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Assessment of Dissolved-Selenium Concentrations and Loads in the Lower Gunnison River Basin, Colorado, as Part of the Selenium Management Program, 2011–17

Open-File Report 2020–1078

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

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DAVID BERNHARDT, Secretary

U.S. Geological Survey
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U.S. Geological Survey, Reston, Virginia: 2020

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Area	
mile (mi^2)	2.590	square kilometer (km^2)
	Length	
foot (ft)	0.3048	meter (m)
	Volume	
cubic foot (ft^3)	0.02832	cubic meter (m^3)

Multiply	By	To obtain
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Mass	
pound, avoirdupois (lb)	0.4536	kilogram (kg)

International System of Units to U.S. customary units

Multiply	By	To obtain
	Volume	
liter (L)	0.2642	gallon (gal)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)

Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Supplemental Information

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

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Water year is defined as the 12-month period from October 1 through September 30 and is designated by the year in which it ends.

Abbreviations

NWQL	National Water Quality Laboratory
Q_n	mean daily
SMP	Selenium Management Program
USGS	U.S. Geological Survey
WY	water year

Assessment of Dissolved-Selenium Concentrations and Loads in the Lower Gunnison River Basin, Colorado, as Part of the Selenium Management Program, 2011–17

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Abstract

The Gunnison Basin Selenium Management Program implemented a water-quality monitoring network in 2011 to measure concentrations of selenium in the lower Gunnison River Basin in Colorado. Selenium is a trace element that bioaccumulates in aquatic food chains. Selenium is essential for life, but elevated amounts can cause reproductive failure, deformities, and other harmful effects. The primary goal of the Selenium Management Program is to meet the State of Colorado water-quality standard of 4.6 micrograms per liter (μg/L) for dissolved selenium at the U.S. Geological Survey (USGS) streamflow-gaging station number 09152500—Gunnison River near Grand Junction, Colorado—herein referred to as "Whitewater." The U.S. Geological Survey, in cooperation with the Bureau of Reclamation, has completed a review of dissolved-selenium data collected from the Selenium Management Program network during Water Year (WY) 2017 (October 1, 2016 through September 30, 2017) to further the understanding of the status and trends of selenium in the basin. This report presents the percentile values for selenium because regulatory agencies in Colorado make decisions based on the U.S. Environmental Protection Agency's Clean Water Act section 303(d), which uses percentile values for concentrations. Also presented are dissolved-selenium loads at 14 sites in the lower Gunnison River Basin for WYs 2011–17. Annual dissolved-selenium loads were calculated for six sites with continuous U.S. Geological Survey streamflow-gaging stations. These six sites are referred to as "core" sites in this report. The remaining sites, which do not have streamflow-gaging stations, are referred to as "ancillary" sites in this report. During WY 2017, the loads calculated at the six core sites ranged from 306 pounds (lb) at Uncompahgre River at Colona to 12,600 lb at Whitewater, respectively.

By using discrete water-quality samples and the associated discharge measurements, instantaneous loads were calculated for 14 sites in WYs 2011–17 where discrete water-quality sampling took place. Median instantaneous loads ranged from 0.52 pounds per day (lb/d) at Uncompahgre River at Colona to 35.7 lb/d at Whitewater. Mean instantaneous loads ranged from 0.63 lb/d at Cummings Gulch at mouth to 35.5 lb/d at Whitewater. Most tributary sites in the basin had a median instantaneous dissolved-selenium load of less than 20.0 lb/d. In general, dissolved-selenium loads at Gunnison River main-stem sites showed an increase from upstream to downstream.

The State of Colorado's water-quality standard for dissolved selenium of 4.6 μg/L was compared to the 85th percentiles for dissolved selenium at selected sites. Annual 85th percentiles for dissolved selenium were calculated by using estimated dissolved-selenium concentrations from linear regression models for the six core sites with U.S. Geological Survey streamflow-gaging stations. The 85th-percentile concentrations for WY 2017 based on this method ranged from 0.68 μg/L at Uncompahgre River at Colona to 140 μg/L at Loutzenhizer Arroyo at North River Road. The 85th percentiles for concentrations of dissolved selenium also were calculated from water-quality samples collected during WY 2017 from sites with sufficient data. The annual 85th-percentile concentrations based on the discrete samples ranged from 0.75 μg/L at Uncompahgre River at Colona to 106 μg/L at Loutzenhizer Arroyo at North River Road.

An analysis was completed for Whitewater to determine if an upward or downward trend exists for dissolved-selenium loads during two time periods. The first time period included all data at Whitewater, whereas the second time period focused on more recent data. The trend analysis indicates a decrease from 22,200 to 12,600 lb, which is a 43.1 percent (9,600 lb) reduction during the time period WY 1986 through WY 2017. The trend analysis for the annual dissolved-selenium load for WY 1995 through WY 2017 indicates a decrease of 6,600 lb per year, or 35.5 percent. An evaluation of laboratory bias was completed for selenium data which was used in the trend analysis. Findings indicated a potential positive bias of approximately 12 percent may exist in the data from October 2005 through August 2015.

Introduction

The lower Gunnison River Basin Selenium Management Program is a private and public partnership of concerned parties working together to identify and implement solutions to reduce selenium concentration in the Gunnison and Colorado Rivers (Bureau of Reclamation [Reclamation], 2011). Selenium is a trace element that bioaccumulates in aquatic-food chains. Selenium is essential for life, but elevated amounts, such as those found in the Gunnison River Basin, can cause reproductive failure, deformities, and other harmful effects (Hamilton, 1998; Lemly, 2002). The primary goal of the Selenium Management Program (SMP), as recommended in the U.S. Fish and Wildlife Service's "Gunnison River Basin Programmatic Biological Opinion," (U.S. Fish and Wildlife Service, 2009), is to meet the State of Colorado water-quality standard of 4.6 micrograms per liter (µg/L) for dissolved selenium at the U.S. Geological Survey (USGS) streamflow-gaging station number 09152500—Gunnison River near Grand Junction, Colorado—herein referred to as "Whitewater." A parallel goal is to continue implementation, monitoring, and evaluation of management practices that will maintain or continue to reduce dissolved-selenium concentration in the river. Mayo and Leib (2012) documented a downward trend in dissolved-selenium load from 1986 through 2008 at Whitewater. The SMP's long-term objective is to improve water quality by reducing dissolved-selenium concentrations sufficiently to assist in the recovery of the Colorado *Ptchocheilus lucius* (pikeminnow) and *Xyrauchen texanus* (razorback sucker) (Reclamation, 2011).

The SMP implemented a water-quality monitoring network in 2011 at 18 USGS sites in the lower Gunnison River Basin (Reclamation, 2011). Five of the sites have had streamflow-gaging stations for the entire period of water years (WY) 2011–17. At one site, Loutzenhizer Arroyo at North River Road, the streamflow-gaging station began operation during WY 2014. These six sites are referred to as "core" sites in this report. The remaining sites, which do not have streamflow-gaging stations, are referred to as "ancillary" sites in this report. The USGS had also previously collected water-quality data at several of the 18 sites prior to operation of the SMP network. The USGS, in cooperation with Reclamation, has completed a review of dissolved-selenium data collected from 14 of the 18 sites (fig. 1) during WY 2017 (October 1, 2016 through September 30, 2017) to further the understanding of the status and trends of selenium in the basin. This review builds on the work presented in Henneberg (2018). The USGS review included the following four types of analyses, which are further broken down into five tasks (A through E) (table 1):

1. Task A. Calculation of annual dissolved-selenium loads by using linear regression models in R-LOADEST at six core sites with continuous USGS streamflow-gaging stations.
2. Task B. Instantaneous dissolved-selenium loading analyses at six core and eight ancillary sites where discrete water-quality sampling took place. The instantaneous dissolved-selenium load can be calculated if the collection of the dissolved-selenium sample was accompanied by a streamflow measurement.
3. Tasks C and D. Annual (C) and instantaneous (D) 85th-percentile analyses for dissolved selenium at 14 sites.
4. Task E. Trend analyses of dissolved-selenium concentrations and loads at Whitewater.

Description of Study Area

The Gunnison River Basin has a drainage area of almost 8,000 square miles (mi^2) at its confluence with the Colorado River at Grand Junction, Colorado. Most of the main-stem runoff is generated by spring snowmelt; however, upstream reservoirs have altered the timing and magnitude of Gunnison River flood peaks since 1966. Flood magnitudes of given recurrence intervals have decreased substantially since 1966 (Elliot and Hammack, 1999). The lower Gunnison River Basin, for the purposes of this analysis and report, includes the Gunnison River and all tributaries downstream of Cimarron, Colorado.

Purpose and Scope

This report presents the percentiles of selenium concentrations and dissolved-selenium loads at 14 of the 18 SMP monitoring sites in the lower Gunnison River Basin for WY 2011–17 to provide historical context for the sampling period. Site-specific sampling-date ranges are presented in table 1. Trend analyses of selenium concentrations and loads at Whitewater are presented for WY 1986 through WY 2017 and also from data recently collected from WY 1995 through WY 2017. An assessment of potential laboratory bias was also completed for the selenium data used in the trend analysis.

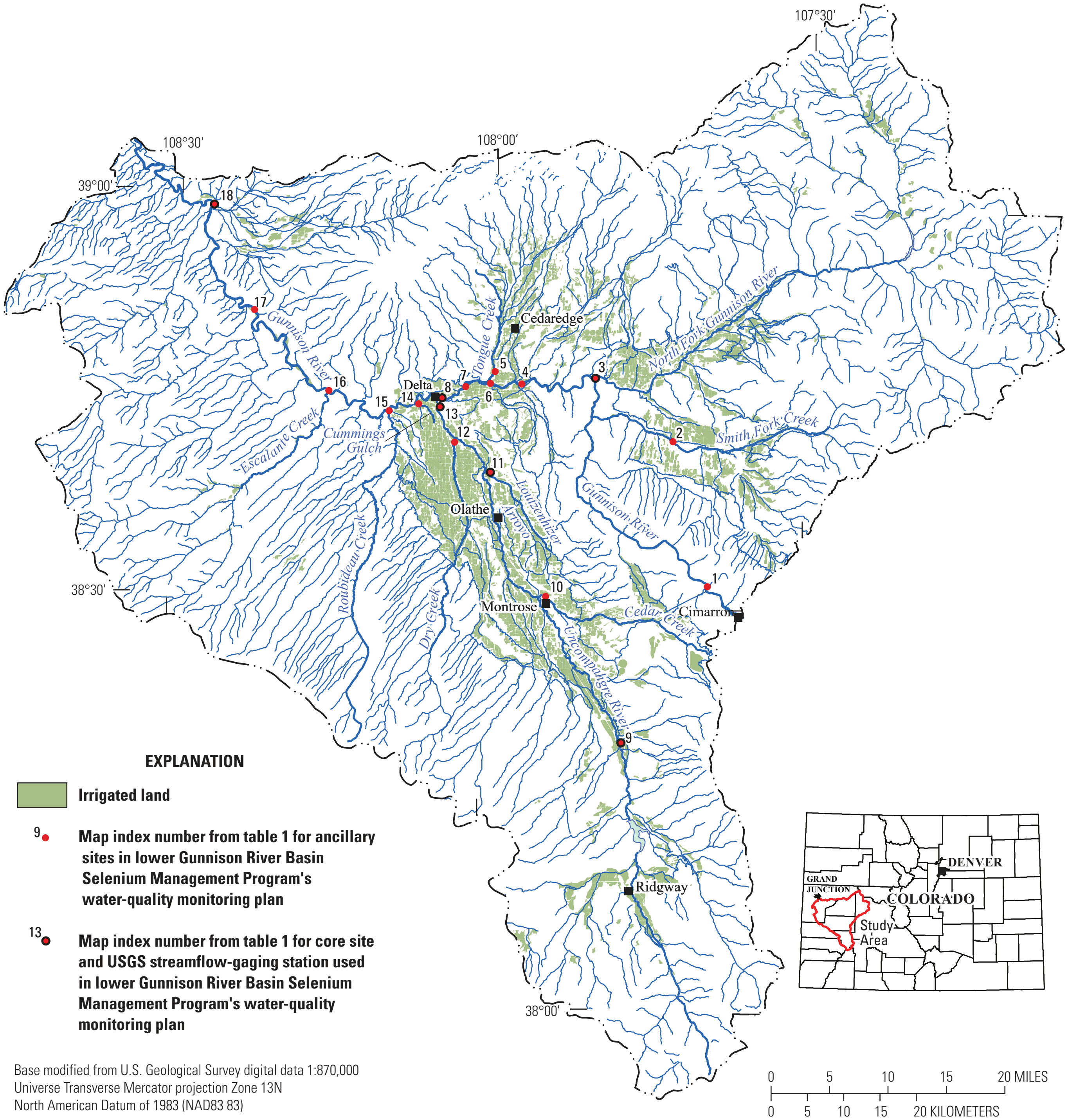

Figure 1. Map of the lower Gunnison River Basin showing the locations of six U.S. Geological Survey streamflow-gaging stations (core sites) and 12 water-quality sampling stations (ancillary sites) in the lower Gunnison River Basin Selenium Management Program. (USGS, U.S. Geological Survey).

Table 1. Tasks completed at 18 U.S. Geological Survey sites in the lower Gunnison River Basin.

[Tasks are (A) annual dissolved-selenium loading analysis, (B) instantaneous dissolved-selenium loading analysis, (C) annual dissolved-selenium 85th-percentile load estimation, (D) instantaneous dissolved-selenium 85th-percentile load estimation, and (E) trend analyses of dissolved-selenium concentrations and loads at Whitewater. Sites are shown on fig. 1. USGS, U.S. Geological Survey; WY, water year, is defined as October 1 through September 30 of the following year; site types are (core) which include a U.S. Geological Survey streamflow-gaging station, and (ancillary) which do not include a U.S. Geological Survey streamflow-gaging station]

Map index number (fig. 1)	USGS station short name (USGS station number)	Site type	Sampling dates (WY)	Analysis types (Tasks)
1	Gunnison River below Gunnison Tunnel (09128000) (Sampling terminated after water year 2012)	Ancillary[1]	2011–12	—
2	Smith Fork near Lazear (09129600)	Ancillary[1]	2012–16	—
3	North Fork Gunnison River near Lazear (09136100)	Core	2011–17	A, B, C
4	Gunnison River at Austin (384624107570701)	Ancillary	2011–17	B, D
5	Tongue Creek at Cory (09144200)	Ancillary	2011–17	B, D
6	Gunnison River near Cory (09137500)	Ancillary	2011–17	B, D
7	Gunnison River near Hartland Dam (384617108022901)	Ancillary[1]	2011–15	—
8	Gunnison River at Delta (09144250)	Core	2011–17	A, B, C
9	Uncompahgre River at Colona (09147500)	Core	2011–17	A, B, C
10	Cedar Creek near mouth (383041107544201)	Ancillary	2014–17	B, D
11	Loutzenhizer Arroyo at North River Road (383946107595301)	Core	2011–17	A, B, C
12	Dry Creek at mouth near Delta (384202108032001)	Ancillary	2014–17	B, D
13	Uncompahgre River at Delta (09149500)	Core	2011–17	A, B, C
14	Cummings Gulch at mouth (384448108070301)	Ancillary	2014–17	B, D
15	Roubideau Creek near mouth (09150500)	Ancillary[1]	2012–16	—
16	Gunnison River above Escalante Creek (384527108152701)	Ancillary	2012–16	B, D
17	Gunnison River below Dominguez Creek (385011108225401)	Ancillary	2013–17	B, D
18	Gunnison River near Grand Junction (Whitewater) (09152500)	Core	2011–17	A, B, C, E

[1]No data were collected during water year 2017.

Methods

This section of the report discusses the technique of flow-adjusted trend analysis, the methods used for regression analysis, the use of regression-analysis software in the study, and the evaluation of laboratory bias in the dataset related to trend analysis. The concept of normalized streamflow is explained, and the methods of estimating load and concentration trends are shown. Streamflow and water-quality data are available in the USGS National Water Information System (https://doi.org/10.5066/F7P55KJN) (USGS, 2017).

General Approach of the Analysis

Regression analysis is a long-accepted and widely used method for analyzing trends in water-quality constituents (Kirscher and others, 1984; Butler, 1996; Richards and Leib, 2011). Variables selected to estimate trends in the concentrations of water-quality constituents in these types of studies commonly include daily streamflow, time, and the measured concentration of the constituent (selenium for this assessment). Several transformations are commonly used to enhance the estimation accuracy of several variables (logarithmic [log] transformation, quadratic terms, decimal time, centered time, and sinusoidal transformations of time). For this study, daily streamflow, decimal time, and various transformations were used in estimating trends in selenium loads and concentrations (Mayo and Leib, 2012). Calibration datasets included the current and previous WY's streamflow, specific conductance, and dissolved-selenium concentration for each discrete water-quality sample collected.

Flow-Adjusted Trend Analysis

Trends in loads and concentrations of water-quality constituents can be approached from two perspectives: not flow-adjusted (which shows the overall influence from both human and natural factors) and flow-adjusted (which removes natural streamflow variability) (Sprague and others, 2006). Only flow-adjusted trends were analyzed in this study (Mayo and Leib, 2012).

Normalized Mean Daily Streamflow

Daily mean streamflow values for each day of the calendar year over the 31-year period of record were averaged to produce a normalized daily mean streamflow value (Q_n), herein referred to as a “mean daily” value. An averaging function available on the USGS National Water Information System website (https://doi.org/10.5066/F7P55KJN) was used to calculate these values. For example, a mean of all the January 1st daily mean streamflow values was calculated for January 1, 1986, through January 1, 2017. This creates a Q_n (mean daily) value for January 1st for the entire 31-year period. By calculating a similar Qn for every day of the year, the year-to-year fluctuations in daily mean streamflow are removed. The Q_n was used only to compare the changes in selenium loads and concentrations between WY 1986 and WY 2017. It is important to remember that because the estimated loads and concentrations given for WY 1986 and WY 2017 were based on the mean daily streamflow, the results were illustrative of the change in selenium loads and concentrations only over the period of study. They were not the actual loads and concentrations that occurred in WY 1986 and WY 2017 (Mayo and Leib, 2012).

Regression-Analysis Software

To build the regression model, the software program R-LOADEST (Version 0.4.5) was selected because it is designed to calculate constituent loads by using daily mean streamflow, time, seasonality, and other explanatory variables. R-LOADEST was derived from LOADEST and was used in the R statistical environment (Version 3.6.1) (Runkel and others, 2004R Core Team, 2019). R-LOADEST was used to calculate daily and annual selenium loads and concentrations from measured selenium concentration calibration data from WY 1986 through WY 2017 (Mayo and Leib, 2012).

Evaluation of Potential Laboratory Bias in Reported Selenium Concentrations

National Water Quality Laboratory (NWQL) Technical Memorandum 2019.01, dated February 19, 2019, characterized bias and variability in dissolved trace-element concentrations determined by inductively coupled plasma-mass spectrometry from October 2005 through August 2015 at NWQL as a result of a deviation in the acid concentration of the calibration standards (Stetson, 2019). Selenium is one of the potentially affected analytes. Selenium data affected by the acid-concentration deviation were potentially biased high by a median of 8.0 percent. Because these data were used in the trend analysis discussed in this report, the potential bias was evaluated.

First, relationships between selenium and several analytes (calcium, magnesium, sodium, chloride, and sulfate) unaffected by the potential bias were evaluated by using linear regression to determine whether the relations were significant (p-value < 0.05). Second, if the relationships were significant, a Mann-Whitney-Wilcoxon test was used to compare ratios of discrete-sample concentrations for selenium and the unaffected analytes by group . The Mann-Whitney-Wilcoxon test is a nonparametric test for identifying differences between groups (Helsel and Hirsch, 2002). The groups were differentiated by time period, with one group including all potentially affected data (October 1, 2005 through August 8, 2015) and the second group (unaffected) including data after the calibration error had been resolved (August 9, 2015 through September 30, 2018). Third, an additional Mann-Whitney-Wilcoxon test was completed on two related but unaffected analytes (calcium and sodium) to test for any environmental changes during the period (environmental control). Finally, linear regression models were developed by using the data from only the unaffected period as the calibration data. The strongest model was used to compare selenium concentrations predicted by using a model calibrated with unaffected data to observations made during the potentially affected period. This comparison was used to estimate the magnitude of bias during the affected period. Residual concentration values were determined for each sample by deducting the predicted selenium concentration from the observed concentration. As a result of the laboratory’s intermittent application of the acid-concentration deviation during the potentially affected period, identification and correction of discrete-sample data was not appropriate. Instead, characterization of laboratory bias was limited to an assessment of the sample population during the potentially affected time period, not to each individual sample within the time period.

Assessment of Dissolved-Selenium Concentrations and Loads

Dissolved-Selenium Concentrations

Boxplots of dissolved-selenium concentrations in discrete water-quality samples are plotted from left to right in an upstream-to-downstream order for WYs 2011–17 in figure 2. In general, the dissolved-selenium concentration increased from upstream to downstream at Gunnison River main-stem sites (blue boxes in fig. 2; Uncompahgre River at Colona and Uncompahgre River at Delta are designated as Gunnison River main-stem sites to conform with previous selenium studies in the area). Dissolved-selenium concentrations at most sites ranged from 1.0 to 10.0 µg/L. Samples from the Gunnison River below Gunnison Tunnel had the lowest dissolved-selenium concentrations (less than 1.0 µg/L) for all samples, and samples from the Loutzenhizer Arroyo at North River Road had the highest (greater than 100 µg/L).

Laboratory Bias of Reported Selenium Concentrations

Mann-Whitney-Wilcoxon tests performed on ratios of selenium concentrations to those of unaffected analytes indicated statistically significant differences between the ratios when comparing the potentially affected and unaffected periods, except for the environmental control (table 2). P-values resulting from statistical tests were less than 0.05 for every ratio except the environmental control. These results indicate that the data used for the trend analysis may be biased high for the period October 1, 2005 through August 8, 2015, the potentially affected period. In each comparison, the median value for the ratio of selenium to analyte was higher during the potentially affected period than during the unaffected period (fig. 3). Selenium concentrations predicted by the strongest linear regression model calibrated with unaffected data were compared to observations made during the potentially affected period by the use of residual concentration values. The residual values were plotted by time to illustrate the differences between the concentration values during and after the potentially affected and unaffected periods (fig. 4).

The regression model used to predict selenium concentrations from the unaffected calibration dataset was plotted with 95-percent confidence and prediction intervals. Measured selenium concentrations were grouped by period and overlain on the regression plot. Most sample concentrations from the potentially affected period were plotted above the model, with several plotting outside the upper 95-percent prediction interval (fig. 5). Percent differences between sampled and predicted selenium concentrations were compared by group. The median percent difference during the unaffected period was approximately −2 percent, whereas the potentially affected period had a median percent difference of approximately 12 percent (fig. 6). The USGS NWQL reported a median bias of 8 percent in technical memorandum 2019.01 (Stetson and others, 2019).

Dissolved-Selenium Loads

Annual dissolved-selenium loads in pounds per year (lb/yr) for the six core sites are summarized in table 3. Annual load estimates for WY 2017 were lowest at 09147500, Uncompahgre River at Colona (306 lb/yr) and highest at 09152500, Whitewater (12,600 lb/yr). Equation forms, regression- model coefficients, and diagnostics, are provided in Appendix 1.

Median and mean instantaneous dissolved-selenium loads, in pounds per day (lb/d), were calculated for 14 sites by using discrete water-quality samples and the associated discharge measurements for WY 2017 (if available) and at 18 sites from WY 2011–17 (table 4). Median instantaneous loads ranged from 0.52 lb/d at Uncompahgre River at Colona (table 4) to 35.7 lb/d at Whitewater for WY 2017. Mean instantaneous loads ranged from 0.63 lb/d at Cummings Gulch at mouth to 35.5 lb/d at Whitewater for WY 2017. Most sites in the basin had a median dissolved-selenium load of less than 20.0 lb/d. In general, dissolved-selenium loads at main-stem Gunnison River sites increased from upstream to downstream (fig. 7).

Changes in median instantaneous dissolved-selenium loads between selected sites along the main-stem Gunnison River are reported in table 5 for WYs 2011–17. The largest increase in dissolved-selenium load was measured between Gunnison River at Delta and Gunnison River above Escalante Creek; the increase is due primarily to the Uncompahgre River at Delta, which contributes a median load of 16.8 lb/d of dissolved selenium to this reach (table 4).

Concentration Percentiles for Dissolved Selenium

The 85th-percentile values of estimated selenium concentrations were calculated for WY 2017. This report presents the percentile values of selenium because regulatory agencies in Colorado make decisions based on the U.S. Environmental Protection Agency's Clean Water Act Section 303(d), which uses percentile values of concentration (Federal Water Pollution Control Act, 1972; Mayo and Leib, 2012). The annual 85th-percentile concentrations for dissolved selenium were derived for the 14 sites for WY 2017 with the exceptions of Gunnison River below Gunnison Tunnel, Smith Fork near Lazear, Gunnison River near Harland Dam, and Roubideau Creek near mouth, none of which had any samples collected in WY 2017. The annual 85th percentiles presented in table 6 for the six core sites were estimated as part of the R-LOADEST daily mean load calculations, whereas the 85th percentiles presented in table 7 for 14 of the 18 sites were calculated from the discrete water-quality samples.

The annual 85th-percentile concentrations (table 6) for WY 2017 based on the R-LOADEST estimated daily mean loads ranged from 0.68 µg/L at Uncompahgre River at Colona to 140 µg/L at Loutzenhizer Arroyo at North River Road. The only core sites that exceeded the State of Colorado water-quality standard of 4.6 µg/L during WY 2017 were Loutzenhizer Arroyo at North River Road and Uncompahgre River at Delta (table 6).

The annual 85th-percentile concentrations based on the discrete water-quality samples in table 7 ranged from 0.75 µg/L at Uncompahgre River near Colona to 106 µg/L at Loutzenhizer Arroyo at North River Road for WY 2017. Tongue Creek at Cory, Cedar Creek near mouth, Loutzenhizer Arroyo at North River Road, Uncompahgre River at Delta, and Cummings Gulch at mouth were the only sites to exceed the State of Colorado water-quality standard of 4.6 µg/L on the basis of discrete samples collected during WY 2017.

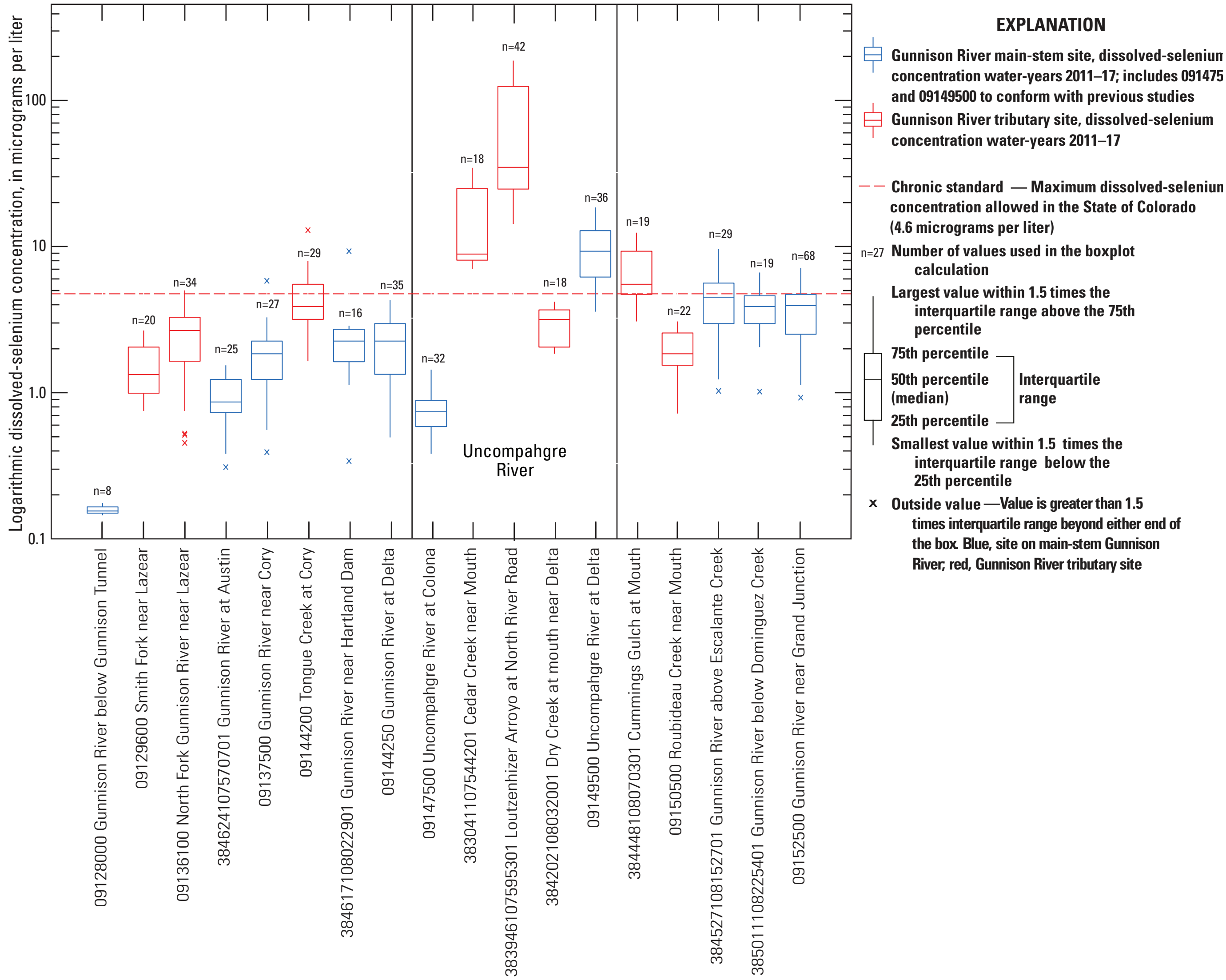

Figure 2. Boxplots of dissolved-selenium concentrations, in micrograms per liter, for discrete water-quality samples collected during water years 2011–17. Uncompahgre River at Colona and Uncompahgre River at Delta are designated as Gunnison River main-stem sites to conform with previous selenium studies in the area.

Table 2. Mann-Whitney-Wilcoxon tests of potential laboratory bias in selenium values at Gunnison River near Grand Junction, Colorado (09152500) for October 2005 through September 2018.

[Potentially affected period, October 1, 2005 through August 8, 2015; unaffected period, August 9, 2015 through September 30, 2018; p-value, significance level]

Selected analyte ratio	Mann-Whitney-Wilcoxon test p-value	Potentially affected period, median ratio	Unaffected period, median ratio	Difference in median ratios between potentially affected and unaffected periods
Selenium to Calcium	6.94E-05	2.31E-05	1.79E-05	5.16E-06
Selenium to Magnesium	6.87E-06	4.47E-05	3.70E-05	7.73E-06
Selenium to Sodium	1.10E-05	2.67E-05	2.35E-05	3.22E-06
Selenium to Chloride	0.00809	0.000263	0.00024	2.27E-05
Selenium to Sulfate	4.96E-06	1.91E-05	1.57E-05	3.42E-06
Calcium to Sodium	0.097173	1.222352	1.305898	−0.08355

Trend Analysis of Dissolved-Selenium Concentrations and Loads

By using methods described in (Mayo and Leib, 2012), a trend analysis of dissolved-selenium concentrations and loads was completed by using water-quality data collected at Whitewater. The calibration dataset contained data from all available discrete water-quality samples from WY 1986 through WY 2017. This process ensured that all data (WY 1986–2008) used by Mayo and Leib (2012) were included in the dataset used for model development through WY 2017. A second period from WY 1995 through WY 2017 was analyzed, and the trend analysis used the same methods as used by Mayo and Leib (2012) to provide emphasis on the more recently collected data.

A continuing downward trend in annual dissolved-selenium loads was observed at Whitewater for both time periods, as indicated in tables 8 and 9. The dissolved-selenium loads decreased from 22,200 pounds (lb) in WY 1986 to 12,600 lb in WY 2017, a decrease of 9,600 lb (table 8). This decrease represents a 43.1 percent reduction during the period and an additional 14.5 percent reduction from the 28.6 percent reduction reported through WY 2008 in Mayo and Leib (2012). As shown in table 8, the 95-percent confidence levels for the dissolved-selenium load in WY 1986 were 20,000 lb (lower) and 24,600 lb (upper); the 95-percent confidence levels for the dissolved-selenium load for 2017 were 11,700 lb (lower) and 13,600 lb (upper). There is no overlap of values predicted within the 95-percent confidence levels for 1986 and 2017, providing further evidence for the downward trend (table 8). For WY 1995 through WY 2017 (table 9), the annual dissolved-selenium load decreased from 18,600 lb in 1995 to 12,000 lb in 2017, a decrease of 6,600 lb, or 35.5 percent.

The time component was removed from the R-LOADEST regression model to graphically describe the trend in dissolved-selenium concentrations that had been adjusted only for flow (Mayo and Leib, 2012). The calibration dataset was then used to predict dissolved-selenium concentrations for each water sample and to compute a partial residual by subtracting the predicted concentrations from the measured concentration. The resulting partial residuals were plotted by year with a Locally Weighted Scatterplot Smoothing fit line in figure 8 for WYs 1986–2017 and in figure 9 for WYs 1995–2017. Both figures 8 and 9 confirm a continuing decrease in dissolved-selenium concentration during the trend periods. Both figures also illustrate the possible laboratory bias in the selenium dataset during the potentially affected period (2005–15). Laboratory values, which were biased high, would result in higher partial residuals when compared to unaffected values. A small inflection can be observed in the Locally Weighted Scatterplot Smoothing trend line centered around 2006 in figure 8 and 2009 in figure 9; both indicate that the partial residuals may be biased high during the period. The potential positive bias of selenium data used in the analysis does not affect the downward trend identified at Whitewater. If actual selenium values were lower than reported because of bias, the downward trend may be greater than identified in this study.

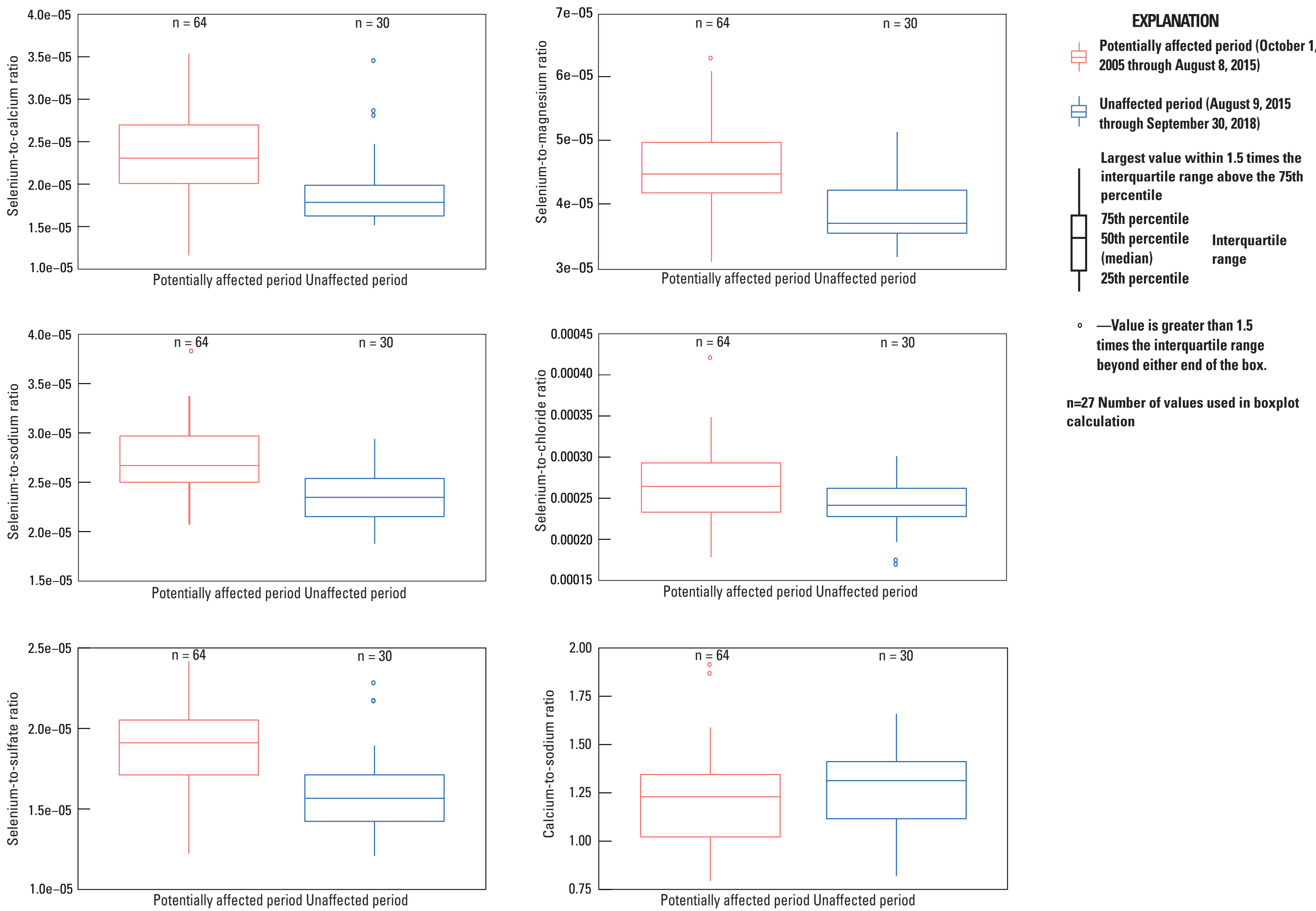

Figure 3. Boxplots of analyte ratios at Gunnison River near Grand Junciton, Colorado (09152500) for potentially affected and unaffected time periods.

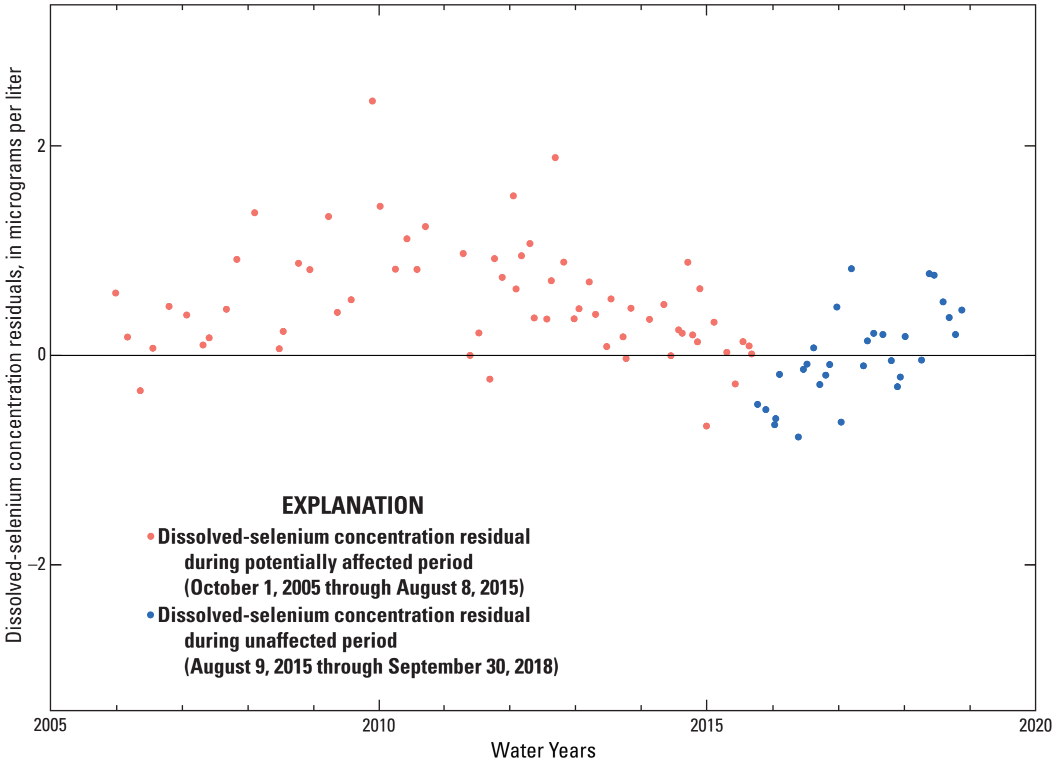

Figure 4. Time series of residual selenium concentrations at Gunnison River near Grand Junction, Colorado (09152500) for potentially affected and unaffected periods.

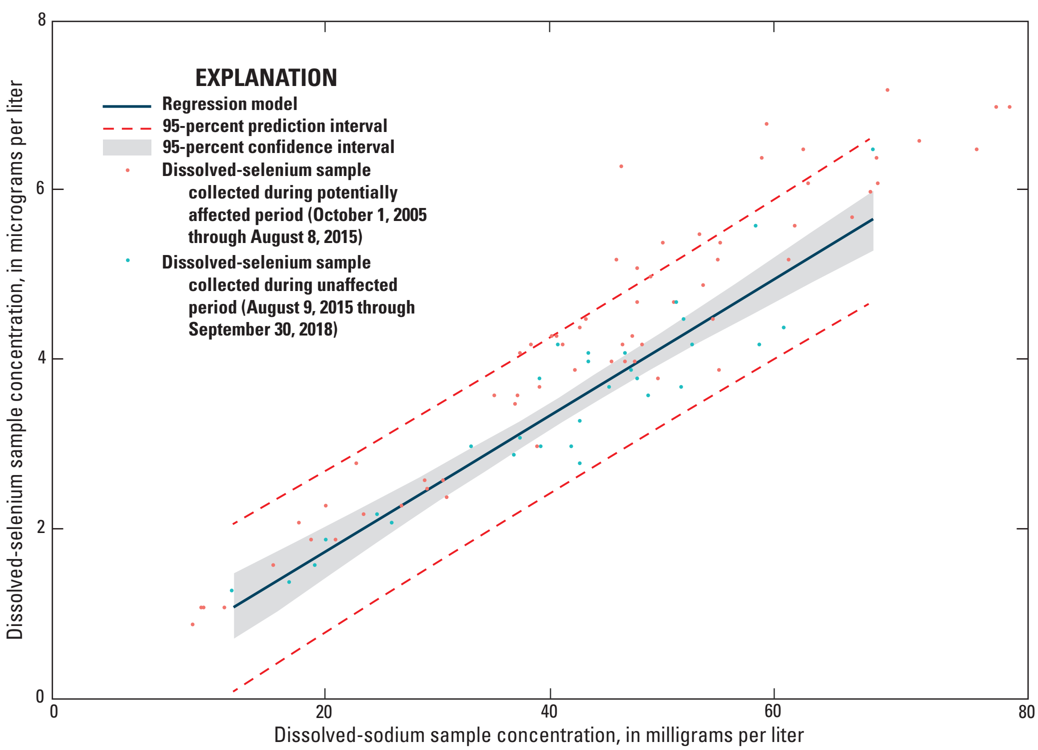

Figure 5. Selenium-prediction regression model calibrated with unaffected data and selenium-sample concentrations during potentially affected and unaffected periods at Gunnison River near Grand Junction, Colorado (09152500).

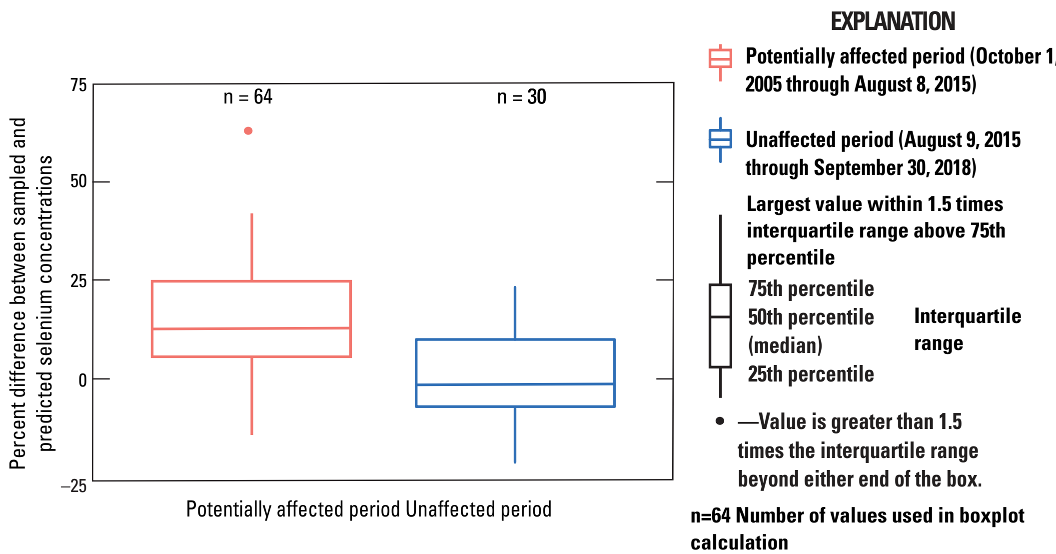

Figure 6. Boxplots of percent differences between predicted and sampled selenium concentrations by group during potentially affected and unaffected periods at Gunnison River near Grand Junction, Colorado (09152500).

Table 3. Estimated annual dissolved-selenium load, in pounds per year, calculated by using multiple linear- regression techniques in R-LOADEST (Runkel and others, 2004) at six core sites with U.S. Geological Survey streamflow-gaging stations for water years 2011–17.

[USGS, U.S. Geological Survey; WY, water year, is defined as October 1 through September 30 of the following year; lb, pounds; yr, year]

Map index number (fig. 1)	USGS station number	WY 2017 Annual dissolved-selenium load (lb/yr)	Total dissolved-selenium load for WYs 2011–17 (lb)[1,2]
3	09136100	1,200	8,180
8	09144250	5,390	34,790
9	09147500	306	2,070
11	383926107593001	3,830	[3]3,830
13	09149500	5,590	42,300
18	09152500	12,600	91,200

[1]Summation of WY 2017 annual loads and annual load values from Henneberg, 2016.

[2]May include values affected by laboratory bias (Stetson, 2019).

[3]WY 2017 is the first year regression techniques were able to be used at this site.

Table 4. Median and mean instantaneous dissolved-selenium load, in pounds per day, at 14 sites for water year 2017 and at 18 sites for 2011–17.

[USGS, U.S. Geological Survey; WY, water year, defined as October 1 through September 30 of the following year; lb/d, pounds per day; blw, below; site types are (C) core which include a U.S. Geological Survey streamflow-gaging station, and (A) ancillary which do not include a U.S. Geological Survey streamflow-gaging station, core; ---, no data available]

Map index number (fig. 1)	USGS station number	USGS station short name	Site type	Number of samples WY 2017	Median selenium load for WY 2017 (lb/d)	Mean selenium load WY 2017 (lb/d)	Number of samples WY 2011–17	Median selenium load for WY 2011–17 (lb/d)[1]	Mean selenium load for WY 2011–17 (lb/d)[1]
1	09128000	Gunnison River blw Gunnison Tunnel	A	0	---	---	[2]8	[2]0.57	[2]1.2
2	09129600	Smith Fork near Lazear	A	0	---	---	[3]20	[3]0.01	[3]0.06
3	09136100	North Fork Gunnison River near Lazear	C	4	3.3	4	34	2.7	3.5
4	384624107570701	Gunnison River at Austin	A	1	3.3	3.3	25	3.9	5.2
5	09144200	Tongue Creek at Cory	A	4	0.78	0.79	29	0.6	0.71
6	09137500	Gunnison River near Cory	A	4	10.3	10.2	27	8.1	9.5
7	384617108022901	Gunnison River near Hartland Dam	A	0	---	---	[4]16	[4]8.6	[4]10.7
8	09144250	Gunnison River at Delta	C	5	15.3	15.2	35	12.9	14.5
9	09147500	Uncompahgre River at Colona	C	4	0.52	0.78	32	0.43	0.77
10	383041107544201	Cedar Creek near mouth	A	4	3.2	3.3	[5]18	[5]3.3	[5]3.4
11	383946107595301	Loutzenhizer Arroyo at North River Road	C	11	10.1	10.2	42	10.3	12
12	384202108032001	Dry Creek at mouth nr Delta	A	4	1.1	1.3	[5]18	[5]1.3	[5]1.2
13	09149500	Uncompahgre River at Delta	C	5	18.1	18.4	36	16.8	17
14	384448108070301	Cummings Gulch at mouth	A	4	0.66	0.63	[5]19	[5]0.99	[5]0.76
15	09150500	Roubideau Creek near mouth	A	0	---	---	[3]22	[3]0.46	[3]0.53
16	384527108152701	Gunnison River above Escalante Creek	A	2	26.5	26.5	29	31.2	33.6
17	385011108225401	Gunnison River below Dominguez Ck.	A	1	28.7	28.7	[6]19	[6]32	[6]31.6
18	09152500	Gunnison River near Grand Junction (Whitewater)	C	12	35.7	35.5	68	33.4	36.1

[1]May include values affected by laboratory bias (Stetson, 2019).

[2]Samples collected during WY 2011–12.

[3]Samples collected during WY 2012–16.

[4]Samples collected during WY 2011–15.

[5]Samples collected during WY 2014–17.

[6]Samples collected during WY 2013–17.

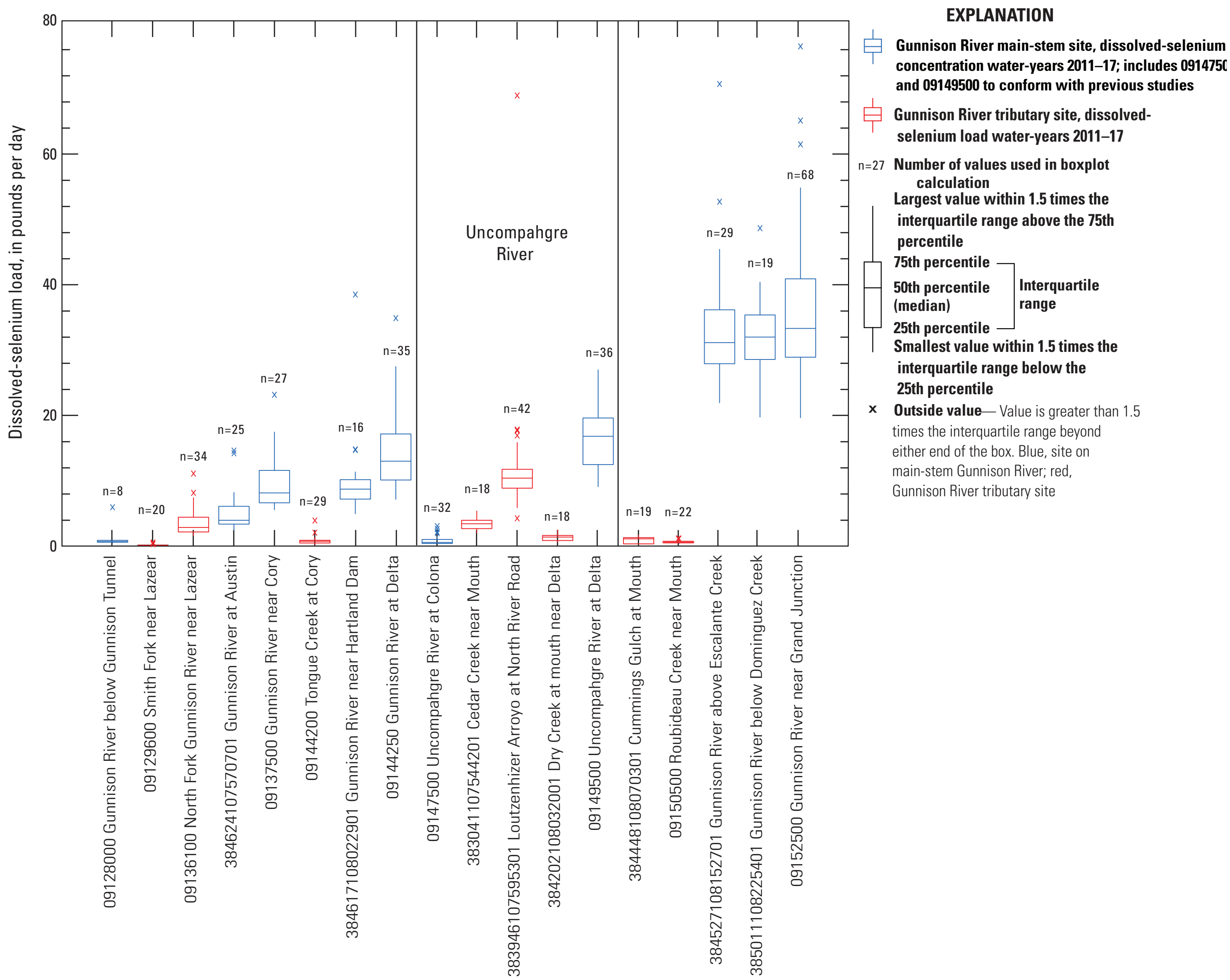

Figure 7. Boxplots representing dissolved-selenium loads, in pounds per day, measured in discrete water-quality samples for water years 2011–17. Uncompahgre River at Colona and Uncompahgre River at Delta are designated as Gunnison River main-stem sites to conform with previous selenium studies in the area.

Summary

The Gunnison Basin Selenium Management Program implemented a water-quality monitoring network in 2011 in the lower Gunnison River Basin in Colorado. Selenium is a trace element that bioaccumulates in aquatic food chains. Selenium is essential for life, but elevated amounts can cause reproductive failure, deformities, and other harmful effects. The primary goal of the Selenium Management Program is to meet the State of Colorado water-quality standard of 4.6 micrograms per liter (µg/L) for dissolved selenium at the U.S. Geological Survey (USGS) streamflow-gaging station number 09152500—Gunnison River near Grand Junction, Colorado—herein referred to as “Whitewater.” The U.S. Geological Survey (USGS), in cooperation with the Bureau of Reclamation, has completed a review of dissolved-selenium data collected from the Selenium Management Program network during water year (WY) 2017 (October 1, 2016 through September 30, 2017) to further the understanding of the status and trends of selenium in the basin. This report presents the percentile values of selenium because regulatory agencies in Colorado make decisions based on the U.S. Environmental Protection Agency’s Clean Water Act Section 303(d), which uses percentile values of concentration.

An assessment of potential laboratory bias was completed for selenium data used in the trend analysis. A potential positive bias of approximately 12 percent was observed in the data from October 2005 through August 2015.

Also presented are dissolved-selenium loads at 14 sites in the lower Gunnison River Basin for WY’s 2011–17 and WY 2017 (October 1, 2016 through September 30, 2017). Annual

Table 5. Changes in median instantaneous dissolved-selenium loads along the main stem of the Gunnison River based on discrete water-quality samples for water years 2011–17.

[USGS, U.S. Geological Survey; WY, water year, defined as October 1 through September 30 of the following year]

Map index number (fig.1)	USGS station number	USGS station short name	Number of samples WY 2011–17	Median selenium load for WY 2011–17, in pounds per day[1]	Change in median dissolved-selenium load between stations for WY 2011–17, in pounds per day[1]
4	384624107570701	Gunnison River at Austin	25	3.9	
					4.2
6	09137500	Gunnison River near Cory	27	8.1	
					0.5
7	384617108022901	Gunnison River near Hartland Dam	[2]16	[2]8.6	
					4.3
8	09144250	Gunnison River at Delta	35	12.9	
					18.3
16	384527108152701	Gunnison River above Escalante Creek	29	31.2	
					2.2
18	09152500	Gunnison River near Grand Junction (Whitewater)	68	33.4	

[1]May include values affected by laboratory bias (Stetson, 2019).

[2]Samples collected during WY 2011–15.

Table 6. Estimated dissolved-selenium annual 85th-percentile concentrations, in micrograms per liter, from daily dissolved-selenium loads calculated by multiple linear-regression techniques in the program R-LOADEST (Runkel and others, 2004) for data collected at six core sites with U.S. Geological Survey streamflow-gaging stations during water years 2011 and 2017.

[Core sites are those which include a U.S. Geological Survey streamflow-gaging station. USGS, U.S. Geological Survey; WY, water year, is defined as October 1 through September 30 of the following year; --, no data]

Map index number (fig. 1)	USGS station number	USGS station short name	85th-percentile concentrations for dissolved selenium, in micrograms per liter		Difference in dissolved-selenium concentration, in micrograms per liter, between WY 2011 and WY 2017
			WY 2011[1,2]	WY 2017	
3	09136100	North Fork Gunnison River near Lazear	3.4	2.8	–0.6
8	09144250	Gunnison River at Delta	3	3	–0.0
9	09147500	Uncompahgre River at Colona	0.91	0.68	–0.23
11	383946107595301	Loutzenhizer Arroyo at North River Road	--	[3]140	--
13	09149500	Uncompahgre River at Delta	18.7	13	–5.7
18	09152500	Gunnison River near Grand Junction, Colorado (Whitewater)	6.6	4.6	–2.0

[1]Values from Henneberg, 2016.

[2]May include values affected by laboratory bias (Stetson, 2019).

[3]WY 2017 is the first year regression techniques were able to be used at this site.

Table 7. Annual 85th-percentile concentrations of dissolved selenium measured at six core sites with U.S. Geological Survey streamflow-gaging stations and at eight ancillary sites, in micrograms per liter in discrete water-quality samples collected during water year 2017.

[Core sites are those which include a U.S. Geological Survey streamflow-gaging station, ancillary sites are those which do not. USGS, U.S. Geological Survey; WY, water year, is defined as October 1 through September 30 of the following year; ---, no samples collected WY 2017; concentrations are in (µg/L), micrograms per liter; site types are (C) core which include a U.S. Geological Survey streamflow-gaging station, and (A) ancillary which do not include a U.S. Geological Survey streamflow-gaging station]

Map index number	USGS station number	Site type	USGS station short name	85th-percentile concentrations WY 2017
1	09128000	A	Gunnison River below Gunnison Tunnel	---
2	09129600	A	Smith Fork near Lazear	---
3	09136100	C	North Fork Gunnison River near Lazear	2.6
4	384624107570701	A	Gunnison River at Austin	0.82
5	09144200	A	Tongue Creek at Cory	5.1
6	09137500	A	Gunnison River near Cory	2.4
7	384617108022901	A	Gunnison River near Hartland Dam	---
8	09144250	C	Gunnison River at Delta	2.4
9	09147500	C	Uncompahgre River at Colona	0.75
10	383041107544201	A	Cedar Creek near mouth	24.9
11	383946107595301	C	Loutzenhizer Arroyo at North River Road	106
12	384202108032001	A	Dry Creek at mouth near Delta	2.8
13	09149500	C	Uncompahgre River at Delta	13.6
14	384448108070301	A	Cummings Gulch at mouth	8.8
15	09150500	A	Roubideau Creek near mouth	---
16	384527108152701	A	Gunnison River above Escalante Creek	4.2
17	385011108225401	A	Gunnison River below Dominguez Creek	4.4
18	09152500	C	Gunnison River near Grand Junction (Whitewater)	4.5

Table 8. Annual dissolved-selenium trends from water years 1986 through 2017 at U.S. Geological Survey streamflow-gaging station 09152500, Gunnison River near Grand Junction, Colorado.[1]

[A water year is defined as October 1 through September 30 of the following year; %, percent; ---, not applicable]

Water year	Normalized mean-daily streamflow for 1986–2016, in cubic feet per second	Estimated dissolved- selenium annual load, in pounds	Lower 95%-confidence level for estimated annual dissolved-selenium load, in pounds	Upper 95%-confidence level for estimated annual dissolved-selenium load, in pounds	Estimated annual dissolved-selenium load reduction, in percent	50th percentile of estimated daily dissolved-selenium concentration, in micrograms per liter	85th percentile of estimated daily dissolved-selenium concentration, in micrograms per liter
1986	2,340	22,200	20,000	24,600	---	6.4	7.1
2017	2,340	12,600	11,700	13,600	43.1	3.6	4.0
Difference	---	–9,600	---	---	---	–2.8	–3.1

[1]Might include values affected by laboratory bias (Stetson and others, 2019).

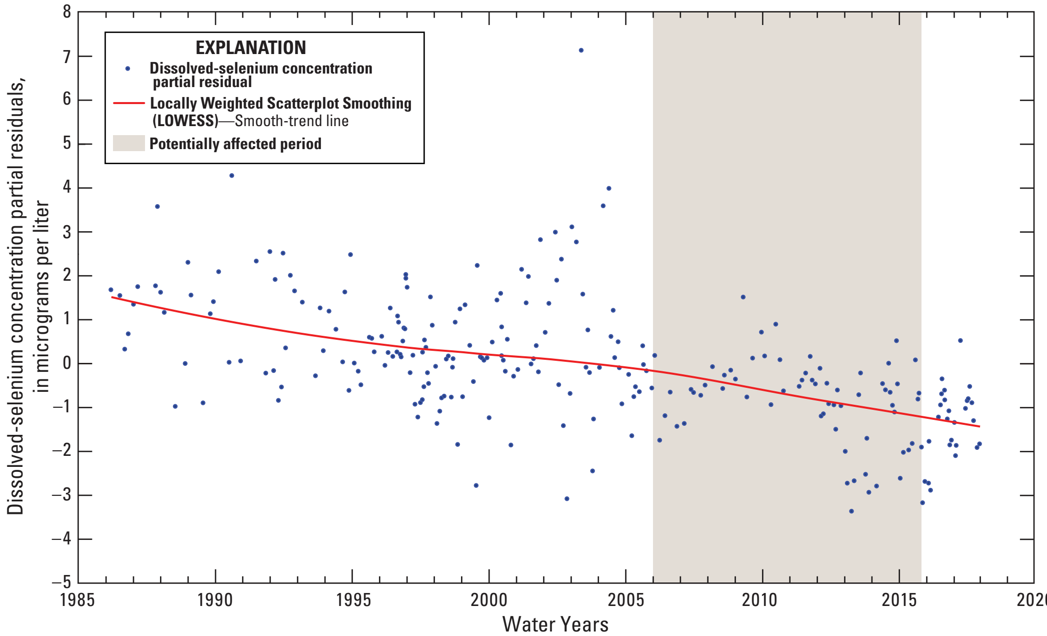

Figure 8. Plot of partial residuals of dissolved-selenium concentrations and the Locally Weighted Scatterplot Smoothing fit line for Gunnison River near Grand Junction (09152500; also known as Whitewater) for water years 1986–2017.

Table 9. Annual dissolved-selenium trends from water years 1995 through 2017 at U.S. Geological Survey streamflow-gaging station 09152500, Gunnison River near Grand Junction, Colorado.[1]

[A water year is defined as October 1 through September 30 of the following year; %, percent; ---, not applicable]

Water year	Normalized mean- daily streamflow for 1994 to 2016, in cubic feet per second	Estimated dissolved-selenium annual load, in pounds	Lower 95%-confidence level for estimated annual dissolved-selenium load, in pounds	Upper 95%-confidence level for estimated annual dissolved-selenium load, in pounds	Estimated annual dissolved-selenium load reduction, in percent	50th percentile of estimated daily dissolved-selenium concentration, in micrograms per liter	85th percentile of estimated daily dissolved-selenium concentration, in micrograms per liter
1995	2,320	18,600	17,100	20,100	---	5.3	6.1
2017	2,320	12,000	11,000	13,000	35.5	3.4	4.0
Difference	---	–6,600	---	---	---	–1.9	–2.1

[1]Might include values affected by laboratory bias (Stetson and others, 2019).

dissolved-selenium loads were calculated for six core sites with continuous USGS streamflow-gaging stations. Annual dissolved-selenium loads for WY 2017 ranged from 306 pounds (lb) at Uncompahgre River at Colona to 12,600 lb at Whitewater, respectively.

Instantaneous loads were calculated for six core sites with data from discrete water-quality samples collected at continuous USGS streamflow-gaging stations and at eight ancillary sites where discrete water-quality sampling also took place and the associated discharge measurements collected during the period. Median instantaneous loads ranged from 0.52 pounds per day (lb/d) at Uncompahgre River at Colona to 35.7 lb/d at Whitewater for WY 2017. Mean instantaneous loads ranged from 0.63 lb/d at Cummings Gulch at mouth to 35.5 lb/d at Whitewater for WY 2017. Most tributary sites in the basin had a median instantaneous dissolved-selenium load of less than 20.0 lb/d. In general, dissolved-selenium loads at Gunnison River main-stem sites showed an increase from upstream to downstream.

The State of Colorado water-quality standard of 4.6 µg/L for dissolved selenium was compared to the 85th percentiles for dissolved selenium at selected

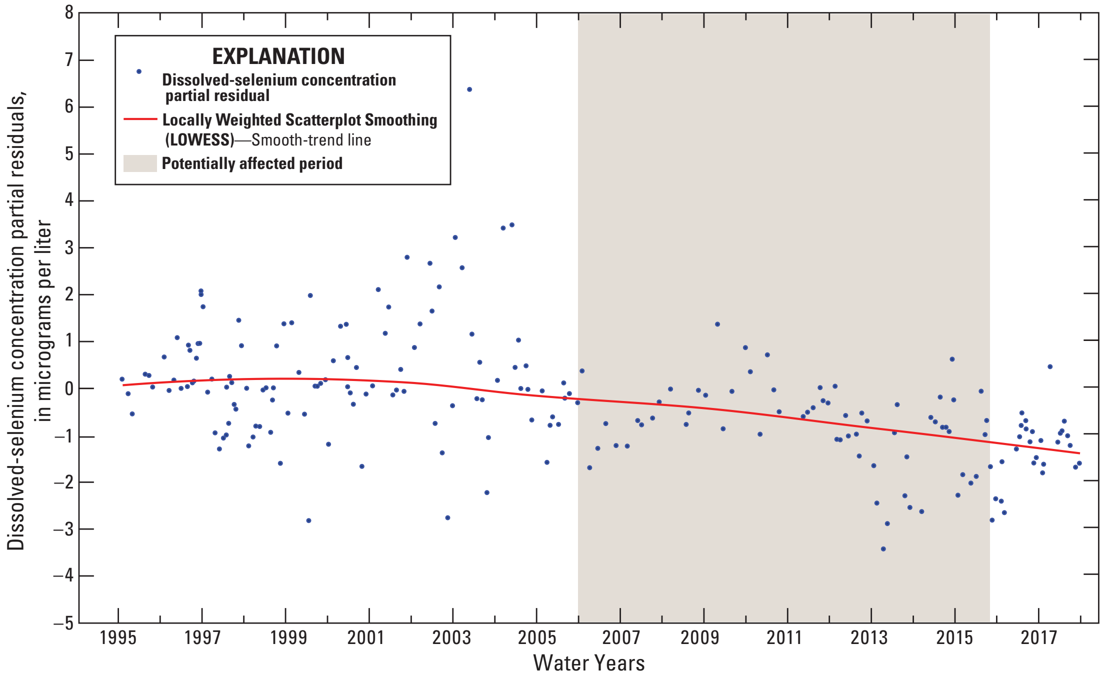

Figure 9. Plot of partial residuals of dissolved-selenium-concentrations and the Locally Weighted Scatterplot Smoothing fit line for Gunnison River near Grand Junction (09152500; also known as Whitewater) for water years 1995–2017.

sites. Annual 85th percentiles for dissolved selenium were calculated for the six core sites with USGS streamflow-gaging stations and estimated dissolved-selenium concentrations from linear regression models. The 85th-percentile concentrations for WY 2017 based on this method ranged from 0.68 µg/L at Uncompahgre River at Colona to 140 µg/L at Loutzenhizer Arroyo at North River Road. The 85th percentiles for dissolved selenium also were calculated for discrete water-quality samples collected during WY 2017 at sites with sufficient data. The annual 85th-percentile concentrations based on the discrete samples ranged from 0.75 µg/L at Uncompahgre River at Colona to 106 µg/L at Loutzenhizer Arroyo at North River Road.

An analysis was completed for Whitewater to determine if an upward or downward trend exists for dissolved-selenium loads during two time periods. The first time period includes all data at Whitewater, whereas the second time period focuses on more recent data. The trend analysis indicates a decrease of 9,600 lb from WY 1986 through WY 2017, a 43.1-percent reduction during the time period. The trend analysis for the annual dissolved-selenium load for WY 1995 through WY 2017 indicates a decrease of 6,600 lb per year, or 35.5 percent. An evaluation of laboratory bias was completed for selenium data used in the trend analysis. This potential positive bias of selenium data used in the analysis does not affect the downward trend identified at Whitewater. If actual selenium values are lower than reported because of bias, the downward trend may be greater than identified in this study.

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Appendix 1. R-LOADEST Equation Forms, Regression-Model Coefficients, and Statistical Diagnostics

A summary of the equation forms used to estimate annual dissolved-selenium loads at the six core sites in the lower Gunnison River Basin for water year 2017 is presented in table 1.1. Table 1.2 provides regression-model coefficients and statistical diagnostics for the six core sites.

Table 1.1. Summary of equation forms used to estimate annual dissolved-selenium loads at six core sites with U.S. Geological Survey streamflow-gaging stations in the lower Gunnison River Basin. Core sites are those which include a U.S. Geological Survey streamflow-gaging station.

[USGS, U.S. Geological Survey; ln, natural logarithm; load, dissolved-selenium load in pounds per day (lb/d); β_0, intercept of the regression on the y-axis; β_1–β_5, regression coefficients; Q, centered daily streamflow in cubic feet per second (ft^3/s); sin(2πdectime), sine function of a Fourier Series; π, approximately 3.141593; dectime, centered decimal time in decimal years; cos(2πdectime), cosine function of a Fourier Series; ε, remaining unexplained variability in the data (error); SC, daily mean specific conductance in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C)]

USGS station number	Equation form[1]
09136100	$\ln(\text{load}) = \beta_0 + \beta_1\ln(Q) + \beta_2\text{dectime} + \varepsilon$
09144250	$\ln(\text{load}) = \beta_0 + \beta_1\ln(Q) + \beta_2\text{SC} + \varepsilon$
09147500	$\ln(\text{load}) = \beta_0 + \beta_1\ln(Q) + \varepsilon$
09149500	$\ln(\text{load}) = \beta_0 + \beta_1\ln(Q) + \beta_2\text{SC} + \varepsilon$
09152500	$\ln(\text{load}) = \beta_0 + \beta_1\ln(Q) + \beta_2\text{SC} + \varepsilon$
09152500[2]	$\ln(\text{load}) = \beta_0 + \beta_1\ln(Q) + \beta_2\ln(Q)^2 + \beta_3\text{dectime} + \beta_4(\text{dectime})^2 + \beta_5\sin(2\pi\text{dectime}) + \beta_6\cos(2\pi\text{dectime}) + \varepsilon$
09152500[3]	$\ln(\text{load}) = \beta_0 + \beta_1\ln(Q) + \beta_2\ln(Q)^2 + \beta_3\text{dectime} + \beta_4(\text{dectime})^2 + \beta_5\sin(2\pi\text{dectime}) + \beta_6\cos(2\pi\text{dectime}) + \varepsilon$
383926107593001	$\ln(\text{load}) = \beta_0 + \beta_1\ln(Q) + \beta_2\sin(2\pi\text{dectime}) + \beta_3\cos(2\pi\text{dectime}) + \varepsilon$

[1]Any bias that is introduced by the log transformation needs to be corrected if the results are transformed out of log space (Cohn and others, 1989), but this correction is automatically applied by the statistical software used for the regression analysis (Mayo and Leib, 2012).

[2]Equation form used for 1986–2017 trend analysis.

[3]Equation form used for 1995–2017 trend analysis.

Table 1.2. Regression-model coefficients and statistical diagnostics at six core sites with U.S. Geological Survey streamflow-gaging stations in the lower Gunnison River Basin. Core sites are those which include a U.S. Geological Survey streamflow-gaging station.

[USGS, U.S. Geological Survey; ln, natural logarithm; Q, centered daily streamflow in cubic feet per second (ft^3/s); dectime, centered decimal time in decimal years; sin(2πdectime), sine function of a Fourier Series; π, approximately 3.141593; cos(2πdectime), cosine function of a Fourier Series; SC, daily mean specific conductance in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C); ERV, estimated residual variance; R^2, coefficient of determination; SCR, serial correlation of the residuals; ---, no coefficient available]

USGS station number	Y-axis Intercept	ln(Q)	$ln(Q)^2$	dectime	$dectime^2$	sin(2ϖdectime)	cos(2ϖdectime)	SC	ERV	R^2	SCR
09136100	1.223	0.380	---	0.2415	---	---	---	---	0.001	99.9	–0.514
09144250	–8.051	1.168	---	---	---	---	---	0.004	0.012	88.2	–0.026
09147500	–0.462	0.889	---	---	---	---	---	---	0.053	95.6	–0.298
09149500	–2.505	0.666	---	---	---	---	---	0.001	0.014	73.5	0.311
09152500	–2.964	0.707	---	---	---	---	---	0.001	0.010	69.9	–0.056
09152500[1]	3.906	0.350	0.064	–0.019	–0.001	–0.217	0.054	---	0.052	65.4	0.185
09152500[2]	3.879	0.366	0.087	–0.020	–0.001	–0.212	–0.060	---	0.050	63.7	0.232
383926107593001	1.628	0.011	---	---	---	0.090	0.544	---	0.031	91.2	–0.004

[1]Equation form used for 1986–2017 trend analysis.

[2]Equation form used for 1995–2017 trend analysis.

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