 source-solution blanks and 1 of 8 equipment blanks collected October 2009–October 2018 (fig. 3*S*). The detection limit for vanadium changed once during the current review period. Beginning in October 2013, the detection limit for vanadium was 0.08 µg/L. In October 2014, it was raised to 0.1 µg/L. Based on the field blanks collected during the current review period, the SRL for vanadium was not updated from the previous SRL of “none” (table 2).

Trace Elements Detected in Greater Than 5 Percent of Field Blanks

One species of the trace element chromium (Cr[VI]), and cobalt, copper, lead, and zinc had detection frequencies in field blanks greater than 5 percent between October 2013 and October 2018 (table 1). Detection frequencies of cobalt, lead, and zinc decreased when compared to the previous review period (October 2009–March 2013), while copper detections increased (table 1). Detected concentrations of cobalt in field blanks decreased significantly (Wilcoxon rank-sum $p < 0.0001$, $\alpha = 0.05$) when comparing the previous and current review periods. Copper, lead, and zinc had insignificant differences between the median detected concentrations when comparing the review periods, with rank-sum $p = 0.74$, $p = 0.11$, and $p = 0.70$ ($\alpha = 0.05$), respectively (figs. 6–8). Collection of Cr(VI) samples submitted to Weck for analysis began during the second half of 2015 and were therefore not part of the previous review by Davis and others (2014).

Except for Cr(VI), SRLs for the trace elements with detection levels greater than 5 percent were determined based on the BD-90/90 of each trace element's concentrations in field blanks collected during the current review period. For Cr(VI), additional data from the equipment and source-solution blanks were included when calculating the BD-90/90 concentration that defined the SRL. Groundwater results with concentrations less than the SRL have an unacceptably high likelihood of significant contamination bias and will be reported as less than the SRL.

Hexavalent Chromium (Cr[VI])

From August 2015 through October 2018, 33 of the 51 field blanks (65 percent) collected had a detection of Cr(VI) (fig. 4; table 1). Concentrations of Cr(VI) in the field blank detections ranged from 0.02 to 0.60 µg/L (fig. 4). Cr(VI) was detected in 4 of the 7 source-solution blanks with concentrations ranging from 0.03 to 0.34 µg/L. Cr(VI) was also detected in 4 of 5 equipment blanks with concentrations ranging from 0.02 to 0.20 µg/L. The detection limit for Cr(VI) used by Weck for Cr(VI) analyses is 0.02 µg/L. The median concentration of detections observed in field, source-solution, and equipment blanks was 0.04 µg/L.

The high detection frequency of Cr(VI) in field, source-solution, and equipment blanks indicates a persistent source of low-level Cr(VI) contamination. An examination of the IBW used found that total chromium (a measure which includes all chromium species) was detected in QC tests conducted by the USGS National Water Quality Laboratory (NWQL) in all eight lots of IBW used over the current review period (Lot numbers 81506, 81507, 81601, 81608, 81705, 81708, 81802, and 81805; table 4).

Table 4. Concentrations of chromium in blank water tested by the U.S. Geological Survey National Water Quality Laboratory (NWQL) for use in the collection of trace-element blanks—September 2015–May 2018.

[mm/dd/yyyy, month/day/year; µg/L, microgram per liter; nd, not detected]

Blank water lot number	Date tested (mm/dd/yyyy)	Laboratory detection level	Chromium concentration[1] (µg/L)				
			Bottle #1	Bottle #2	Bottle #3	Bottle #4	Average
81506	09/30/2015	0.3	0.013	0.0089	0.19	0.0088	0.054
81507	03/31/2015	0.3	0.0013	0.0019	0.0011	0.0003	0.0012
81608	08/31/2016	0.3	nd	0.0009	0.0073	0.018	0.0039
81601	10/31/2016	0.5	0.05	0.07	0.03	0.05	0.05
81705	04/30/2017	0.5	0.33	0.31	0.20	0.24	0.27
81708	07/31/2018	0.5	0.12	0.079	0.087	0.06	0.087
81802	01/31/2018	0.5	0.068	0.03	nd	nd	0.02
81805	05/31/2018	0.5	0.16	0.05	nd	nd	nd

[1] Reported concentrations are uncensored instrument readings provided by NWQL. Values are not significantly different from "zero" and should be interpreted to be "non-detections."

The NWQL ran tests on four separate bottles from each IBW lot to determine average trace-element concentrations in each lot (table 4). Concentrations of total chromium reported by the NWQL from these tests ranged from <0.003 to 0.326 µg/L, which is very close to the range of concentrations measured in the field, source-solution, and equipment blanks collected (fig. 4). The NWQLs testing of IBW does not include Cr(VI). Although the IBW tests only reported total chromium, a statewide assessment of Cr(VI) occurrence in California found that 90 percent of the dissolved chromium in groundwater samples was Cr(VI), suggesting that Cr(VI) is the dominant chromium species in most environmental water samples (Izbicki and others, 2015). While the IBW isn't an environmental water sample it is assumed that the predominant chromium species in the IBW is Cr(VI). The IBW certified by NWQL for use when conducting trace-element blanks was not flagged for low-level chromium concentrations because the detection limit for total chromium analyses conducted by the NWQL is 0.5 µg/L, which is greater than the highest concentration of total chromium measured in the eight IBW lots (0.326 µg/L) tested by NWQL during this review.

The SRL for Cr(VI) was determined by calculating the BD-90/90 concentration from the 63 Cr(VI) results from the combined dataset of field, source-solution, and equipment blanks. Using this combined dataset, the SRL for Cr(VI) reported from Weck was determined to be 0.34 µg/L (table 2). For 63 ranked values, the 3rd highest value statistically defines the BD-90/90 concentration. The 3rd highest concentration of Cr(VI) from the combined field, source-solution, and equipment-blank dataset was from a source-solution blank collected in April 2018 (fig. 4). Because the IBW itself contains low level concentrations of Cr(VI), it was not possible to determine if low-level field contamination of Cr(VI) is occurring. Field and equipment blanks did not have noticeably higher concentrations of Cr(VI) than the source-solution blanks (fig. 4). Despite low-level detections of Cr(VI) in blanks not being attributed to field contamination, an SRL of 0.34 µg/L was still implemented to be conservative when reporting low-level detections of Cr(VI) in environmental samples. The range of Cr(VI) concentrations in the environmental samples associated with the field blanks was 0.03 to 24 µg/L. About 24 percent of those samples had Cr(VI) concentrations less than 0.34 µg/L (Jurgens and others, 2018).

Cobalt (Co)

Cobalt was detected in 99 percent of field blanks between October 2009 and March 2013 (Davis and others, 2014). As was discussed in the manganese section, the high detection frequency of cobalt in field blanks is attributed to the high-capacity capsule filters used to collect samples for trace-element analyses starting October 2009 and continuing through September 2014 (U.S. Geological Survey, 2016). The calculated BD-90/90 concentration using field blanks collected October 2009 through March 2013 was 0.038 µg/L; however, that SRL was not assigned. Instead, the samples were considered “reviewed and rejected” (Davis and others, 2014). This was done in part because of the pervasiveness of cobalt detections in field blanks during this time period and because cobalt does not have a regulatory benchmark for drinking water, meaning that rejecting the data did not affect the ability of the GAMA-PBP to assess groundwater quality within the framework of drinking-water benchmarks.

From October 2013 through October 2018, 32 of the 77 field blanks (42 percent) collected had a detection of cobalt (fig. 5; table 1). Concentrations in the field blanks ranged from 0.03 to 0.21 µg/L. There were no detections of cobalt in the 19 source-solution blanks collected October 2009–October 2018. Cobalt was detected in three of five equipment blanks with concentrations ranging from 0.04 to 0.08 µg/L within the current review period and two of three equipment blanks during the previous review period (fig. 5). The frequency and concentration of cobalt in field blanks dropped considerably in 2014, suggesting the increased awareness of contamination bias associated with the capsule filters and suggesting mitigation strategies by the USGS OWQ have been effective to some degree (fig. 5; table 3). This resulted in a reconsideration of the previous determination by Davis and others (2014) that all cobalt detections in groundwater samples be reported as “reviewed and rejected.” Cobalt was detected in about 40 percent (339 of 849) of the groundwater samples collected by GAMA during the current review period with concentrations ranging from 0.03 to 22.5 µg/L and a median concentration of 0.09 µg/L (Jurgens and others, 2018). The BD-90/90 concentration for cobalt based on the field-blank data for the current review period is 0.16 µg/L. Applying an SRL of 0.16 µg/L for cobalt to the dataset reduces the detection frequency to about 10 percent (84 of 849), effectively screening low-level detections of cobalt for which contamination bias cannot be ruled out.

Copper (Cu)

During the previous review period, 36 percent of field blanks collected for copper had detections, and the BD-90/90 concentration calculated based on those field blanks was 2.1 µg/L (Davis and others, 2014; tables 1, 2). From October 2013 through October 2018, 34 of 77 field blanks (44 percent) had detections of copper with concentrations ranging from 0.21 to 6.31 µg/L (fig. 6). One of 19 source-solution blanks and 6 of 8 equipment blanks had detections of copper between October 2009 and October 2018 (fig. 6). The copper concentration in the source-solution blank was 1.50 µg/L, and concentrations in the equipment blanks ranged from 0.51 to 6.7 µg/L (fig. 6).

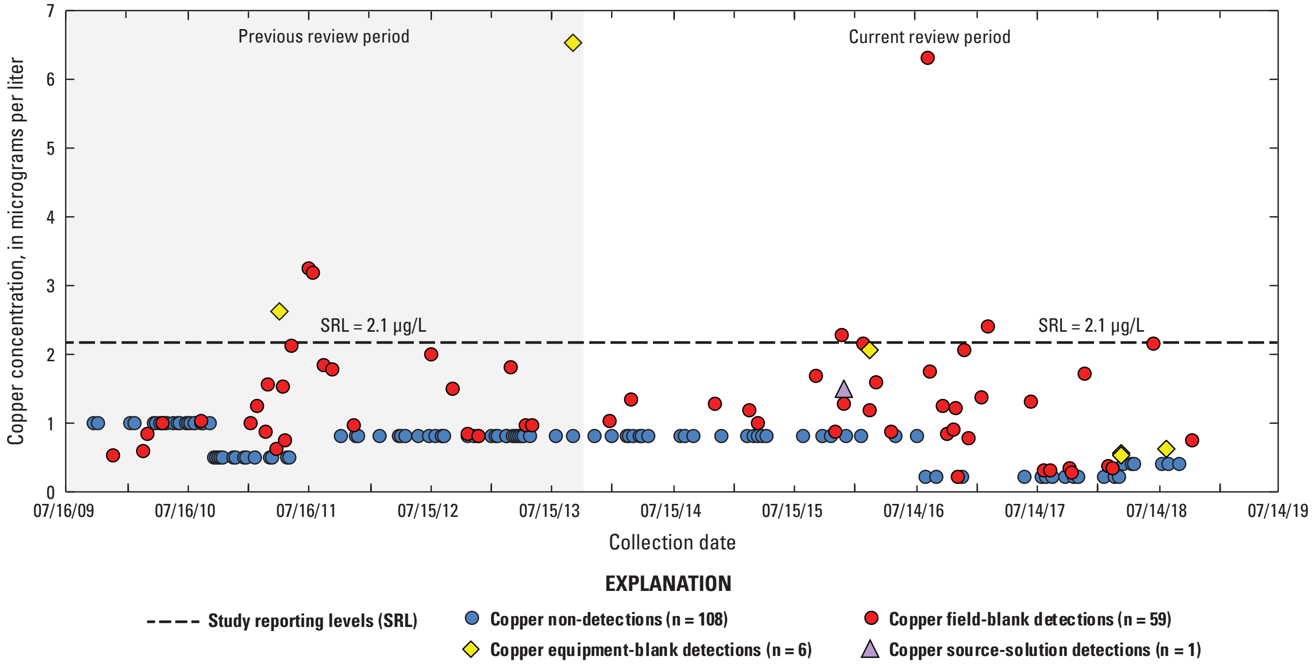


Figure 6. Copper concentrations in field, source-solution, and equipment blanks collected October 2009 through October 2018 plotted in time series and study reporting levels (SRLs), Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project. [µg/L, microgram per liter]

The contamination bias for copper was determined to be more likely caused by the equipment and processes used to collect samples in the field than by laboratory processes (Davis and others, 2014). Copper is one of the primary metals in the brass alloy plumbing hardware used to connect sampling equipment to the well. Some stainless steels also can contain low concentrations of copper. This bias has showed no improvement since the last review. The SRL for copper based on the BD-90/90 concentration using field-blank detections during the current review period (2.1 µg/L) is the same as the SRL determined after the previous review by Davis and others (2014; table 2). The SRL of 2.1 µg/L is far less than the U.S. Environmental Protection Agency Action Level (AL-US) for copper of 1,300 µg/L.

Lead (Pb)

During the previous review period (October 2009 through March 2013), 57 percent of field blanks collected for lead had detections, and the BD-90/90 concentration calculated from those field blanks was 0.82 µg/L (tables 1, 2). From October 2013 through October 2018, 23 of 77 field blanks (30 percent) had detections of lead with concentrations ranging from 0.021 to 1.29 µg/L (fig. 7). Lead was not detected in any of the 19 source-solution blanks collected but was detected in 4 of 8 equipment blanks collected over the entire review period with concentrations ranging from 0.04 µg/L to 0.35 µg/L (fig. 7). The detection limit for lead dropped from 0.04 to 0.02 µg/L in August of 2016; however, this change did not appear to result in an increase in detections in field blanks. Concentrations of lead in field blanks during the current review period were highest between 2015 and 2016 with more recent field blanks having relatively low concentrations or non-detections (fig. 7).

As noted in Davis and others (2014), the sampling equipment is likely the main source of lead contamination observed in the field blanks. The contamination bias for lead observed by Davis and others (2014) showed little sign of improvement between October 2013 and December 2016, with 39 percent of field blanks (19 of 49) having detections of lead (fig. 7). However, since the beginning of 2017, only 14 percent (4 of 28) of the field blanks had a lead detection. Despite this apparent improvement, an SRL for lead was calculated based on the BD-90/90 concentration using field-blank data from the current review period. The resulting SRL, 0.83 µg/L, is nearly the same as the SRL calculated during the previous review period (0.82 µg/L; Davis and others, 2014). As before, the newly established SRL of 0.83 µg/L is far less than the AL-US for lead of 15 µg/L.

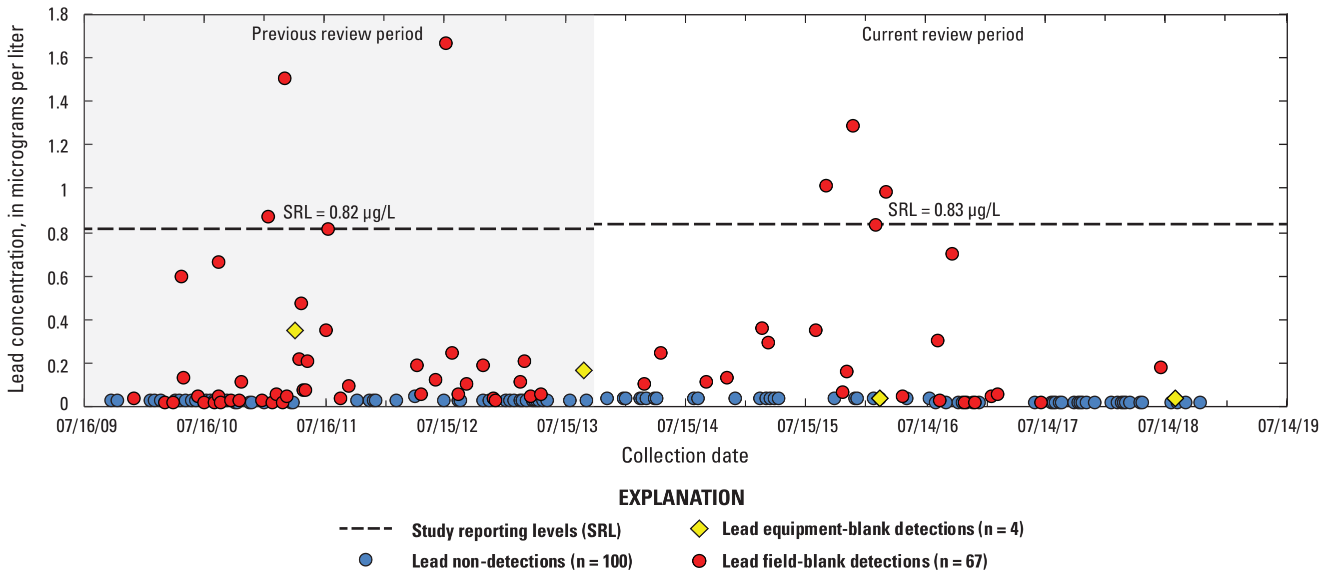


Figure 7. Lead concentrations in field, source-solution, and equipment blanks collected October 2009 through October 2018 plotted in time series and study reporting levels (SRLs), Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project. [µg/L, microgram per liter]

Zinc (Zn)

During the previous review period (October 2009 through March 2013) 36 percent of field blanks collected for zinc had detections and the BD-90/90 concentration calculated from those field blanks was 6.2 µg/L (tables 1, 2). From October 2013 through October 2018, 25 of 77 field blanks (32 percent) had detections of zinc with concentrations ranging from 2.02 to 7.08 µg/L (fig. 8). Zinc was detected in 1 of 19 source-solution blanks and 4 of 8 equipment blanks collected between October 2009 and October 2018 (fig. 8). Like lead, concentrations of zinc in field blanks during the current review period were highest between 2015 and 2016 with more recent field blanks having relatively low concentrations of zinc or non-detections (fig. 8).

The contamination bias for zinc observed by Davis and others (2014) showed little sign of improvement. It is likely that zinc detections in blanks (like lead and copper) are associated with the sampling equipment, specifically the brass (an alloy of copper and zinc) plumbing hardware used to connect sampling equipment to the wells. Between October 2013 and December 2016, 43 percent of blanks (21 of 49) had detections of zinc (fig. 8). However, since the beginning of 2017, only 14 percent of field blanks (4 of 28) had a zinc detection. Despite this apparent improvement, an SRL for zinc was calculated based on the BD-90/90 concentration using field blank data from the current review period. The calculated SRL was 3.9 µg/L, which is less than the SRL of 6.2 µg/L determined during the previous review period. The updated SRL of 3.9 µg/L is far less than the SWRCB Division of Drinking Water Secondary Maximum Contaminant Level (SMCL-CA) for zinc of 5,000 µg/L.

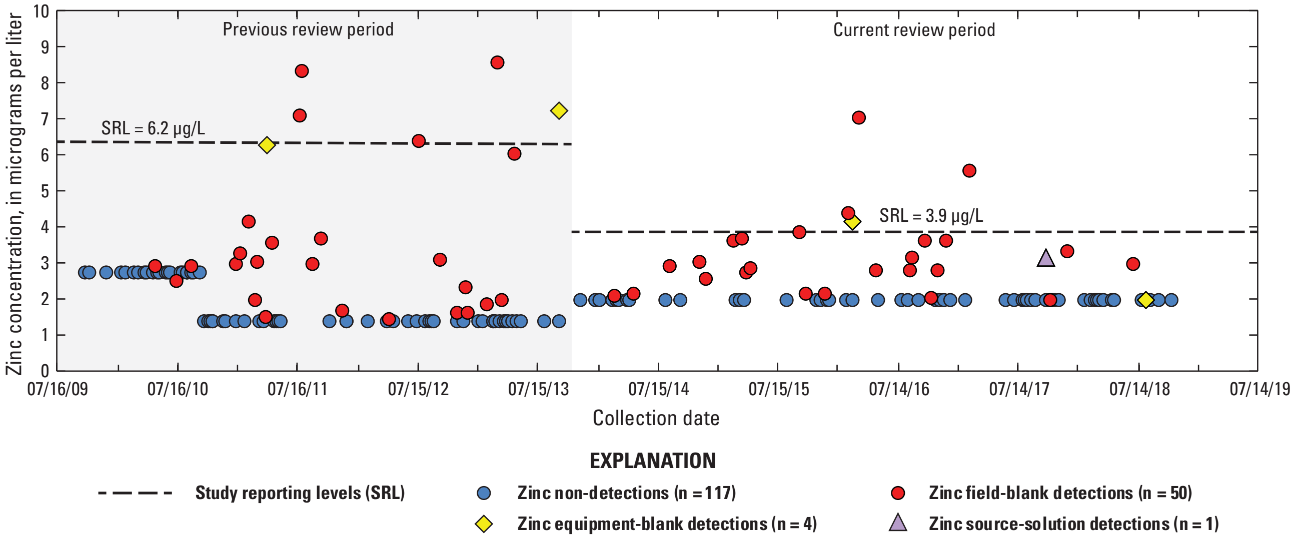


Figure 8. Zinc concentrations in field, source-solution, and equipment blanks collected October 2009 through October 2018 plotted in time series and study reporting levels (SRLs), Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project. [µg/L, microgram per liter]

Summary

The California State Water Resources Control Board in cooperation with the U.S. Geological Survey have been analyzing groundwater quality statewide since 2004 as part of the Groundwater Ambient Monitoring and Assessment (GAMA) Program Priority Basin Project (PBP). The program is a comprehensive assessment of statewide groundwater quality designed to identify and characterize risks to groundwater resources and to increase the availability of information about groundwater quality to the public. Trace-element field blanks were collected as part of the quality-control (QC) process for this program and were reviewed to determine potential bias to environmental sample results. Bias in the environmental data could be attributed to contamination in the field from contact between groundwater and sampling equipment or other contaminant sources, to contamination during processing or shipping, or to method bias during the analysis of samples. Bias can affect the interpretation of results, particularly if any constituents are present in the samples solely because of extrinsic contamination that would otherwise be absent from the groundwater sampled.

Olsen and others (2010) had previously determined study reporting levels (SRLs) for trace-element results based primarily on field-blank samples collected May 2004 through January 2008. Using the same approach as Olsen and others (2010) the SRLs were re-evaluated by Davis and others (2014). Using a modified approach in this report, the SRLs were again reviewed by analyzing field, source-solution, and equipment blanks collected October 2009 through October 2018. As in the previous two reports, results from the field blanks were used to calculate detection frequencies and to estimate the upper 90-percent confidence limit of contamination bias (BD-90/90). Unlike the previous reports, the BD-90/90 was used as the exclusive determinant of the SRL for the current review period (October 2013–October 2018). The BD-90/90 is the upper 90-percent confidence limit of the 90th percentile concentration of potential extrinsic contamination, with greater than 90 percent confidence derived by assuming the binomial probability distribution, from the method reported by Hahn and Meeker (1991).

Ten trace elements analyzed—antimony (Sb), arsenic (As), beryllium (Be), boron (B), cadmium (Cd), lithium (Li), selenium (Se), silver (Ag), thallium (Tl), and uranium (U)—had field-blank results that did not necessitate establishing SRLs during this review or the two previous reviews. Four trace elements analyzed—iron (Fe), manganese (Mn), molybdenum (Mo), and nickel (Ni)—had field-blank results that necessitated establishing an SRL during the previous review but were determined to no longer need an SRL. Copper (Cu) had field-blank results that necessitated keeping the previous SRL (2.1 µg/L). Two trace elements analyzed, cobalt (Co) and zinc (Zn), had field-blank results that necessitated decreasing the previous SRLs, from “reject all results” to 0.16 µg/L for Co and from 6.2 µg/L to 3.9 µg/L for Zn. Lead (Pb) had field-blank results that necessitated retention of an SRL at a nearly identical concentration (0.83 µg/L) to the one established during the previous review (0.82 µg/L). Hexavalent chromium (Cr[VI]) had field-blank results that necessitated establishing an SRL of 0.34 µg/L for the first time.

The SRLs for Cr(VI) (0.34 µg/L), Co (0.16 µg/L), Cu (2.1 µg/L), Pb (0.83 µg/L), and Zn (3.9 µg/L) were changed to these concentrations beginning October 2013, based on the BD-90/90 concentration in field blanks. The BD-90/90 calculation for Cr(VI) included source-solution and equipment blank results. October 2013 was selected as the start of the current review period because it was around this time that a noteworthy shift occurred with respect to detection frequencies and concentrations of manganese and cobalt. Additionally, between October 2013 and October 2018 (the current review period), there were enough blanks to calculate statistically robust BD-90/90 values. At all times, SRLs for the constituents were at least an order of magnitude less than the benchmarks established for drinking water for health and aesthetic purposes (cobalt does not currently have a benchmark); therefore, the practice of reporting concentrations below the SRLs as less than the SRL would not prevent the identification of values greater than the drinking-water benchmarks.

The primary sources of contamination inferred from this review are biases either from the inorganic blank water (IBW) used to collect the samples or from the equipment and processes used in the field to collect the samples. Reductions in field-blank detection frequencies for Fe, Mn, Mo, and Ni are likely related to increasing laboratory detection limits over time. Contamination in field blanks with Cr(VI), analyzed by Weck Laboratories, Inc., was inferred from this review to be linked to the IBW used when collecting blanks for trace elements.

Contamination in field blanks with Co and Mn reported in a 2014 review of GAMA-PBP blank-sample results was attributed to the high-capacity capsule filters that are still in use by the GAMA-PBP. As of October 2013, issues with the capsule filter appear to have improved with the application of mitigation strategies provided by the U.S. Geological Survey. The abrupt decreases in the frequency and magnitude of cobalt and manganese detections in blanks starting in October 2013 helped define the start date for SRLs resulting from this latest re-evaluation. Even though Co detections in field blanks have seen a significant reduction, Co was still detected in greater than 5 percent of the field blanks, and an SRL was established. The Mn detection frequency in blanks dropped from over 70 percent during the previous review to less than 3 percent during the current review and Mn no longer needs an SRL. Lastly, the sampling equipment is likely the main source of contamination for Co, Pb, and Zn. All three are components of brass, which is consistently a part of the sampling process. For each of these trace elements, there was either little change or a minor reduction in the contamination bias with respect to SRLs determined during this review as compared to the two previous reviews.

The SRLs determined in this report are intended to be used for GAMA groundwater-quality data for samples collected from October 2013 onward, for as long as QC data are consistent with what was observed in this study. The QC data should be continuously reviewed in the context of the findings in this report to reassess the SRLs used by the GAMA-PBP.

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