Prepared in cooperation with the U.S. Environmental Protection Agency

Water-Quality Trends and Constituent-Transport Analysis for Selected Sampling Sites in the Milltown Reservoir/Clark Fork River Superfund Site in the Upper Clark Fork Basin, Montana, Water Years 1996–2015

Scientific Investigations Report 2016–5100

U.S. Department of the Interior
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U.S. Geological Survey
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U.S. Geological Survey, Reston, Virginia: 2016

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Suggested citation:
Sando, S.K., and Vecchia, A.V., 2016, Water-quality trends and constituent-transport analysis for selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 1996–2015: U.S. Geological Survey Scientific Investigations Report 2016–5100, 82 p., http://dx.doi.org/10.3133/sir20165100.

ISSN 2328-0328 (online)

Contents

Figures

Appendix Figures

Tables

Appendix Tables

Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
	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)

Supplemental Information

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

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

Load estimates are given in kilograms per day (kg/d).

Water year is defined as the 12-month period from October 1 through September 30 of the following calendar year. The water year is designated by the calendar year in which it ends. For example, water year 2010 is the period from October 1, 2009, through September 30, 2010.

Abbreviations

AMC	Anaconda Mining Company
FAC	flow-adjusted concentration
LRL	laboratory reporting level
LOWESS	locally weighted scatter plot smooth
NWQL	National Water Quality Laboratory
NWIS	National Water Information System
SEE	standard error of estimate
SRL	study reporting level
TSM	time-series model
USGS	U.S. Geological Survey

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Abstract

During the extended history of mining in the upper Clark Fork Basin in Montana, large amounts of waste materials enriched with metallic contaminants (cadmium, copper, lead, and zinc) and the metalloid trace element arsenic were generated from mining operations near Butte and milling and smelting operations near Anaconda. Extensive deposition of mining wastes in the Silver Bow Creek and Clark Fork channels and flood plains had substantial effects on water quality. Federal Superfund remediation activities in the upper Clark Fork Basin began in 1983 and have included substantial remediation near Butte and removal of the former Milltown Dam near Missoula. To aid in evaluating the effects of remediation activities on water quality, the U.S. Geological Survey began collecting streamflow and water-quality data in the upper Clark Fork Basin in the 1980s.

Trend analysis was done on specific conductance, selected trace elements (arsenic, copper, and zinc), and suspended sediment for seven sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site for water years 1996–2015. The most upstream site included in trend analysis is Silver Bow Creek at Warm Springs, Montana (sampling site 8), and the most downstream site is Clark Fork above Missoula, Montana (sampling site 22), which is just downstream from the former Milltown Dam. Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. Trend analysis was done by using a joint time-series model for concentration and streamflow. To provide temporal resolution of changes in water quality, trend analysis was conducted for four sequential 5-year periods: period 1 (water years 1996–2000), period 2 (water years 2001–5), period 3 (water years 2006–10), and period 4 (water years 2011–15). Because of the substantial effect of the intentional breach of Milltown Dam on March 28, 2008, period 3 was subdivided into period 3A (October 1, 2005–March 27, 2008) and period 3B (March 28, 2008–September 30, 2010) for the Clark Fork above Missoula (sampling site 22). Trend results were considered statistically significant when the statistical probability level was less than 0.01.

In conjunction with the trend analysis, estimated normalized constituent loads (hereinafter referred to as "loads") were calculated and presented within the framework of a constituent-transport analysis to assess the temporal trends in flow-adjusted concentrations (FACs) in the context of sources and transport. The transport analysis allows assessment of temporal changes in relative contributions from upstream source areas to loads transported past each reach outflow.

Trend results indicate that FACs of unfiltered-recoverable copper decreased at the sampling sites from the start of period 1 through the end of period 4; the decreases ranged from large for one sampling site (Silver Bow Creek at Warm Springs [sampling site 8]) to moderate for two sampling sites (Clark Fork near Galen, Montana [sampling site 11] and Clark Fork above Missoula [sampling site 22]) to small for four sampling sites (Clark Fork at Deer Lodge, Montana [sampling site 14], Clark Fork at Goldcreek, Montana [sampling site 16], Clark Fork near Drummond, Montana [sampling site 18], and Clark Fork at Turah Bridge near Bonner, Montana [sampling site 20]). For period 4 (water years 2011–15), the most notable changes indicated for the Milltown Reservoir/Clark Fork River Superfund Site were statistically significant decreases in FACs and loads of unfiltered-recoverable copper for sampling sites 8 and 22. The period 4 changes in FACs of unfiltered-recoverable copper for all other sampling sites were not statistically significant.

Trend results indicate that FACs of unfiltered-recoverable arsenic decreased at the sampling sites from period 1 through period 4 (water years 1996–2015); the decreases ranged from minor (sampling sites 8–20) to small (sampling site 22). For period 4 (water years 2011–15), the most notable changes indicated for the Milltown Reservoir/Clark Fork River Superfund Site were statistically significant decreases in FACs and loads of unfiltered-recoverable arsenic for sampling site 8 and near statistically significant decreases for sampling site 22. The period 4 changes in FACs of unfiltered-recoverable arsenic for all other sampling sites were not statistically significant.

Trend results indicate that FACs of suspended sediment decreased at the sampling sites from period 1 through period 4 (water years 1996–2015); the decreases ranged from moderate (sampling site 8) to small (sampling sites 11–22). For period 4 (water years 2011–15), the changes in FACs of suspended sediment were not statistically significant for any sampling sites.

The reach of the Clark Fork from Galen to Deer Lodge is a large source of metallic contaminants and suspended sediment, which strongly affects downstream transport of those constituents. Mobilization of copper and suspended sediment from flood-plain tailings and the streambed of the Clark Fork and its tributaries within the reach results in a contribution of those constituents that is proportionally much larger than the contribution of streamflow from within the reach. Within the reach from Galen to Deer Lodge, unfiltered-recoverable copper loads increased by a factor of about 4 and suspended-sediment loads increased by a factor of about 5, whereas streamflow increased by a factor of slightly less than 2. For period 4 (water years 2011–15), unfiltered-recoverable copper and suspended-sediment loads sourced from within the reach accounted for about 41 and 14 percent, respectively, of the loads at Clark Fork above Missoula (sampling site 22), whereas streamflow sourced from within the reach accounted for about 4 percent of the streamflow at sampling site 22. During water years 1996–2015, decreases in FACs and loads of unfiltered-recoverable copper and suspended sediment for the reach generally were proportionally smaller than for most other reaches.

Unfiltered-recoverable copper loads sourced within the reaches of the Clark Fork between Deer Lodge and Turah Bridge near Bonner (just upstream from the former Milltown Dam) were proportionally smaller than contributions of streamflow sourced from within the reaches; these reaches contributed proportionally much less to copper loading in the Clark Fork than the reach between Galen and Deer Lodge. Although substantial decreases in FACs and loads of unfiltered-recoverable copper and suspended sediment were indicated for Silver Bow Creek at Warm Springs (sampling site 8), those substantial decreases were not translated to downstream reaches between Deer Lodge and Turah Bridge near Bonner. The effect of the reach of the Clark Fork from Galen to Deer Lodge as a large source of copper and suspended sediment, in combination with little temporal change in those constituents for the reach, contributes to this pattern.

With the removal of the former Milltown Dam in 2008, substantial amounts of contaminated sediments that remained in the Clark Fork channel and flood plain in reach 9 (downstream from Turah Bridge near Bonner) became more available for mobilization and transport than before the dam removal. After the removal of the former Milltown Dam, the Clark Fork above Missoula (sampling site 22) had statistically significant decreases in FACs of unfiltered-recoverable copper in period 3B (March 28, 2008, through water year 2010) that continued in period 4 (water years 2011–15). Also, decreases in FACs of unfiltered-recoverable arsenic and suspended sediment were indicated for period 4 at this site. The decrease in FACs of unfiltered-recoverable copper for sampling site 22 during period 4 was proportionally much larger than the decrease for the Clark Fork at Turah Bridge near Bonner (sampling site 20). Net mobilization of unfiltered-recoverable copper and arsenic from sources within reach 9 are smaller for period 4 than for period 1 when the former Milltown Dam was in place, providing evidence that contaminant source materials have been substantially reduced in reach 9.

Introduction

Mining in the upper Clark Fork Basin in Montana began in 1864 when small-scale placer mining operations extracted gold from Silver Bow Creek and its tributaries in and near Butte (Freeman, 1900; U.S. Environmental Protection Agency, 2005; fig. 1). By the early 1900s, the small gold mining operations had transitioned to larger scale underground silver and copper mining owned by the former Anaconda Mining Company (AMC), with most of the ore being processed at AMC milling and smelting facilities near Anaconda (U.S. Environmental Protection Agency, 2005, 2010; Gammons and others, 2006). In 1955, the AMC mining operations began to transition from underground to open-pit mining, with the opening of the Berkeley Pit north of Butte. The Berkeley Pit mining operations and AMC milling and smelting operations continued until closure in the early 1980s.

During the extended history of mining in the upper Clark Fork Basin, large amounts of waste materials enriched with metallic contaminants (cadmium, copper, lead, and zinc) and the metalloid trace element arsenic were generated from mining operations near Butte and the milling and smelting operations near Anaconda (Andrews, 1987; Gammons and others, 2006). Extensive deposition of mining wastes in the Silver Bow Creek and Clark Fork channels and flood plains had substantial effects on water quality. Federal Superfund remediation activities in the upper Clark Fork Basin began in 1983 and have included substantial remediation near Butte and removal of the former Milltown Dam near Missoula in 2008 (U.S. Environmental Protection Agency, 2004, 2010; CDM, 2005; Sando and Lambing, 2011). The various Superfund activities are distributed among three National Priorities List sites: the Silver Bow Creek/Butte Area Site, the Anaconda Smelter Site, and the Milltown Reservoir/Clark Fork River Superfund Site, which are described in the "Description of Study Area" section of this report.

Water-quality data collection by the U.S. Geological Survey (USGS) in the upper Clark Fork Basin began during 1985–88 with the establishment of a small long-term monitoring program that has expanded through time and continued through present (2016). Sando and others (2014) analyzed the monitoring data and characterized flow-adjusted trends in mining-related contaminants for 22 sampling sites in the Silver Bow Creek/Butte Area Site, the Anaconda Smelter Site, and the Milltown Reservoir/Clark Fork River Superfund Site in the

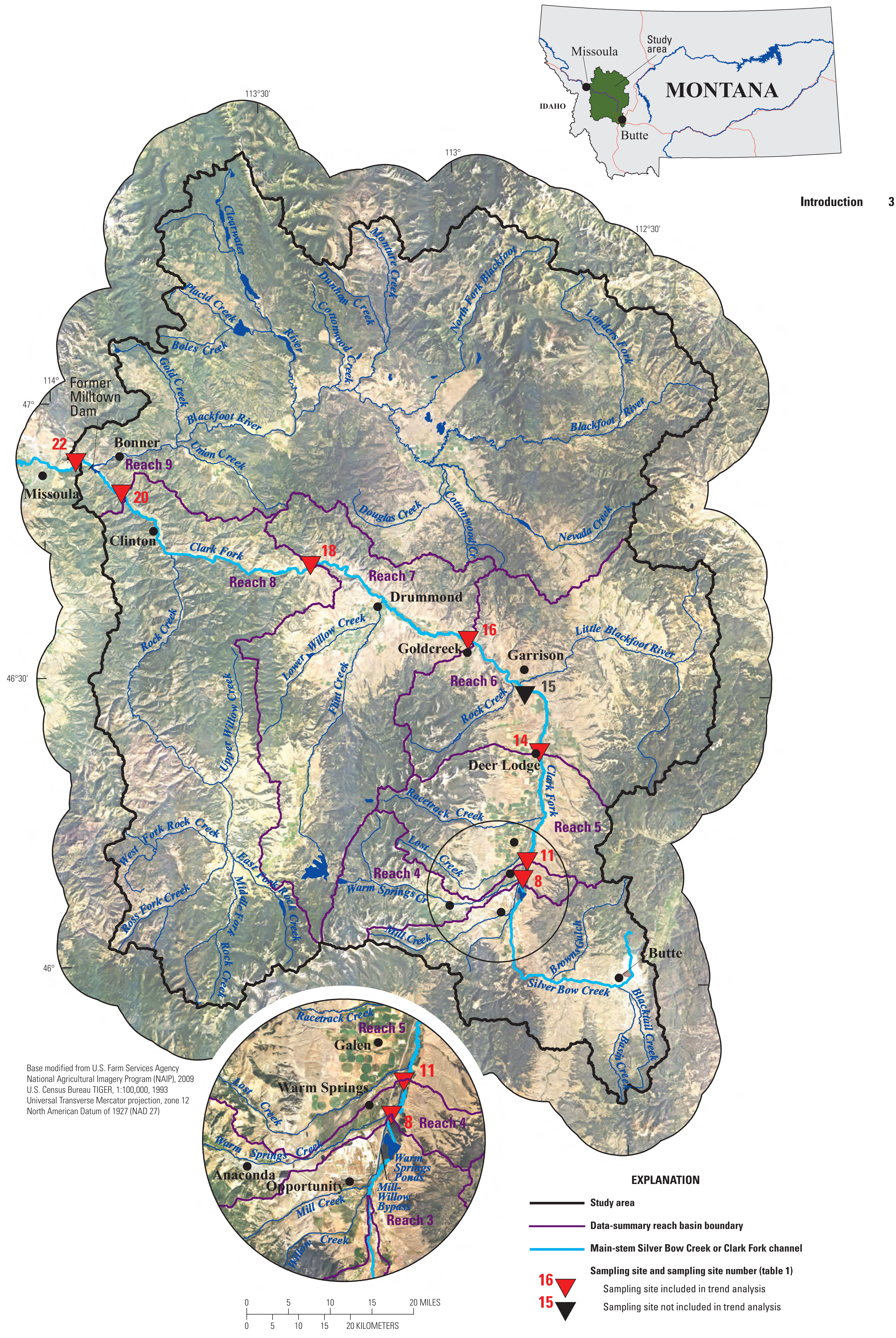


Figure 1. Location of study area, selected sampling sites, and data-summary reaches in the upper Clark Fork Basin, Montana; the Milltown Reservoir/Clark Fork River Superfund Site includes the reaches from sampling site 8 to sampling site 22.

upper Clark Fork Basin for water years 1996–2010 (water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends). An update of flow-adjusted water-quality trends for the monitoring data was needed for seven sampling sites to provide timely information for the 2016 5-year review for the Milltown Reservoir/Clark Fork River Superfund Site. The USGS, in cooperation with the U.S. Environmental Protection Agency, conducted this study to test for flow-adjusted trends (water years 1996–2015) in water quality at seven sampling sites (fig. 1, table 1) in the Milltown Reservoir/Clark Fork River Superfund Site by using a joint time-series model (TSM; Vecchia, 2005) for concentration and streamflow; an eighth site (Clark Fork above Little Blackfoot River near Garrison, Montana [sampling site 15; fig. 1, table 1]) was included in the study for the purpose of statistically summarizing water-quality data collected during water years 2011–15, but the period of water-quality data collection was insufficient for trend analysis.

Purpose and Scope

The primary purposes of this report are to (1) characterize temporal trends in flow-adjusted concentrations (filtered and unfiltered) of mining-related contaminants and (2) assess those trends in the context of source areas and transport of those contaminants through the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin. Trend analysis was done on specific conductance, selected trace elements (arsenic, copper, and zinc), and suspended sediment for seven sampling sites for water years 1996–2015. This report provides an update of and supersedes the trend results reported by Sando and others (2014) for seven sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site. This report presents the trend results and information on trend-analysis methods, streamflow conditions, and various data-related factors that affect trend results. This information is presented to assist in evaluating trend results; however, it is beyond the scope of this report to provide detailed explanations for all observed temporal changes.

Description of Study Area

The Clark Fork drains an extensive region in western Montana and northern Idaho in the Columbia River Basin (not shown on fig. 1). The main-stem Clark Fork begins at the confluence of Silver Bow and Warm Springs Creeks near Warm Springs, Montana, and flows about 485 miles (mi) through Montana and Idaho. The study area (fig. 1) encompasses the upper Clark Fork Basin in west-central Montana upstream from Clark Fork above Missoula, Montana (sampling site 22, table 1), with a drainage area of 5,999 square miles (mi^2). Sando and others (2014) presented somewhat detailed information describing the hydrographic, physiographic, climatic, and geologic characteristics of the upper Clark Fork Basin and an overview of mining and remediation activities.

Early Federal Superfund activities in the upper Clark Fork Basin involved designation of three areas as National Priorities List sites in 1983: the Silver Bow Creek Site, the Anaconda Smelter Site, and the Milltown Reservoir Site. The Silver Bow Creek Site was redesignated as the Silver Bow Creek/Butte Area Site in 1987 and includes remnants from mining operations near Butte and about 26 river miles of Silver Bow Creek extending from near Butte to the outlet of Warm Springs Ponds (U.S. Environmental Protection Agency, 2000; CDM, 2005). The Anaconda Smelter Site includes about 300 mi^2, primarily in the Mill, Willow, Warm Springs, and Lost Creek drainage basins near Anaconda (U.S. Environmental Protection Agency, 2010). Many remediation activities within the Anaconda Smelter Site are administered within the Regional Water, Waste, and Soils Operable Unit (Henry Elsen, U.S. Environmental Protection Agency, written commun., January 2016). The Milltown Reservoir Site was redesignated as the Milltown Reservoir/Clark Fork River Superfund Site in 1992. The Milltown Reservoir/Clark Fork River Superfund Site includes two primary operable units: the Milltown Reservoir Operable Unit and the Clark Fork Operable Unit. The Milltown Reservoir Operable Unit includes about 0.84 mi^2 defined by the area inundated by maximum pool elevation of the former Milltown Reservoir (U.S. Environmental Protection Agency, 2004). The Clark Fork Operable Unit includes streamside areas of the 115-mi reach of the Clark Fork extending from the Warm Springs Ponds outlet to the start of Milltown Reservoir Operable Unit (Montana Department of Environmental Quality, 2016).

The specific focus of this study is the Milltown Reservoir/Clark Fork River Superfund Site, which includes the Clark Fork Operable Unit and the Milltown Reservoir Operable Unit, and extends about 123 river miles from the outlet of Warm Springs Ponds on Silver Bow Creek (represented by sampling site 8) to the outlet of the former Milltown Reservoir (represented by sampling site 22, which is about 3 river miles downstream from the former Milltown Dam). Sampling sites included in this study are located on the main-stem channels of Silver Bow Creek and the Clark Fork. Sando and others (2014) included trend analyses for several sampling sites on tributaries to Silver Bow Creek or the Clark Fork in the Milltown Reservoir/Clark Fork River Superfund Site; however, data collection for most of the tributary sampling sites was discontinued in water year 2004. No tributary sampling sites were included in this study. The sampling site numbers and reach designations assigned by Sando and others (2014) generally have been retained to facilitate comparisons. An exception is Clark Fork above Little Blackfoot River near Garrison (USGS streamgage 12324400), for which data collection began in water year 2009. Streamgage 12324400 was not included in Sando and others (2014). A discontinued tributary sampling site (Little Blackfoot River near Garrison, Montana; USGS streamgage 12324590) was designated as sampling site 15 in Sando and others (2014), but in this study Clark Fork above Little Blackfoot River near Garrison (USGS streamgage 12324400) is designated as sampling site 15. The period of

Table 1. Information for selected sampling sites and data-summary reaches in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. USGS, U.S. Geological Survey; NA, not applicable]

Sampling site number[1] (fig. 1)	USGS site identification number	USGS site name	Abbreviated sampling site name	Data-summary reach[1,2]	Drainage area, in square miles	Period of water-quality data collection	Median annual sampling frequency, in samples per year (range)	Trend analysis periods[3]
8	12323750	Silver Bow Creek at Warm Springs, Montana	Silver Bow Creek at Warm Springs	3 and 4	473	3/1993–8/2015	8 (6–11)	1, 2, 3, 4
11	12323800	Clark Fork near Galen, Montana	Clark Fork near Galen	4 and 5	651	7/1988–8/2015	8 (1–13)	1, 2, 3, 4
14	12324200	Clark Fork at Deer Lodge, Montana	Clark Fork at Deer Lodge	5 and 6	995	3/1985–8/2015	8 (4–20)	1, 2, 3, 4
15	12324400	Clark Fork above Little Blackfoot River near Garrison, Montana	Clark Fork near Garrison	6	1,139	3/2009–8/2015	8 (7-8)	NA[4]
16	12324680	Clark Fork at Goldcreek, Montana	Clark Fork at Goldcreek	6 and 7	1,704	3/1993–8/2015	8 (6–10)	1, 2, 3, 4
18	12331800	Clark Fork near Drummond, Montana	Clark Fork near Drummond	7 and 8	2,501	3/1993–8/2015	8 (6–10)	1, 2, 3, 4
20	12334550	Clark Fork at Turah Bridge near Bonner, Montana	Clark Fork at Turah Bridge	8 and 9	3,641	3/1985–8/2015	8 (6–23)	1, 2, 3, 4
22	12340500	Clark Fork above Missoula, Montana	Clark Fork above Missoula	9	5,999	7/1986–8/2015	8 (2–18)	1, 2, 3A, 3B, 4

[1]For this study, the sampling site numbers and reach designations assigned by Sando and others (2014) generally have been retained to facilitate comparisons.

[2]Where two reach numbers are shown, the site is both an outflow from the upstream reach and an inflow to the downstream reach.

[3]The numerical designations of the trend analysis periods are defined as
1: water years 1996–2000;
2: water years 2001–5;
3: water years 2006–10;
4: water years 2011–15.
Because of the substantial effect of the breach and removal of Milltown Dam in 2008, for Clark Fork above Missoula (station 12340500), period 3 was subdivided into period 3A (October 1, 2005–March 27, 2008) and period 3B (March 28, 2008–September 30, 2010).

[4]Period of water-quality data collection is insufficient for trend analysis. Site was included in the study for the purpose of statistically summarizing water-quality data collected during water years 2011–15.

water-quality data collection is insufficient for trend analysis for sampling site 15, but this site was included in the study for the purpose of statistically summarizing water-quality data collected during water years 2011–15.

Data-Collection and Analytical Methods

Sando and others (2014) present information concerning historical aspects of data-collection and analytical methods used in the monitoring program. Data collected in the monitoring program are published (typically on an annual basis) in data reports that present the methods of data collection, water-quality data, quality-assurance data, and statistical summaries of the data (for example, Dodge and others, 2015). A brief overview of field and laboratory data-collection and analytical methods is presented in the following paragraphs.

The sampling design of the monitoring program provides information relevant to several objectives, including evaluating constituent transport, regulatory compliance, and long-term trends. Since 1993, the sampling frequency of the main-stem sampling sites in the monitoring program generally has been consistent, with the sites sampled eight times per year in most years. In the monitoring program, the seasonal timing of sample collection placed greater emphasis on the snowmelt runoff period (typically April–July), when streamflow conditions are high and variable and constituent transport is large. About 75 percent of samples were collected during April–July. In general, the frequency and timing of sample collection throughout the period of data collection among the sites are reasonably consistent to provide reasonable consistency in trend-analysis results.

In the monitoring program, water samples were collected from vertical transits throughout the entire stream depth at multiple locations across the stream by using standard USGS depth- and width-integration methods (U.S. Geological Survey, variously dated). Those methods provide a vertically and laterally discharge-weighted composite sample that is intended to be representative of the entire flow passing through the cross section of a stream (Dodge and others, 2015). Specific conductance was measured onsite in subsamples from the composite water samples. Subsamples of the composite water samples were analyzed at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, for filtered (0.45-micrometer pore size) and unfiltered-recoverable concentrations of the trace-element constituents (table 2) by using methods described by Garbarino and Struzeski (1998) and Garbarino and others (2006). Water samples also were analyzed for suspended-sediment concentrations by the USGS sediment laboratory in Helena, Montana. All water-quality data are available in the USGS National Water Information System (NWIS; U.S. Geological Survey, 2015).

Quality Assurance

Sando and others (2014) present information concerning historical aspects of quality-assurance procedures used in the monitoring program. Quality-assurance data collected in the monitoring program are reported and statistically summarized in annual data reports (for example, Dodge and others, 2015). Selected quality-assurance information relevant to this study is presented in the following paragraphs.

Analytical results for field quality-assurance samples (including field blank and replicate samples) that were collected in the monitoring program during water years 1993–2015 were compiled and statistically summarized (table 1–1 in appendix 1 at the back of the report). Those data provide information on the consistency and environmental representativeness of data collection. Representative sampling for trace elements in streams is particularly difficult because of low concentrations in stream waters and ubiquitous presence in the sampling environment that produce an associated large potential for contamination.

Summary of analytical results for field blank samples (table 1–1 in appendix 1 at the back of the report) provides information on potential effects of contamination during the sampling process on trend-analysis results. For the trace-element constituents included in the trend analysis (table 2), the frequency of detection in field blank samples at concentrations greater than the laboratory reporting level (LRL) at the time of analysis ranged from 0.5 percent (filtered arsenic) to 10.7 percent (unfiltered-recoverable zinc). Precise statistical analysis of the analytical results of field blank samples is difficult because of the multiple LRLs used by NWQL during the study period (table 2). Also, it is difficult to precisely quantify the field blank sample results with respect to the study datasets because contamination indicated by field blank samples was routinely monitored in the Clark Fork monitoring program, and stream-sample data judged to be affected by persistent contamination issues were identified during periodic reviews of the data and excluded from data analysis. However, it is important that trend-analysis procedures are structured to minimize potential effects of sampling contamination on low-concentration data included in the trend analysis. Specific procedures used in application of the trend-analysis method with respect to handling of low-concentration and censored data (that is, analytical results reported as less than the LRL; Helsel, 2005) are described in the section of this report “General Description of the Time-Series Model.”

Summary of analytical results for field replicate samples (table 1–1 in appendix 1 at the back of the report) provides information on data precision. For the entire study period, the relative standard deviations (a measure of overall precision) for field replicate sample pairs were within 20 percent for all constituents, indicating reasonable precision (Taylor, 1987; Dodge and others, 2015).

Table 2. Properties, constituents, and associated information relating to laboratory and study reporting levels.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. NWQL, U.S. Geological Survey National Water Quality Laboratory; µS/cm, microsiemen per centimeter at 25 degrees Celsius; NA, not applicable; mg/L, milligram per liter; µg/L, microgram per liter]

Property or constituent	Units of measurement	Number of NWQL laboratory reporting levels during water years 1993–2015	Range in NWQL laboratory reporting levels	Study reporting level used in application of the time-series model[1]
Specific conductance[2]	µS/cm	NA	NA	NA
pH, standard units	standard units	NA	NA	NA
Calcium, filtered	mg/L	5	0.005–0.022	NA
Magnesium, filtered	mg/L	7	0.002–0.011	NA
Cadmium, filtered	µg/L	7	0.01–1.0	NA
Cadmium, unfiltered-recoverable	µg/L	10	0.007–1.0	NA
Copper, filtered[2]	µg/L	4	0.2–1	1.0
Copper, unfiltered-recoverable[2]	µg/L	6	0.3–2	1.0
Lead, filtered	µg/L	10	0.015–5	NA
Lead, unfiltered-recoverable	µg/L	6	0.03–5	NA
Zinc, filtered	µg/L	7	0.9–20	NA
Zinc, unfiltered-recoverable[2]	µg/L	4	2–31	2.0
Arsenic, filtered[2]	µg/L	7	0.022–1	1.0
Arsenic, unfiltered-recoverable[2]	µg/L	7	0.06–1	1.0
Suspended sediment[2]	mg/L	NA	NA	1

[1]Procedures for determining and applying the study reporting level used in the application of the time-series model are discussed in the section of this report "General Description of the Time-Series Model."

[2]Property or constituent was analyzed for temporal trends.

Analytical results for laboratory-spiked deionized-water blank samples and stream-water samples that were collected in the monitoring program during water years 1993–2015 are presented in tables 1–2 and 1–3, respectively, in appendix 1 at the back of the report. Annual mean recoveries for laboratory-spiked deionized-water blank samples for all constituents combined have ranged from 82.3 to 118 percent (mean of 104 percent). Annual mean recoveries for laboratory-spiked stream-water samples for all constituents combined have ranged from 84.3 to 114 percent (mean of 105 percent). Potential effects of temporal variability in spike recoveries on trend results are described in appendix 1 and also the section "Specific Aspects of the Application of the Time-Series Model in this Study" in appendix 2. Based on analysis of all quality-assurance data, the quality of the study datasets were determined to be suitable for trend analysis.

Overview of Streamflow and Water-Quality Characteristics for Water Years 2011–15

Statistically summarizing recent streamflow and water-quality characteristics of the study sampling sites (fig. 1, table 1) is useful for generally describing water quality and in providing comparative information relevant for interpreting trend results. Data are summarized for water years 2011–15, a summary period that represents recent water-quality conditions and the increment of data collected after the study period 1996–2010 reported by Sando and others (2014).

General Streamflow Characteristics for Water Years 2011–15

To aid in interpreting water-quality characteristics of the sampling sites, statistical summaries of continuous streamflow data are presented in table 3. The continuous streamflow data are available in NWIS (U.S. Geological Survey, 2015). In general, streamflow conditions during water years 2011–15 were somewhat high. Mean annual streamflows for water years 2011–15 generally were about 10–20 percent higher than period-of-record mean annual streamflows.

Water-Quality Characteristics for Water Years 2011–15

Statistical summaries of water-quality data (water years 2011–15) for sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin are presented in table 4. The statistical summaries in table 4 are based on unadjusted trace-element concentrations (the observed concentrations before flow adjustment). Flow adjustment, described in the sections of this report "General Description of the Time-Series Model" and "Factors that Affect Trend Results and Interpretation," is relevant when interpreting trends in concentrations of water-quality constituents that are strongly dependent on streamflow conditions. However, flow adjustment is not relevant for statistically summarizing the observed water-quality data during water years 2011–15.

In addition to statistical summaries of unadjusted concentrations, ratios of median filtered to unfiltered-recoverable trace-element concentrations are reported in table 4 to provide general information on the predominant phase (that is, dissolved or particulate) of transport. Values of aquatic-life standards (Montana Department of Environmental Quality, 2012; based on median hardness for each site for water years 2011–15) for cadmium, copper, lead, and zinc are presented in table 1–4 in appendix 1 at the back of the report; those values were used for plotting the standards in relation to statistical distributions of selected trace elements. The arsenic human-health standard is 10 micrograms per liter (µg/L; Montana Department of Environmental Quality, 2012). Percentages of samples (water years 2011–15) with unadjusted unfiltered-recoverable concentrations exceeding water-quality standards for each site are presented in table 5. The exceedance percentages for the hardness-based aquatic-life standards for cadmium, copper, lead, and zinc in table 5 were based on comparison of trace-element concentrations of each individual sample with the aquatic-life standards that were calculated by using the hardness for each individual sample.

Statistical distributions of water-quality characteristics of the sampling sites are illustrated in figure 2 by using boxplots of selected example constituents (unadjusted specific conductance and unadjusted concentrations of copper, arsenic, and suspended sediment); the boxplots provide an overview of important water-quality characteristics in the upper Clark Fork Basin. Also shown in figure 2 are applicable water-quality standards. Specific conductance is presented as an example because it is an index of ionic strength, is strongly correlated with hardness (which is used in calculations of aquatic-life standards), and provides information on the extent of water contact with geologic materials, types of geologic materials present in the sampling-site basins, and potential effects of remediation activities on ionic strength. Copper and arsenic are presented as examples of trace elements because they are constituents of concern with respect to potential toxicity issues, but they have much different geochemical characteristics. Spatial and temporal variability in copper concentrations in the upper Clark Fork Basin generally is similar to variability in other metallic contaminants that tend to adsorb to particulates in water (Sando and others, 2014) and is considered generally representative of those constituents. In contrast, arsenic in the upper Clark Fork Basin tends to largely exist in the dissolved phase and does not exhibit the same variability as metallic contaminants (Sando and others, 2014). Suspended sediment is presented because it provides information on transport of particulate materials, which is a factor that can strongly affect transport of metallic contaminants.

To assist in the presentation of results, Sando and others (2014) divided Silver Bow Creek and the Clark Fork into nine data-summary reaches based on the location of sampling sites along the main-stems of those streams. The sampling site numbers and reach designations assigned by Sando and others (2014) generally have been retained to facilitate comparisons, and water-quality characteristics for sampling sites in six reaches (reaches 4–9) are presented. Water-quality characteristics within the six reaches are affected by environmental characteristics within the delineated reach basin boundaries (fig. 1). Water-quality characteristics of the sampling sites are described for each of the data-summary reaches. Emphasis is placed on describing spatial differences in observed water quality in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin during water years 2011–15.

Table 3. Statistical summaries of continuous streamflow data for selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft³/s, cubic foot per second; POR, period of record]

Sampling site number (fig. 1, table 1)	Abbreviated sampling site name (table 1)	Drainage area, in square miles	Analysis period, in water years (number of years)	Statistical summaries of daily mean streamflow, in ft³/s					
				Minimum	25th percentile	Median	Mean (also referred to as "mean annual streamflow")	75th percentile	Maximum
8	Silver Bow Creek at Warm Springs	473	2011–15 (5)	22	51	65	96	97	1,060
			POR: 1994–2015 (22)	15	41	59	88	88	1,060
11	Clark Fork near Galen	651	2011–15 (5)	35	92	130	172	174	1,390
			POR: 1989–2015 (27)	13	70	100	143	152	1,390
14	Clark Fork at Deer Lodge	995	2011–15 (5)	55	187	237	283	302	1,960
			POR: 1979–2015 (37)	22	159	219	257	298	2,390
15	Clark Fork near Garrison	1,139	2011–15 (5)	61	198	263	315	331	2,560
			POR: 2010–15 (6)	61	209	267	323	334	2,560
16	Clark Fork at Goldcreek	1,704	2011–15 (5)	112	320	409	570	583	6,100
			POR: 1978–2015 (38)	55	280	380	519	556	9,100
18	Clark Fork near Drummond	2,501	2011–15 (5)	185	461	595	771	813	7,740
			POR: 1994–2015 (22)	77	419	563	718	758	8,430
20	Clark Fork at Turah Bridge	3,641	2011–15 (5)	250	790	990	1,490	1,560	12,700
			POR: 1985–2015 (31)	177	678	870	1,260	1,260	12,700
22	Clark Fork above Missoula	5,999	2011–15 (5)	500	1,400	1,730	3,330	3,760	28,100
			POR: 1930–2015 (86)	340	1,270	1,650	2,930	2,960	30,800

Table 4. Statistical summaries of water-quality data collected at selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 2011–15.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft^3/s, cubic foot per second; NA, not applicable; µS/cm, microsiemen per centimeter at 25 degrees Celsius; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, unadjusted (not flow adjusted) units of measurement	Statistical summaries of water-quality data[1]							Ratios of median filtered to median unfiltered-recoverable concentrations for trace elements, in percent[3]
	Number of samples (values in parentheses indicate number of censored values)	Minimum uncensored value[2]	25th percentile	Median	Mean	75th percentile	Maximum	
Silver Bow Creek at Warm Springs, Montana (sampling site 8, fig. 1, table 1)								
Streamflow, instantaneous, ft^3/s	40	20	66	89	146	161	1,030	NA
Specific conductance, µS/cm	40	182	342	394	407	489	577	NA
pH, standard units	40	8.1	8.5	8.8	NA	9.1	9.4	NA
Hardness, filtered, mg/L as $CaCO_3$	40	74.9	136	170	169	203	253	NA
Calcium, filtered, mg/L	40	22.5	39.7	48.4	48.7	58.6	73.3	NA
Magnesium, filtered, mg/L	40	4.52	9.10	11.8	11.5	14.4	16.9	NA
Cadmium, filtered, µg/L	40 (4)	0.023	0.031	0.038	0.044	0.054	0.096	45
Cadmium, unfiltered-recoverable, µg/L	40	0.027	0.065	0.085	0.119	0.125	0.567	
Copper, filtered, µg/L	40	1.6	2.6	3.5	4.3	4.7	21.4	51
Copper, unfiltered-recoverable, µg/L	40	2.8	5.0	6.8	9.5	11.2	35.2	
Iron, filtered, µg/L	40	7.0	16.2	30.0	30.0	38.7	63.0	13
Iron, unfiltered-recoverable, µg/L	40	61.1	159	225	256	313	839	
Lead, filtered, µg/L	40	0.044	0.103	0.158	0.162	0.186	0.566	14
Lead, unfiltered-recoverable, µg/L	40	0.37	0.81	1.16	1.80	2.07	6.39	
Manganese, filtered, µg/L	40	27.1	42.7	61.2	72.6	84.7	208	64
Manganese, unfiltered-recoverable, µg/L	40	60.1	77.5	95.2	116	130	332	
Zinc, filtered, µg/L	40 (11)	1.5	1.7	2.8	2.8	3.3	6.1	33
Zinc, unfiltered-recoverable, µg/L	40 (2)	2.3	5.5	8.6	13.3	14.1	69.8	
Arsenic, filtered, µg/L	40	8.4	13.4	19.2	20.9	28.0	38.1	86
Arsenic, unfiltered-recoverable, µg/L	40	10.4	16.9	22.4	22.8	28.8	37.9	
Suspended sediment, mg/L	40	1	3	6	6	7	21	NA
Suspended sediment, percent fines[4]	40	60	84	88	87	92	98	NA

Table 4. Statistical summaries of water-quality data collected at selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 2011–15.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft^3/s, cubic foot per second; NA, not applicable; µS/cm, microsiemen per centimeter at 25 degrees Celsius; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, unadjusted (not flow adjusted) units of measurement	Statistical summaries of water-quality data[1]							Ratios of median filtered to median unfiltered-recoverable concentrations for trace elements, in percent[3]
	Number of samples (values in parentheses indicate number of censored values)	Minimum uncensored value[2]	25th percentile	Median	Mean	75th percentile	Maximum	
Clark Fork near Galen, Montana (sampling site 11, fig. 1, table 1)								
Streamflow, instantaneous, ft^3/s	40	38	110	175	249	284	1,380	NA
Specific conductance, µS/cm	40	182	292	367	360	434	498	NA
pH, standard units	40	8.2	8.4	8.6	NA	8.7	9.1	NA
Hardness, filtered, mg/L as $CaCO_3$	40	76.4	125	164	158	191	225	NA
Calcium, filtered, mg/L	40	23.2	37.1	47.9	46.4	55.4	65.1	NA
Magnesium, filtered, mg/L	40	4.44	7.75	10.6	10.2	12.7	15.1	NA
Cadmium, filtered, µg/L	40 (2)	0.020	0.037	0.041	0.044	0.049	0.111	42
Cadmium, unfiltered-recoverable, µg/L	40	0.034	0.076	0.098	0.115	0.160	0.287	
Copper, filtered, µg/L	40	1.4	3.1	3.7	4.3	4.7	19.8	31
Copper, unfiltered-recoverable, µg/L	39	4.8	9.2	11.9	15.4	17.5	51.6	
Iron, filtered, µg/L	40	7.5	11.7	20.0	20.2	27.1	43.0	8
Iron, unfiltered-recoverable, µg/L	40	67.5	167	248	297	370	860	
Lead, filtered, µg/L	40	0.037	0.074	0.112	0.116	0.132	0.387	7
Lead, unfiltered-recoverable, µg/L	40	0.40	1.10	1.51	2.06	2.82	6.33	
Manganese, filtered, µg/L	40	13.1	37.8	41.8	54.7	63.8	130	48
Manganese, unfiltered-recoverable, µg/L	40	40.9	73.0	87.5	102	122	220	
Zinc, filtered, µg/L	40 (7)	1.4	1.8	2.6	2.8	3.3	9.4	24
Zinc, unfiltered-recoverable, µg/L	40	2.8	7.1	10.7	13.5	18.0	45.1	
Arsenic, filtered, µg/L	40	7.0	10.4	12.7	13.8	18.0	27.5	82
Arsenic, unfiltered-recoverable, µg/L	40	8.9	12.4	15.4	16.0	19.0	31.5	
Suspended sediment, mg/L	40	2	5	8	12	12	59	NA
Suspended sediment, percent fines[4]	40	32	68	76	75	87	96	NA

Table 4. Statistical summaries of water-quality data collected at selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 2011–15.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft^3/s, cubic foot per second; NA, not applicable; µS/cm, microsiemen per centimeter at 25 degrees Celsius; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, unadjusted (not flow adjusted) units of measurement	Statistical summaries of water-quality data[1]							Ratios of median filtered to median unfiltered-recoverable concentrations for trace elements, in percent[3]
	Number of samples (values in parentheses indicate number of censored values)	Minimum uncensored value[2]	25th percentile	Median	Mean	75th percentile	Maximum	
Clark Fork at Deer Lodge, Montana (sampling site 14, fig. 1, table 1)								
Streamflow, instantaneous, ft^3/s	40	44	197	265	353	357	2,000	NA
Specific conductance, µS/cm	40	228	346	436	412	481	525	NA
pH, standard units	40	7.9	8.2	8.3	NA	8.4	8.9	NA
Hardness, filtered, mg/L as $CaCO_3$	40	97.1	154	200	183	214	231	NA
Calcium, filtered, mg/L	40	29.1	46.0	58.8	54.0	62.8	68.8	NA
Magnesium, filtered, mg/L	40	5.92	9.56	13.1	11.8	13.7	15.5	NA
Cadmium, filtered, µg/L	40	0.035	0.049	0.065	0.069	0.072	0.280	43
Cadmium, unfiltered-recoverable, µg/L	40	0.046	0.094	0.152	0.203	0.221	0.784	
Copper, filtered, µg/L	40	3.4	5.6	7.0	8.3	7.7	45.9	25
Copper, unfiltered-recoverable, µg/L	40	9.4	15.2	27.6	46.3	49.3	220	
Iron, filtered, µg/L	40	5.5	11.7	18.5	18.7	24.9	45.8	4
Iron, unfiltered-recoverable, µg/L	40	63.0	224	436	708	788	4,290	
Lead, filtered, µg/L	40 (1)	0.041	0.082	0.142	0.152	0.189	0.372	4
Lead, unfiltered-recoverable, µg/L	40	0.55	1.61	3.28	5.70	6.63	32.8	
Manganese, filtered, µg/L	40	11.7	22.6	30.0	32.6	38.7	70.8	36
Manganese, unfiltered-recoverable, µg/L	40	22.9	57.4	82.9	97.5	115	364	
Zinc, filtered, µg/L	40	1.6	3.6	5.5	6.5	6.6	50.6	23
Zinc, unfiltered-recoverable, µg/L	40	5.0	15.3	23.2	34.9	37.6	164	
Arsenic, filtered, µg/L	40	7.7	10.3	13.3	14.0	16.2	36.6	81
Arsenic, unfiltered-recoverable, µg/L	40	9.7	13.8	16.4	19.2	20.3	46.6	
Suspended sediment, mg/L	40	2	8	17	33	31	218	NA
Suspended sediment, percent fines[4]	40	39	72	81	77	86	96	NA

Table 4. Statistical summaries of water-quality data collected at selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 2011–15.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft^3/s, cubic foot per second; NA, not applicable; µS/cm, microsiemen per centimeter at 25 degrees Celsius; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, unadjusted (not flow adjusted) units of measurement	Statistical summaries of water-quality data[1]							Ratios of median filtered to median unfiltered-recoverable concentrations for trace elements, in percent[3]
	Number of samples (values in parentheses indicate number of censored values)	Minimum uncensored value[2]	25th percentile	Median	Mean	75th percentile	Maximum	
Clark Fork above Little Blackfoot River near Garrison, Montana (sampling site 15, fig. 1, table 1)								
Streamflow, instantaneous, ft^3/s	39	71	227	289	410	418	2,310	NA
Specific conductance, µS/cm	39	249	363	449	421	479	527	NA
pH, standard units	39	7.9	8.2	8.4	NA	8.6	8.9	NA
Hardness, filtered, mg/L as $CaCO_3$	39	107	162	202	186	213	228	NA
Calcium, filtered, mg/L	39	31.9	47.4	58.8	54.1	61.7	66.5	NA
Magnesium, filtered, mg/L	39	6.65	10.4	13.4	12.3	14.4	15.5	NA
Cadmium, filtered, µg/L	39 (1)	0.024	0.050	0.065	0.067	0.072	0.227	42
Cadmium, unfiltered-recoverable, µg/L	39	0.027	0.117	0.155	0.227	0.272	0.835	
Copper, filtered, µg/L	39	2.8	6.2	7.9	9.2	9.7	40.6	25
Copper, unfiltered-recoverable, µg/L	39	10.0	19.1	31.9	51.3	54.0	222	
Iron, filtered, µg/L	38	5.2	9.2	15.7	19.0	25.2	64.4	3
Iron, unfiltered-recoverable, µg/L	38	40.7	256	505	806	823	3,860	
Lead, filtered, µg/L	39 (1)	0.048	0.086	0.135	0.181	0.247	0.715	4
Lead, unfiltered-recoverable, µg/L	39	0.33	2.08	3.74	6.40	6.63	32.3	
Manganese, filtered, µg/L	39	8.6	20.7	27.2	29.4	35.7	65.1	32
Manganese, unfiltered-recoverable, µg/L	39	13.4	63.4	84.5	105	129	344	
Zinc, filtered, µg/L	39 (2)	1.9	3.1	4.9	5.6	6.9	37.1	18
Zinc, unfiltered-recoverable, µg/L	39 (1)	3.2	15.9	26.7	43.9	44.5	181	
Arsenic, filtered, µg/L	39	7.8	10.9	15.2	15.0	17.3	36.7	87
Arsenic, unfiltered-recoverable, µg/L	39	10.5	15.2	17.4	20.3	21.2	46.0	
Suspended sediment, mg/L	39	1	11	21	37	37	205	NA
Suspended sediment, percent fines[4]	39	46	72	79	77	83	92	NA

Table 4. Statistical summaries of water-quality data collected at selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 2011–15.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft³/s, cubic foot per second; NA, not applicable; µS/cm, microsiemen per centimeter at 25 degrees Celsius; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, unadjusted (not flow adjusted) units of measurement	Statistical summaries of water-quality data[1]							Ratios of median filtered to median unfiltered-recoverable concentrations for trace elements, in percent[3]
	Number of samples (values in parentheses indicate number of censored values)	Minimum uncensored value[2]	25th percentile	Median	Mean	75th percentile	Maximum	
Clark Fork at Goldcreek, Montana (sampling site 16, fig. 1, table 1)								
Streamflow, instantaneous, ft³/s	40	137	393	522	820	902	4,450	NA
Specific conductance, µS/cm	40	216	297	364	353	411	456	NA
pH, standard units	40	7.9	8.1	8.3	NA	8.6	9.1	NA
Hardness, filtered, mg/L as $CaCO_3$	40	98.5	131	165	158	186	211	NA
Calcium, filtered, mg/L	40	29.6	38.7	48.2	46.5	55.0	62.1	NA
Magnesium, filtered, mg/L	40	5.96	8.21	10.6	10.2	12.2	13.6	NA
Cadmium, filtered, µg/L	40 (3)	0.020	0.031	0.041	0.044	0.050	0.124	40
Cadmium, unfiltered-recoverable, µg/L	40	0.021	0.072	0.102	0.158	0.209	0.530	
Copper, filtered, µg/L	40	2.1	4.3	5.1	6.1	6.4	23.3	27
Copper, unfiltered-recoverable, µg/L	40	5.6	11.4	18.6	32.1	41.3	133	
Iron, filtered, µg/L	40 (1)	3.8	8.8	18.6	25.9	36.0	93.7	5
Iron, unfiltered-recoverable, µg/L	40	31.8	182	360	699	922	2,940	
Lead, filtered, µg/L	40 (2)	0.035	0.056	0.111	0.141	0.170	0.677	5
Lead, unfiltered-recoverable, µg/L	40	0.14	1.31	2.24	4.33	5.99	19.9	
Manganese, filtered, µg/L	40	5.5	12.8	16.1	18.3	20.0	45.1	24
Manganese, unfiltered-recoverable, µg/L	40	9.3	46.9	67.4	84.4	107	253	
Zinc, filtered, µg/L	40 (5)	1.8	2.3	3.5	4.1	5.7	17.7	20
Zinc, unfiltered-recoverable, µg/L	40 (1)	2.9	11.0	17.3	29.9	41.7	113	
Arsenic, filtered, µg/L	40	5.6	7.9	9.0	9.9	11.5	22.5	79
Arsenic, unfiltered-recoverable, µg/L	40	7.5	9.7	11.4	13.3	14.4	28.4	
Suspended sediment, mg/L	40	2	8	16	35	40	176	NA
Suspended sediment, percent fines[4]	40	56	71	82	78	87	94	NA

Table 4. Statistical summaries of water-quality data collected at selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 2011–15.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft^3/s, cubic foot per second; NA, not applicable; µS/cm, microsiemen per centimeter at 25 degrees Celsius; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, unadjusted (not flow adjusted) units of measurement	Statistical summaries of water-quality data[1]							Ratios of median filtered to median unfiltered-recoverable concentrations for trace elements, in percent[3]
	Number of samples (values in parentheses indicate number of censored values)	Minimum uncensored value[2]	25th percentile	Median	Mean	75th percentile	Maximum	
Clark Fork near Drummond, Montana (sampling site 18, fig. 1, table 1)								
Streamflow, instantaneous, ft^3/s	40	248	563	781	1,040	1,090	5,540	NA
Specific conductance, µS/cm	40	243	346	417	403	458	560	NA
pH, standard units	40	7.9	8.1	8.1	NA	8.2	8.5	NA
Hardness, filtered, mg/L as $CaCO_3$	40	109	158	190	184	211	265	NA
Calcium, filtered, mg/L	40	32.6	45.1	54.3	52.7	59.7	74.9	NA
Magnesium, filtered, mg/L	40	6.75	10.7	13.2	12.9	15.0	19.0	NA
Cadmium, filtered, µg/L	40 (2)	0.021	0.032	0.043	0.045	0.053	0.101	35
Cadmium, unfiltered-recoverable, µg/L	40 (1)	0.026	0.072	0.124	0.168	0.241	0.536	
Copper, filtered, µg/L	40	1.9	3.9	4.8	5.6	6.2	19.8	24
Copper, unfiltered-recoverable, µg/L	40	5.4	9.8	19.4	29.9	36.7	107	
Iron, filtered, µg/L	40 (2)	3.6	9.0	15.0	20.7	26.9	88.7	3
Iron, unfiltered-recoverable, µg/L	40	24.8	180	440	710	979	3,170	
Lead, filtered, µg/L	40 (2)	0.039	0.059	0.115	0.142	0.152	0.592	4
Lead, unfiltered-recoverable, µg/L	40	0.17	1.27	3.02	4.61	6.29	19.8	
Manganese, filtered, µg/L	40	4.2	12.4	15.5	17.4	22.0	37.7	20
Manganese, unfiltered-recoverable, µg/L	40	9.9	49.7	76.6	96.0	121	294	
Zinc, filtered, µg/L	40 (1)	2.2	3.5	4.3	4.7	5.3	13.2	19
Zinc, unfiltered-recoverable, µg/L	40 (1)	4.6	12.0	22.7	35.0	48.3	134	
Arsenic, filtered, µg/L	40	6.3	8.0	9.7	10.1	11.3	23.9	86
Arsenic, unfiltered-recoverable, µg/L	40	7.7	10.6	11.3	13.3	13.9	30.7	
Suspended sediment, mg/L	40	2	9	22	40	57	216	NA
Suspended sediment, percent fines[4]	40	42	68	79	76	86	93	NA

Table 4. Statistical summaries of water-quality data collected at selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 2011–15.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft^3/s, cubic foot per second; NA, not applicable; µS/cm, microsiemen per centimeter at 25 degrees Celsius; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, unadjusted (not flow adjusted) units of measurement	Statistical summaries of water-quality data[1]							Ratios of median filtered to median unfiltered-recoverable concentrations for trace elements, in percent[3]
	Number of samples (values in parentheses indicate number of censored values)	Minimum uncensored value[2]	25th percentile	Median	Mean	75th percentile	Maximum	
Clark Fork at Turah Bridge near Bonner, Montana (sampling site 20, fig. 1, table 1)								
Streamflow, instantaneous, ft^3/s	40	462	1,050	1,500	2,230	2,640	10,600	NA
Specific conductance, µS/cm	40	140	214	285	277	340	385	NA
pH, standard units	40	7.8	8.0	8.1	NA	8.2	8.4	NA
Hardness, filtered, mg/L as $CaCO_3$	40	60.1	97.6	132	127	156	186	NA
Calcium, filtered, mg/L	40	17.3	27.8	35.9	35.6	43.5	52.8	NA
Magnesium, filtered, mg/L	40	4.11	6.76	9.57	9.27	11.6	13.1	NA
Cadmium, filtered, µg/L	40 (12)	0.017	0.019	0.027	0.031	0.037	0.083	37
Cadmium, unfiltered-recoverable, µg/L	40 (3)	0.025	0.048	0.073	0.104	0.132	0.404	
Copper, filtered, µg/L	40	1.3	2.2	2.9	3.8	3.9	17.9	27
Copper, unfiltered-recoverable, µg/L	40	3.8	5.9	10.5	16.8	20.1	61.9	
Iron, filtered, µg/L	40 (3)	3.3	7.1	20.4	29.7	34.0	359	6
Iron, unfiltered-recoverable, µg/L	40	47.7	132	316	507	527	2,450	
Lead, filtered, µg/L	40 (6)	0.030	0.039	0.069	0.134	0.137	2.79	4
Lead, unfiltered-recoverable, µg/L	40	0.20	0.58	1.67	2.67	3.33	11.9	
Manganese, filtered, µg/L	40	3.0	5.4	6.9	9.6	9.8	48.6	16
Manganese, unfiltered-recoverable, µg/L	40	9.5	26.9	43.5	57.7	66.7	212	
Zinc, filtered, µg/L	40 (4)	1.5	2.3	3.3	3.9	4.7	17.4	23
Zinc, unfiltered-recoverable, µg/L	40	3.8	8.4	14.2	22.9	27.3	109	
Arsenic, filtered, µg/L	40	2.7	4.5	5.6	5.6	6.0	14.2	90
Arsenic, unfiltered-recoverable, µg/L	40	3.0	5.6	6.2	7.3	8.2	21.0	
Suspended sediment, mg/L	40	3	7	16	32	30	186	NA
Suspended sediment, percent fines[4]	40	44	66	78	74	85	91	NA

Table 4. Statistical summaries of water-quality data collected at selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 2011–15.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft^3/s, cubic foot per second; NA, not applicable; µS/cm, microsiemen per centimeter at 25 degrees Celsius; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, unadjusted (not flow adjusted) units of measurement	Statistical summaries of water-quality data[1]							Ratios of median filtered to median unfiltered-recoverable concentrations for trace elements, in percent[3]
	Number of samples (values in parentheses indicate number of censored values)	Minimum uncensored value[2]	25th percentile	Median	Mean	75th percentile	Maximum	
Clark Fork above Missoula, Montana (sampling site 22, fig. 1, table 1)								
Streamflow, instantaneous, ft^3/s	40	910	1,710	4,100	5,530	7,240	22,900	NA
Specific conductance, µS/cm	40	148	189	230	239	288	341	NA
pH, standard units	40	8.0	8.2	8.3	NA	8.4	8.7	NA
Hardness, filtered, mg/L as $CaCO_3$	40	70.7	88.5	109	113	141	163	NA
Calcium, filtered, mg/L	40	19.3	23.8	29.5	30.3	36.9	44.9	NA
Magnesium, filtered, mg/L	40	5.30	6.98	8.48	9.06	11.3	12.9	NA
Cadmium, filtered, µg/L	40 (25)	0.017	0.014	0.018	0.019	0.023	0.046	47
Cadmium, unfiltered-recoverable, µg/L	40 (12)	0.020	0.021	0.038	0.056	0.067	0.345	
Copper, filtered, µg/L	40	1.0	1.5	1.7	2.1	2.1	7.0	35
Copper, unfiltered-recoverable, µg/L	40	1.9	3.2	4.8	9.0	9.4	53.1	
Iron, filtered, µg/L	40 (1)	3.7	6.6	17.3	22.6	34.2	60.5	7
Iron, unfiltered-recoverable, µg/L	40	40.9	96.3	255	370	344	2,030	
Lead, filtered, µg/L	40 (10)	0.026	0.031	0.054	0.068	0.089	0.212	7
Lead, unfiltered-recoverable, µg/L	40	0.13	0.41	0.80	1.40	1.57	8.04	
Manganese, filtered, µg/L	40	3.5	5.5	6.5	7.7	8.5	20.0	24
Manganese, unfiltered-recoverable, µg/L	40	8.8	19.7	27.5	36.5	41.4	155	
Zinc, filtered, µg/L	40 (16)	1.4	1.4	1.9	2.0	2.4	5.5	26
Zinc, unfiltered-recoverable, µg/L	40 (4)	2.3	4.9	7.2	12.2	12.2	84.4	
Arsenic, filtered, µg/L	40	1.2	2.5	3.1	3.1	3.6	7.1	85
Arsenic, unfiltered-recoverable, µg/L	40	1.4	2.9	3.7	4.1	4.8	13.2	
Suspended sediment, mg/L	40	2	5	13	26	20	176	NA
Suspended sediment, percent fines[4]	40	61	73	82	79	85	95	NA

[1]Distributional parameters affected by censored observations (that is, concentrations reported as less than the laboratory reporting level) were estimated by using adjusted maximum likelihood estimation (Cohn, 1988).

[2]Minimum uncensored value refers to the smallest concentration reported as detected above any of the various laboratory reporting levels applicable for a given constituent.

[3]Ratio of median filtered to unfiltered-recoverable concentration greater than 100 percent affected by low median concentrations near minimum laboratory reporting levels (table 2) and small bias in filtered concentrations.

[4]Percent fines refers to the percentage of suspended sediment smaller than 0.062-millimeter diameter.

Table 5. Percentages of samples with unadjusted unfiltered-recoverable concentrations exceeding water-quality standards for selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, water years 2011–15.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. $CaCO_3$, calcium carbonate]

Sampling site number (fig. 1, table 1)	Abbreviated sampling site name (table 1)	Percentage of samples exceeding indicated standard								
		Arsenic human-health standard	Aquatic-life standards							
			Cadmium		Copper		Lead		Zinc	
			Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Chronic
8	Silver Bow Creek at Warm Springs	100	0	3	8	18	0	3	0	0
11	Clark Fork near Galen	98	0	0	26	41	0	8	0	0
14	Clark Fork at Deer Lodge	95	0	15	58	75	0	23	3	3
15	Clark Fork near Garrison	100	0	18	59	79	0	23	3	3
16	Clark Fork at Goldcreek	68	0	18	48	60	0	28	0	0
18	Clark Fork near Drummond	80	0	15	38	58	0	25	3	3
20	Clark Fork at Turah Bridge	13	0	13	28	48	0	25	0	0
22	Clark Fork above Missoula	3	0	5	15	23	0	13	0	0

Reach 4

Reach 4 extends about 2 river miles from Silver Bow Creek at Warm Springs, Montana (sampling site 8), to Clark Fork near Galen, Montana (sampling site 11). Within the reach, water from Warm Springs Ponds mixes and geochemically reacts with water contributed from the Mill-Willow Bypass and Warm Springs Creek; thus, complex water-quality processes are possible in the short reach.

The Warm Springs Ponds system was originally constructed during 1908–17 (and expanded during the 1950s) to trap sediment enriched in trace elements (CDM, 2005). In about 1967, the AMC started introducing a lime and water suspension into Silver Bow Creek upstream from Warm Springs Ponds to raise pH and promote precipitation and deposition of metals in Warm Springs Ponds (U.S. Environmental Protection Agency, 2000). The Mill-Willow Bypass was constructed in about 1969 to capture streamflows of Mill and Willow Creeks near their mouths and divert the combined streamflows (believed to be relatively clean water; U.S. Environmental Protection Agency, 2000) around Warm Springs Ponds and into Silver Bow Creek between the outlet from the Warm Springs Ponds and sampling site 8 (CDM, 2005). Warm Springs Creek originates in the mountains west of the AMC Smelter, flows generally east through areas adjacent to the AMC Smelter and various tailings piles and ponds, and joins Silver Bow Creek to form the Clark Fork near Warm Springs. The Warm Springs Creek Basin is affected by pollution from milling and smelting operations of the AMC Smelter. Thick tailings deposits are extensive in the Silver Bow Creek and Clark Fork flood plain near Warm Springs (Smith and others, 1998) and provide a source of sediment enriched with metallic contaminants within reach 4.

In reach 4, the mean annual streamflow for water years 2011–15 increased by about 79 percent from 96 cubic feet per second (ft^3/s) at sampling site 8 to 172 ft^3/s at sampling site 11 (table 3) primarily because of contributions from Warm Springs Creek and also ephemeral gulches and groundwater inflow. Near the end of reach 4, Warm Springs Creek and Silver Bow Creek join to form the Clark Fork.

Silver Bow Creek at Warm Springs (sampling site 8) is about 0.2 river mile downstream from Warm Springs Ponds, which were designed to trap suspended sediment and metallic contaminants by physical deposition and treatment (liming; U.S. Environmental Protection Agency, 2000). Median concentrations of unfiltered-recoverable copper and zinc (6.8 and 8.6 µg/L, respectively) and suspended sediment (6 milligrams per liter [mg/L]) are lower than median concentrations of most downstream main-stem Clark Fork sampling sites (fig. 2, table 4). The median concentration of unfiltered-recoverable arsenic (22.4 µg/L) at sampling site 8 is higher than median concentrations at the downstream main-stem Clark Fork sampling sites. The high median arsenic concentration at sampling site 8 is affected by contributions of water with high arsenic concentrations from the Mill-Willow Bypass and by complex hydrologic and limnologic factors that affect arsenic biogeochemical processing in Warm Springs Ponds (Chatham, 2012). The median pH for sampling site 8 is 8.8 standard units, which is higher than the median pH of the downstream main-stem Clark Fork sampling sites (table 4). High pH in Warm Springs Ponds (a result of a combination factors, including liming and nutrient processing by aquatic vegetation; Chatham, 2012) promotes arsenic solubility and mobilization (Stumm and Morgan, 1970). Exceedances of most water-quality standards were infrequent (that is, less than or equal to 20 percent of samples) for sampling site 8; however, the

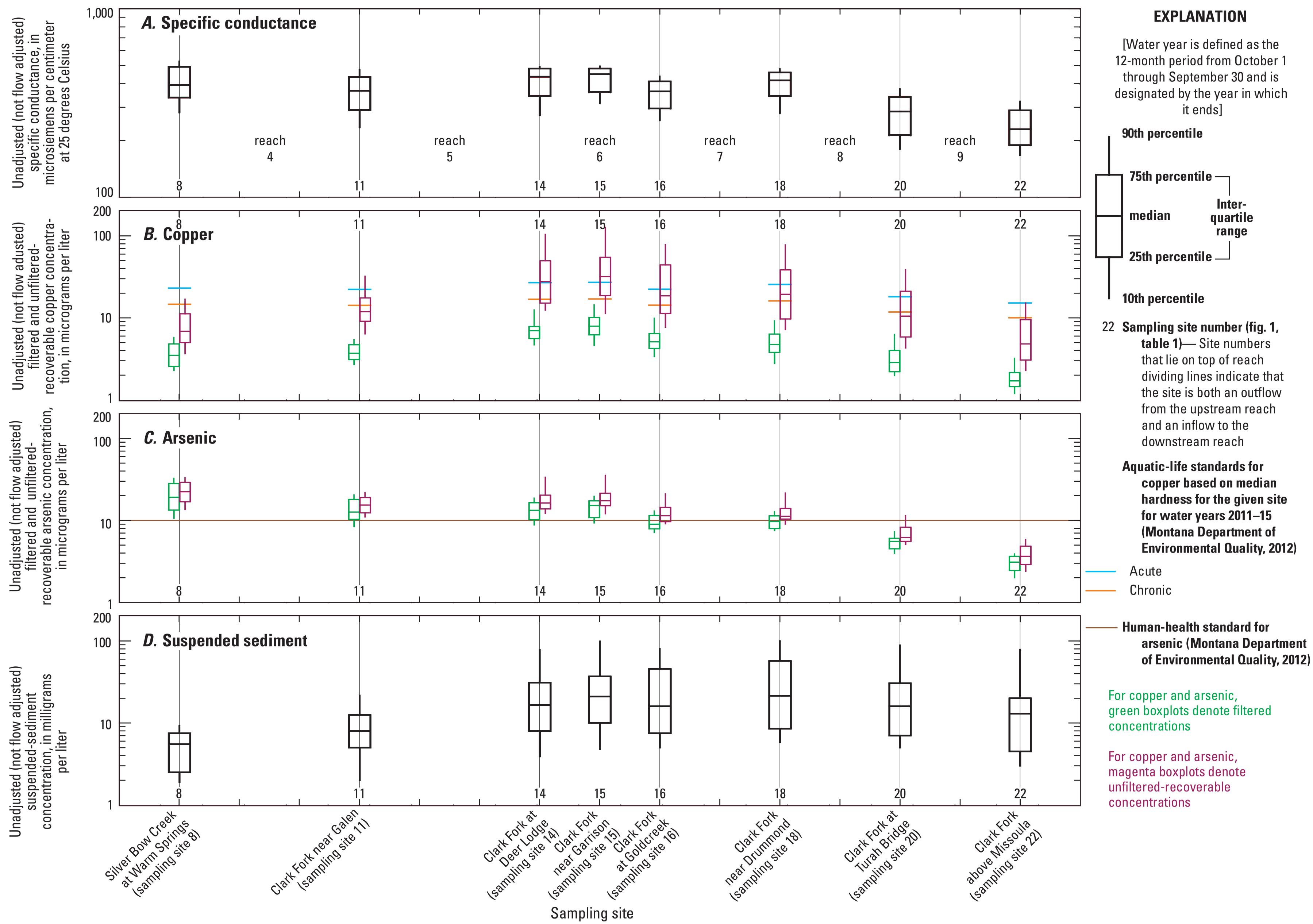


Figure 2. Statistical distributions of selected constituents for selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 2011–15. *A*, specific conductance; *B*, copper; *C*, arsenic; and *D*, suspended sediment.

arsenic human-health standard was exceeded in 100 percent of samples (table 5).

Clark Fork near Galen (sampling site 11) is about 2 river miles downstream from sampling site 8 and about 1 river mile downstream from the start of the Clark Fork at the confluence of Silver Bow Creek and Warm Springs Creek. Spatial changes in water quality between sampling sites 8 and 11 in water years 2011–15 include increases in median concentrations of unfiltered-recoverable metallic trace elements and suspended sediment, as well as decreases in median concentrations of unfiltered-recoverable arsenic (fig. 2, table 4). Factors that might contribute to the patterns include mobilization of materials from flood-plain tailings deposits near Warm Springs and complex processes as water from Warm Springs Ponds mixes and geochemically reacts with water contributed from the Mill-Willow Bypass and Warm Springs Creek. Exceedances of most water-quality standards were somewhat infrequent for sampling site 11, but the acute aquatic-life standard for copper was exceeded in 26 percent of samples, the chronic aquatic-life standard for copper was exceeded in 41 percent of samples, and the arsenic human-health standard was exceeded in 98 percent of samples (table 5).

Reach 5

Reach 5 extends about 21 river miles from Clark Fork near Galen (sampling site 11) to Clark Fork at Deer Lodge, Montana (sampling site 14), and meanders through a broad valley with extensive flood-plain tailings deposits. Lost Creek (a tributary to the Clark Fork in reach 5) originates in the mountains northwest of the AMC Smelter and flows generally east to its confluence with the Clark Fork near Galen. The Lost Creek Basin is affected by pollution from milling and smelting operations of the AMC Smelter (U.S. Environmental Protection Agency, 2010). In reach 5, the mean annual streamflow for water years 2011–15 increased by about 65 percent from 172 ft^3/s at sampling site 11 to 283 ft^3/s at sampling site 14 (table 3) partly because of contributions from Lost Creek and also numerous other tributaries, ephemeral gulches, and groundwater inflow.

Spatial changes in water quality between sampling sites 11 and 14 in water years 2011–15 include substantial increases in median concentrations of unfiltered-recoverable metallic trace elements and suspended sediment (fig. 2, table 4). Mobilization of mining wastes from extensive flood-plain tailings deposits and stream banks contribute to the pattern. Exceedances of water-quality standards were frequent for sampling site 14: the acute aquatic-life standard for copper was exceeded in 58 percent of samples, the chronic aquatic-life standard for copper was exceeded in 75 percent of samples, the chronic aquatic-life standard for lead was exceeded in 23 percent of samples, and the arsenic human-health standard was exceeded in 95 percent of samples (table 5).

Reach 6

Reach 6 extends about 26 river miles from Clark Fork at Deer Lodge (sampling site 14) to Clark Fork at Goldcreek, Montana (sampling site 16). Clark Fork above Little Blackfoot River near Garrison (sampling site 15), is in reach 6 and is located about 14 river miles downstream from sampling site 14 and about 12 river miles upstream from sampling site 16. Water-quality data collection for sampling site 15 began in water year 2009 (table 1); thus, water-quality data for sampling site 15 are suitable for summarizing water years 2011–15 water-quality characteristics but are not adequate for trend analysis.

The Clark Fork meanders through a broad valley from Deer Lodge to Garrison, in which flood-plain tailings along the Clark Fork are present to a similar extent as in the valley upstream from Deer Lodge (Smith and others, 1998). The Little Blackfoot River (a tributary to the Clark Fork in reach 6) drains a basin with moderate density of agricultural and historical mining activity (in comparison with other tributaries downstream from Deer Lodge) and discharges into reach 6 near Garrison (about 1 river mile downstream from sampling site 15) where the Clark Fork Valley begins to narrow. Downstream from Garrison, flood-plain tailings are less extensive than in the valley upstream. In reach 6, the mean annual streamflow for water years 2011–15 increased by about 11 percent from 283 ft^3/s at sampling site 14 to 315 ft^3/s at sampling site 15 and then by about 81 percent to 570 ft^3/s at sampling site 16 (table 3). The overall increase in streamflow from sampling site 14 to sampling site 16 was about 101 percent, mostly because of contributions from the Little Blackfoot River and also numerous other tributaries, ephemeral gulches, and groundwater inflow.

Spatial changes in water quality between sampling sites 14 and 16 in water years 2011–15 include decreases in median concentrations of unfiltered-recoverable metallic trace elements, unfiltered-recoverable arsenic, and suspended sediment, despite small increases in most of these values between sampling sites 14 and 15. Water-quality changes in reach 6 primarily were affected by transport of mining wastes from upstream source areas in combination with streamflow inputs from areas with less mining effects (including the Little Blackfoot River). Dispersion and dilution of mining wastes generally result in decreasing water-quality effects with distance downstream from primary source areas. Exceedances of water-quality standards were frequent for sampling site 15: the acute aquatic-life standard for copper was exceeded in 59 percent of samples, the chronic aquatic-life standard for copper was exceeded in 79 percent of samples, the chronic aquatic-life standard for lead was exceeded in 23 percent of samples, and the arsenic human-health standard was exceeded in 100 percent of samples (table 5). Exceedances of water-quality standards were somewhat frequent for sampling site 16: the acute aquatic-life standard for copper was exceeded in 48 percent of samples, the chronic aquatic-life standard for copper was exceeded in 60 percent of samples, the chronic aquatic-life standard for lead was exceeded in 28 percent of samples, and the arsenic human-health standard was exceeded in 68 percent of samples (table 5).

Reach 7

Reach 7 extends about 31 river miles from Clark Fork at Goldcreek (sampling site 16) to Clark Fork near Drummond, Montana (sampling site 18). In reach 7, channel meandering and exposed flood-plain tailings are less extensive than in upstream reaches (Lambing, 1998; Smith and others, 1998). Flint Creek (a tributary that discharges to the Clark Fork in reach 7 near Drummond) drains a basin with high density of agricultural and historical mining activity (in comparison with other tributaries downstream from Deer Lodge). Downstream from Drummond, the Clark Fork Valley narrows further, and meandering of the Clark Fork decreases further in association with the narrow valley and presence of highway and railroad embankments (Lambing, 1998; Smith and others, 1998). In reach 7, the mean annual streamflow for water years 2011–15 increased by about 35 percent from 570 ft^3/s at sampling site 16 to 771 ft^3/s at sampling site 18 (table 3) mostly because of contributions from Flint Creek and also numerous other tributaries, ephemeral gulches, and groundwater inflow.

Spatial changes in water quality between sampling sites 16 and 18 in water years 2011–15 include generally small increases in median concentrations of unfiltered-recoverable metallic trace elements and suspended sediment. Although the increases were not large, they contrast with the pattern of decreasing water-quality effects with distance downstream from primary mining-waste source areas in the upper Clark Fork Basin. The spatial changes in water quality between sites 16 and 18 probably were affected by streamflow contributions from the Flint Creek Basin, which has high density of agricultural and historical mining activity (in comparison with other tributaries downstream from Deer Lodge). The Clark Fork flood plain and stream banks downstream from Flint Creek probably also contain mining-waste deposits sourced from the Flint Creek Basin. Exceedances of water-quality standards were somewhat frequent for sampling site 18: the acute aquatic-life standard for copper was exceeded in 38 percent of samples, the chronic aquatic-life standard for copper was exceeded in 58 percent of samples, the chronic aquatic-life standard for lead was exceeded in 25 percent of samples, and the arsenic human-health standard was exceeded in 80 percent of samples (table 5).

Reach 8

Reach 8 extends about 34 river miles from Clark Fork near Drummond (sampling site 18) to Clark Fork at Turah Bridge near Bonner, Montana (sampling site 20). In reach 8, the Clark Fork flows through a narrow flood plain (generally less than 1 mi wide) with little or no visible mining tailings. Rock Creek (a tributary to the Clark Fork in reach 8) drains a heavily forested basin with low density of agricultural and historical mining activity (in comparison with other tributaries downstream from Deer Lodge) and discharges into reach 8 near Clinton, Montana. In reach 8, the mean annual streamflow for water years 2011–15 increased by about 93 percent from 771 ft^3/s at sampling site 18 to 1,490 ft^3/s at sampling site 20 (table 3) primarily because of contributions from Rock Creek, as well as numerous other tributaries, ephemeral gulches, and groundwater inflow.

Spatial changes in water quality between sampling sites 18 and 20 in water years 2011–15 include generally substantial decreases in median concentrations of unfiltered-recoverable metallic trace elements, unfiltered-recoverable arsenic, and suspended sediment. Water-quality changes in reach 8 were affected by dilution from Rock Creek. Exceedances of most water-quality standards were somewhat infrequent for sampling site 20, but the acute aquatic-life standard for copper was exceeded in 28 percent of samples, the chronic aquatic-life standard for copper was exceeded in 48 percent of samples, and the chronic aquatic-life standard for lead was exceeded in 25 percent of samples (table 5).

Reach 9

Reach 9 extends about 9 river miles from Clark Fork at Turah Bridge (sampling site 20) to Clark Fork above Missoula, Montana (sampling site 22). Reach 9 includes the former Milltown Reservoir where large amounts of mining wastes had been deposited. The former Milltown Dam was removed in 2008. The Blackfoot River (a tributary that discharges to the Clark Fork in reach 9 near Bonner) drains a largely forested basin with low density of agricultural and historical mining activity (in comparison with other tributaries downstream from Deer Lodge). In reach 9, mean annual streamflow increased by about 123 percent from 1,490 ft^3/s at sampling site 20 to 3,330 ft^3/s at sampling site 22 (table 3) primarily because of contributions from the Blackfoot River.

Spatial changes in water quality between sampling sites 20 and 22 in water years 2011–15 include generally substantial decreases in median concentrations of unfiltered-recoverable metallic trace elements, unfiltered-recoverable arsenic, and suspended sediment. Water-quality changes in reach 9 were affected by dilution from the Blackfoot River. Exceedances of most water-quality standards were infrequent for sampling site 22, but the chronic aquatic-life standard for copper was exceeded in 23 percent of samples (table 5).

Water-Quality Trend- and Constituent-Transport Analysis Methods

This section of the report describes methods used to analyze trends in flow-adjusted concentrations of water-quality constituents. Normalized loads (as defined in the section of this report “Estimation of Normalized Constituent Loads”) were estimated to evaluate temporal changes in relative contributions of selected trace elements and suspended sediment from upstream source areas to the outflows of each data-summary reach. Methods used for estimation of normalized constituent loads also are described.

General Description of the Time-Series Model

The TSM for streamflow and constituent concentration (Vecchia, 2005) was used to detect water-quality trends. Details on theory and parameter estimation for the model are presented in Vecchia (2005), and the model is summarized in appendix 2 of this report. Specific information concerning suitability of application of the TSM to the study datasets and procedures for determination of statistical significance and magnitude of trends also are presented in appendix 2.

The TSM analyzes trends in flow-adjusted concentrations (FACs); that is, the TSM computes FACs, estimates unbiased best-fit trend lines that represent temporal changes in FACs, and determines statistical significance of changes. Flow adjustment is necessary because concentrations of many water-quality constituents are strongly dependent on streamflow conditions, which are primarily affected by climatic variability in the study area. The intent of flow adjustment is to identify and remove streamflow-related variability in concentrations and thereby enhance the capability to detect trends independent from effects of climatic variability. Flow-adjustment procedures produce FACs that are estimates of constituent concentrations after removing effects of streamflow variability.

The TSM uses multiple flow-related variables computed from concurrent (same day as the concentration sample) and antecedent (days before the concentration sample) daily mean streamflow in the flow-adjustment process. The TSM FACs provide detailed accounting by incorporating interannual, seasonal, and short-term streamflow variability (Vecchia, 2005), which compensates for interannual, seasonal, and short-term hysteresis processes that affect concentration and streamflow relations (Colby, 1956; Chanat and others, 2002; Vecchia, 2005). Detailed analysis of continuous streamflow data provides definition of the context of streamflow conditions associated with a given water sample, handling of temporal variability in sampling frequency, and interpolation of trend patterns to periods when water-quality data are sparse or absent. The TSM inherently accounts for effects of serial correlation.

The TSM incorporates base-10 logarithm (hereinafter referred to as “log”) transformation of the concentration and streamflow data. As such, the fitted trends in FACs quantify temporal changes in central tendency represented by the geometric mean of concentration in reference to log-transformed streamflow. The geometric mean is the mean of the logs transformed back into their original units.

All of the study datasets (except for Clark Fork near Garrison [sampling site 15], which was not analyzed for trends) met the data criteria for applying the TSM, which include at least 15 years of continuous streamflow data and at least 15 years of water-quality data with at least 60 total water-quality samples and at least 10 samples total in each 3-month season (Vecchia, 2005). A limitation of the TSM is that it does not handle censored data in a rigorous manner. In the TSM, a single value is substituted for all censored data for a given constituent; thus, criteria must be set to specify the allowable amount of censored data and a consistent substitution value for each constituent. Based on analysis of trial datasets with artificially imposed variable levels of censoring, the TSM generally can be applied to datasets with about 10 percent or less censored data without substantial effects on trend results (Vecchia, 2003). Multiple LRLs (table 2) in the datasets of the Clark Fork monitoring program complicate the task of setting consistent substitution values. In applying the TSM to the study datasets, study reporting levels (SRLs; table 2) were established to set consistent substitution values for each trace-element constituent based on investigation of the time frame during which various NWQL LRLs were used, the frequency of censoring that resulted from each LRL, and field blank sample data that provided information on potential contamination bias of low concentrations. The SRLs were applied to the study datasets by (1) substituting one-half the SRL for all censored observations with LRLs equal or close to the SRL, (2) substituting one-half the SRL for all reported uncensored concentrations (analyzed during times when the LRL was less than the SRL) that were less than the SRL, and (3) excluding censored data with LRLs substantially larger than the SRL. Any analytical result that was revised by either substitution or exclusion was considered to be affected by the recensoring procedures used in applying the SRL. The study datasets largely were unaffected by recensoring for the trace-element constituents included in the trend analysis (table 2); unfiltered-recoverable zinc was the only affected constituent, and no sampling site had more than 8.5 percent of values affected by the recensoring procedures. Further, for individual constituents, the maximum frequency of detection in field blank samples at concentrations greater than the SRL was 2.7 percent (for unfiltered-recoverable zinc; table 1–1).

The TSM accounts for many hydrologic factors that contribute to complexity in concentration and streamflow relations. In this study, the TSM was applied as consistently as possible among sampling-site and constituent combinations and is considered to be a useful tool for simplifying the environmental complexity in the upper Clark Fork Basin to provide a large-scale evaluation of general temporal changes in FACs and constituent transport independent from streamflow variability. As such, the TSM provides a consistent relational framework for evaluating temporal water-quality changes among the sampling sites. The TSM best-fit trend lines were considered to provide important information beyond the strict statistical characteristics of the trend results (in terms of statistical probability levels [*p*-values] and levels of significance) because they aid in comparing and summarizing large-scale patterns among sampling sites.

Selection of Trend-Analysis Time Periods

Appropriate selection of trend-analysis time periods is important because the results of trend analyses are dependent on how the time periods are structured. Factors considered in selection of trend-analysis time periods included providing capability to (1) compare trend results among sampling sites with different periods of data collection, (2) distinguish somewhat short-term timing of changes in concentration and streamflow relations during the long study period, and (3) allow periodic future updates of trend analyses for evaluation of effects of remediation activities. Based primarily on those factors, trend-analysis periods were defined as sequential 5-year periods that extended from near the start of long-term data-collection activities for most sampling sites in the upper Clark Fork Basin to the end of water year 2015. Thus, four trend-analysis time periods were defined: period 1 (water years 1996–2000), period 2 (water years 2001–5), period 3 (water years 2006–10), and period 4 (water years 2011–15).

The TSM-fitted trends for a given trend-analysis period are monotonic trends that are smoothed to produce generally consistent slopes across the middle section of the trend-analysis period that become flatter near the ends of the trend-analysis period. The flatter slopes near the ends provide gradual transition between adjacent trend-analysis periods. In some cases, the fitted trends in a given trend-analysis period do not precisely follow the patterns in FACs, and there are short-term (about 1–2 years) trend patterns in FACs that are unresolved in the fitted trends. In those cases, better temporal resolution might have been attained by defining two or more trend-analysis periods in a given 5-year trend-analysis period. This approach generally was avoided because it would have required detailed trend analysis for potentially inconsistent time periods among the various sampling-site and constituent combinations. An important consideration in the design of the trend-analysis structure of this study was making general comparisons among the sampling-site and constituent combinations to evaluate large-scale effects of mining and remediation activities for consistent time periods. In general, when unresolved trending was apparent, more complicated trend models (with additional trend-analysis periods) were tested, and the more complicated models did not change the general findings and conclusions of this report; that is, the overall fitted trends in the affected trend-analysis periods were consistent with overall patterns in FACs in the period. However, because of the substantial effect of the intentional breach of the former Milltown Dam on March 28, 2008, an exception to consistent trend-analysis periods was made. For Clark Fork above Missoula (sampling site 22), period 3 was subdivided into period 3A (October 1, 2005–March 27, 2008) and period 3B (March 28, 2008–September 30, 2010). The intentional breach of the former Milltown Dam was part of an extensive remediation effort from about 2006–8 that resulted in the removal of the former Milltown Dam (Sando and Lambing, 2011).

Estimation of Normalized Constituent Loads

Normalized constituent loads were estimated to assess the temporal trends in FACs of mining-related contaminants in the context of sources and transport. The fitted trends are unbiased best-fit lines through the FACs, which are independent of streamflow variability. The FAC trends at individual sampling sites are important descriptors of water-quality changes in the upper Clark Fork Basin, but without consideration of differences in streamflow magnitudes among different sampling sites, the trends do not provide direct information on resultant changes in contaminant source-area contributions and transport characteristics. Combining the FAC trends with a stationary streamflow index (that maintains relative differences in streamflow magnitudes among sampling sites but normalizes streamflow for a given sampling site to a constant value through time) allows assessment of how the temporal changes in FACs translate into relative temporal changes in source and transport of mining-related contaminants in the upper Clark Fork Basin. Thus, normalized loads were estimated to conduct a transport analysis.

Normalized loads were estimated for each of the four 5-year trend-analysis periods. The stationary streamflow index used in estimating normalized loads was the geometric mean streamflow for each sampling site for water years 1996–2015. The geometric mean was selected as a measure of central tendency in streamflow to maintain consistency with the TSM analysis, which is conducted on log-transformed data.

For each sampling-site and constituent combination and each of the 5-year periods, the normalized load was estimated by multiplying the mean annual fitted trend FAC during the 5-year analysis period times the geometric mean streamflow for water years 1996–2015 and a units conversion factor, according to the following equation:

$$LOAD = MAC*GMQ*K \tag{1}$$

where

$LOAD$ is the estimated normalized constituent load (in kilograms per day) for the indicated 5-year period;

MAC is the mean annual fitted trend FAC (in micrograms per liter for trace elements or milligrams per liter for suspended sediment) for the indicated 5-year period;

GMQ is the geometric mean of daily mean streamflow for water years 1996–2015, in cubic feet per second; and

K is a units conversion constant (0.00245 for concentrations in micrograms per liter or 2.45 for concentrations in milligrams per liter) to convert instantaneous constituent discharge (in mass units per second) to an equivalent daily constituent load (in kilograms per day).

The *MAC* is calculated by temporally averaging (in each of the four 5-year periods) the fitted trend FACs that quantify temporal changes in central tendency based on the geometric mean. It is notable that the *MAC* is referred to as a “mean annual value”; this terminology indicates temporal averaging of geometric mean concentrations. The temporal averaging of geometric mean concentrations in each 5-year period effectively results in the *MAC* representing the center of the 5-year period, which introduces a conservative approach to the transport analysis. The geometric mean generally is closely associated with the median of the original untransformed units for data that are approximately log-normally distributed. Thus, because of effects of analysis of log-transformed data, the estimated normalized loads generally represent quantification with respect to near-median conditions. As such, the estimated normalized loads do not represent actual magnitudes of total mass transport, but rather provide information on relative temporal changes in constituent transport characteristics of the study sampling sites quantified with respect to near-median conditions.

Factors that Affect Trend Analysis and Interpretation

Several factors affect temporal trends in water quality. Climatic variability (interannual and seasonal) is indicated in variability in streamflow conditions, which strongly affect concentration and streamflow relations. Investigating streamflow conditions during the study period is relevant to interpreting trend results. Other factors relating to data assessment or treatment that also are relevant to understanding trend-analysis procedures and interpreting trend results include relations between unadjusted concentrations and FACs, and data transformation.

Streamflow Conditions

Daily mean streamflows for water years 1993–2015 for selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin are presented in figure 3. Locally weighted scatter plot smooth (LOWESS; Cleveland and McGill, 1984; Cleveland, 1985) lines through the daily mean streamflows also are presented in figure 3 to represent temporal variability in the moving central tendency of streamflow. The geometric mean streamflows for water years 1996–2015 are presented to represent overall central tendency of streamflow during the period of trend analysis. Silver Bow Creek at Warm Springs (sampling site 8), Clark Fork at Deer Lodge (sampling site 14), and Clark Fork at Turah Bridge (sampling site 20) were selected as examples for showing hydrologic patterns (fig. 3) that generally apply to the other sampling sites.

Temporal variability in streamflow conditions during the study period generally is similar among sampling sites. In about water year 1993, streamflow conditions generally increased to above the geometric mean streamflows during a period of several years. Streamflows were high during water years 1996–97, near the start of period 1 (water years 1996–2000). During period 1, streamflows above the geometric mean streamflows generally persisted through water year 1999 and then decreased substantially to below the geometric mean streamflows during water year 2000. High streamflows were prevalent during most of period 1 and are evident in annual maximum streamflows being higher than maximums of most other years and also in annual minimum streamflows being higher than minimums of most other years (fig. 3). Streamflow during water year 1997 was particularly unusual in that the receding limb of snowmelt runoff was less abrupt and less variable than in most years, and post-runoff base streamflows generally were above or near the geometric mean streamflow. Further, the post-runoff base streamflows in water year 1997 at sampling site 14 (fig. 3*B*) sometimes exceeded annual maximum streamflows during the low streamflow years 2000–2002. During period 2 (water years 2001–5), streamflows generally were below the geometric mean streamflows. During period 3 (water years 2006–10), streamflows gradually increased from below the geometric mean streamflows in water year 2006 to above the geometric mean streamflows in water year 2010. During period 4 (water years 2011–15), streamflows generally were above the geometric mean streamflows in water years 2011–12 and then decreased to near the geometric mean streamflows in water year 2013. Streamflows in water year 2011 were especially high and generally similar to streamflows in water year 1997.

Other Factors

Factors relating to data requirements, treatments, and assessment that affect trend analysis and interpretation of results include relations between unadjusted concentrations and FACs, and data transformation. Unadjusted concentrations are the observed concentrations before flow adjustment.

The FACs are estimates of constituent concentrations after removing effects of streamflow variability; thus, FACs typically have less variability than unadjusted concentrations, although the strength of this pattern is variable among sampling-site and constituent combinations, and also can be variable through time for a given sampling-site and constituent combination. Time-series streamflow, unfiltered-recoverable copper, unfiltered-recoverable arsenic, and

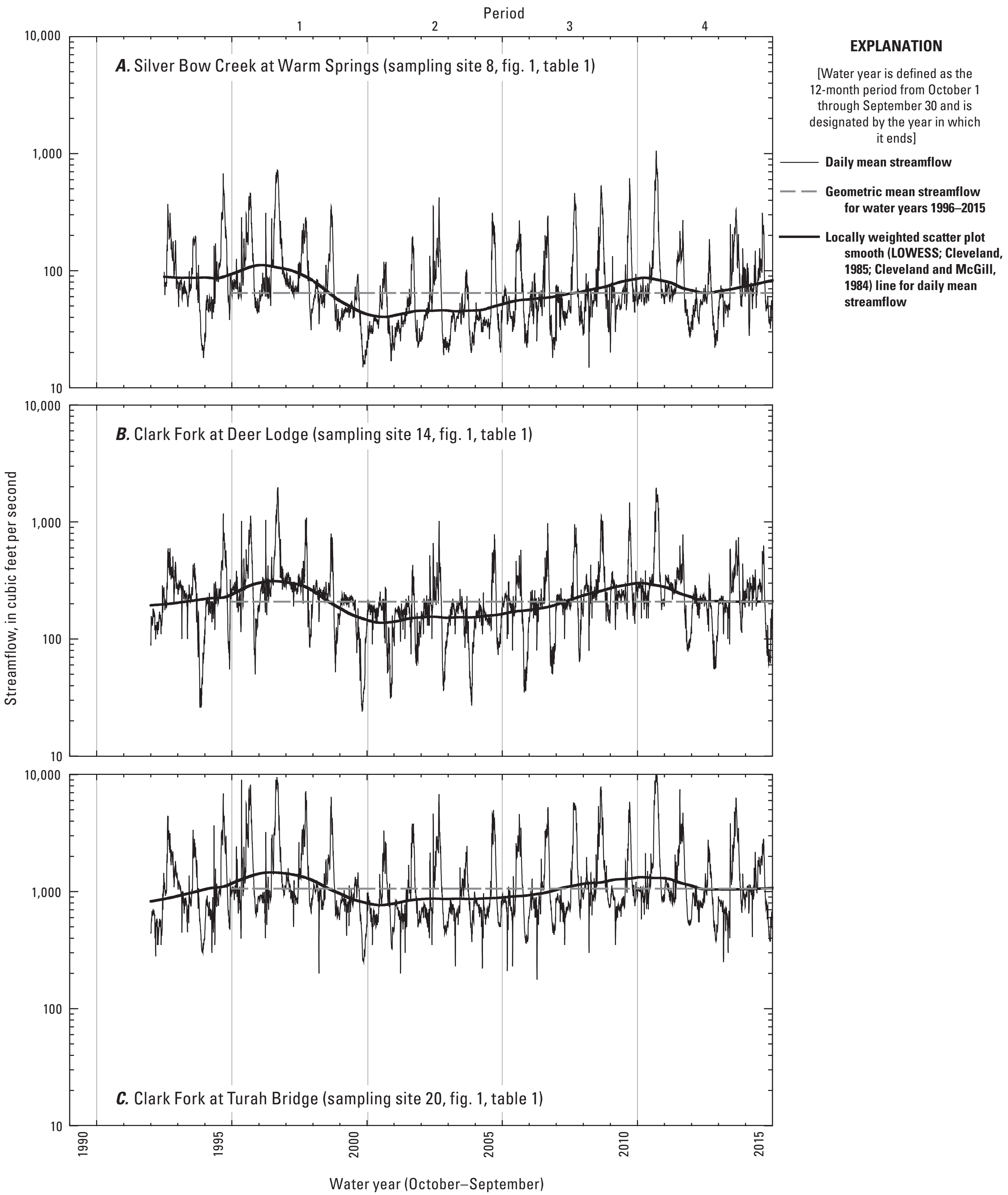


Figure 3. Daily mean streamflow for selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 1993–2015. *A*, Silver Bow Creek at Warm Springs, Montana; *B*, Clark Fork at Deer Lodge, Montana; and *C*, Clark Fork at Turah Bridge near Bonner, Montana.

suspended-sediment data for Clark Fork near Galen (sampling site 11) are presented in figure 4 to provide examples for discussion of relations between unadjusted and flow-adjusted concentrations.

Similarities among the LOWESS lines for streamflow (fig. 4*A*) and unadjusted suspended-sediment concentrations (fig. 4*D*) illustrate the direct relations between streamflow and unadjusted suspended-sediment concentrations. Unadjusted suspended-sediment concentrations tend to be higher during high streamflow conditions than during low streamflow conditions. During high streamflow conditions, with associated high hydraulic energy, particulate material is mobilized and transported in the stream. During low streamflow conditions, streams have less capacity for transporting particulate materials. Flow-adjustment procedures account for the response of suspended-sediment concentrations to variations in streamflow and produce FACs that represent temporal variability in consistent streamflow conditions. In the Clark Fork, suspended-sediment FACs in high streamflow conditions are less variable and lower than unadjusted concentrations (for example, fig. 4*D*, water years 1996–99). Suspended-sediment FACs in low streamflow conditions are less variable and generally centered within unadjusted concentrations (for example, fig. 4*D*, water years 2000–2001).

Unfiltered-recoverable copper has concentration and streamflow relations that are similar to suspended sediment because of adsorption on inorganic and organic particulate materials; these same relations generally apply to other metallic elements. As a result, patterns in unadjusted concentrations and FACs for unfiltered-recoverable copper (fig. 4*B*) are similar to those of suspended sediment (fig. 4*D*).

Arsenic in streams in the upper Clark Fork Basin typically is mostly in dissolved phase and has less variability and a weaker direct relation with streamflow than is the case for metallic elements. Arsenic has been widely dispersed in the upper Clark Fork Basin as a result of deposition of flue dust and smelter emissions with resultant large-scale soil and groundwater contamination (U.S. Environmental Protection Agency, 2010). Further, arsenic generally is more soluble than metallic elements in the geochemical conditions that are prevalent in the upper Clark Fork Basin. These factors result in high arsenic concentrations in groundwater in some areas and also mobilization of arsenic to stream channels for a large range of streamflow conditions. Thus, patterns in unadjusted concentrations and FACs for unfiltered-recoverable arsenic (fig. 4*C*) generally are less variable than for unfiltered-recoverable copper (fig. 4*B*) and suspended sediment (fig. 4*D*). Also, unadjusted concentrations of unfiltered-recoverable arsenic have less correspondence with streamflow than unfiltered-recoverable copper and suspended sediment.

Similarities among the LOWESS lines for streamflow (fig. 4*A*), unfiltered-recoverable copper (fig. 4*B*), and suspended sediment (fig. 4*D*) indicate that temporal variability in streamflow might confound interpretation of temporal variability in unadjusted constituent concentrations. Examination of temporal variability during water years 1993–2015 indicates that, in all cases, the LOWESS lines for streamflow (fig 4*A*), unfiltered-recoverable copper (fig. 4*B*), and suspended sediment (fig. 4*D*) are highest about 1996–97 and lowest about 2000–2001, then variably increase during 2002–11 and generally decrease during 2012–15. Because of the strong association between constituent concentrations and streamflow, interpreting temporal changes in unadjusted constituent concentrations during specific time periods is difficult. For example, in water years 2000–2002, mean annual streamflow was low (about 60 percent of the long-term mean annual streamflow). Annual mean streamflow in water year 2003 somewhat increased to near-normal conditions (about 90 percent of the long-term mean annual streamflow). Associated with the increase in streamflow in 2003 were somewhat abrupt increases in unadjusted concentrations of unfiltered-recoverable copper and suspended sediment that are reflected by somewhat abrupt increases in the LOWESS lines for those constituents. The somewhat abrupt increases in unadjusted concentrations of unfiltered-recoverable copper and suspended sediment in water year 2003 probably were affected by the near-normal streamflow conditions of water year 2003 immediately following the low streamflow conditions of water years 2000–2002. During water years 2000–2002, low streamflow conditions might have promoted storage of particulate materials in the basin; the stored particulate materials might have been readily mobilized during water year 2003. Beginning in water year 2005, streamflow conditions gradually transitioned from generally low streamflow conditions to high streamflow conditions in water year 2011. The gradual transition might have affected the response in unadjusted concentrations of unfiltered-recoverable copper and suspended sediment to the high streamflow conditions of water year 2011, particularly in comparison with the more abrupt increase in streamflow in water year 2003. Thus, various complexities in concentration and streamflow relations contribute to difficulties in interpreting temporal patterns in unadjusted constituent concentrations. Temporal variability in streamflow strongly confounds the ability to interpret temporal variability in unadjusted constituent concentrations.

The TSM flow-adjustment procedure analyzes concentration and streamflow relations on multiple timescales (interannual, seasonal, and short-term) and accounts for streamflow variability. In contrast to the LOWESS lines through the unadjusted constituent concentrations, the TSM-fitted trends in figure 4 indicate consistent decreases in FACs of unfiltered-recoverable copper and suspended sediment. The dissimilar patterns between unadjusted concentrations and FACs indicate the importance of flow-adjusted trend analysis for identifying actual patterns in constituent concentrations independent from variability in streamflow conditions.

An important consideration in interpreting trend results relates to the trend-analysis methods incorporating log transformation of constituent concentrations. Log transformation results in datasets that are approximately normally distributed and allows analysis using rigorous parametric procedures; however, log transformation decreases variability in the data

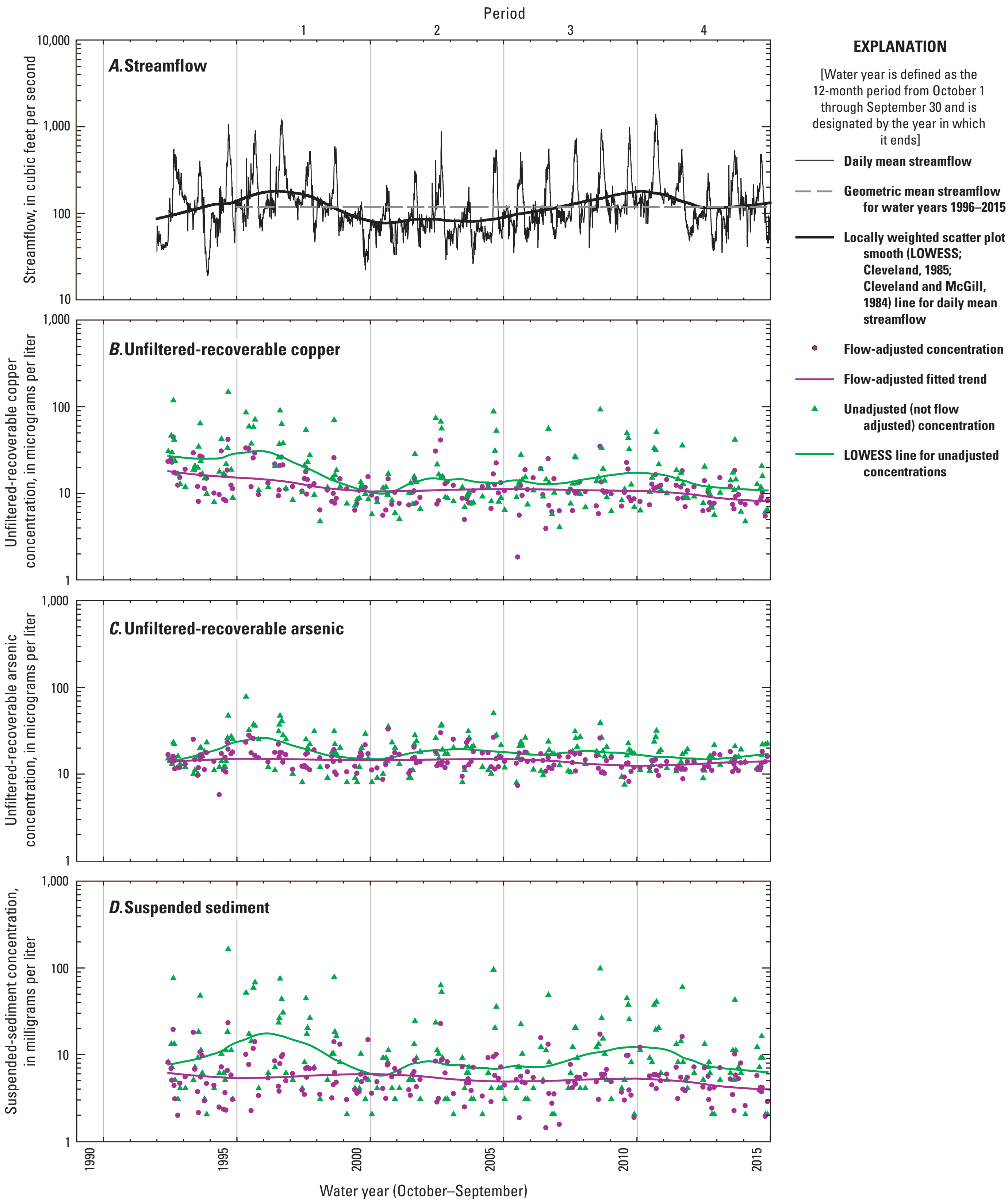


Figure 4. Selected streamflow and constituent concentration information for Clark Fork near Galen, Montana (sampling site 11), water years 1993–2015. *A*, streamflow; *B*, unfiltered-recoverable copper; *C*, unfiltered-recoverable arsenic; and *D*, suspended sediment.

relative to the original untransformed units representative of actual environmental variability. In general, the statistical distributions of constituent concentrations and streamflow (in original untransformed units) for sampling sites in the upper Clark Fork Basin are right skewed, indicating that the extent of data higher than the median is greater than the extent of data lower than the median. Log transformation results in expansion of the lower end of the distribution and compression of the higher end of the distribution. Compression of the higher end of the distribution has a relatively larger effect than expansion of the lower end of the distribution. This factor is important in interpreting trend results with respect to various regulatory issues, including compliance with human-health or aquatic-life standards. Trends in FACs represent changes in central tendency quantified as changes in the geometric mean in reference to log-transformed streamflow. Thus, the trends in FACs provide general information on overall temporal changes (in terms of directions and relative magnitudes) in concentrations but lack the specificity to indicate compliance or noncompliance with various regulatory standards. Effects of data transformation, however, do not negatively affect the primary purpose of this study in determining temporal water-quality trends through time and using the trend results to evaluate relative changes in constituent transport characteristics among sampling sites. In the trend analyses, all data (high as well as low values) affect changes in FAC geometric means; thus, the fitted trends appropriately represent unbiased estimates of overall changes in central tendency.

Water-Quality Trends and Constituent-Transport Analysis Results

This section of the report presents water-quality trend and transport-analysis results for selected sampling sites in the data-summary reaches in the Milltown Reservoir/Clark Fork River Superfund Site for water years 1996–2015. Results are presented for all constituents investigated, but emphasis is placed on copper, arsenic, and suspended sediment in the following subsections.

Water-Quality Trends in Flow-Adjusted Concentrations

For all constituents investigated, detailed results for trend magnitudes, computed as the total percent changes in FAC geometric means from the beginning to the end of each 5-year period, are presented in appendix 3 in tables 3–1 (for most sampling sites) and 3–2 (for Clark Fork above Missoula [sampling site 22]). Detailed trend results are graphically presented in figures 3–1 through 3–7 in appendix 3. The detailed graphical presentations in appendix 3 present fitted trends for all constituents and allow evaluation of the fitted trends for a given sampling site in conjunction with FACs.

Fitted trend values (that quantify the temporal changes in FAC geometric means in terms of concentration units) are summarized in tables 6 (for most sampling sites) and 7 (for Clark Fork above Missoula [sampling site 22]) and graphically summarized in figures 5–10. The summary graphical presentations in figures 5–10 show side-by-side fitted trends for the adjacent sampling sites in a given reach and allow comparisons in temporal patterns between the reach inflow and outflow; these comparisons facilitate interpretation of the constituent-transport analysis results.

In this report, qualitative observations are described for the overall trend magnitude (percent change) from the start of period 1 to the end of period 4. Overall trend magnitude was considered to be (1) large, if the absolute value was greater than about 60 percent; (2) moderate, if the absolute value was in the range of about 40–60 percent; (3) small, if the absolute value was in the range of about 20–40 percent; and (4) minor, if the absolute value was less than about 20 percent.

Trend-magnitude and fitted trend values are considered semiquantitative estimates determined by complex statistical analysis. Throughout this report, trend-magnitude and fitted trend values frequently are mentioned in figures, tables, and discussion of temporal and spatial changes in water quality (reported to two significant figures for all constituents except specific conductance, which is reported to three significant figures). Reference to specific trend-magnitude and fitted trend values is intended to facilitate presentation and discussion of relative spatial and temporal differences between values but is not intended to represent absolute accuracy at two significant figures. The *p*-values and levels of significance (a *p*-value less than 0.01 is considered statistically significant in this report) associated with the trend results are indicated in the tables and figures that present trend results. Significance levels were not the only factor in evaluating the substance of the trends, but rather were considered in conjunction with trend directions and relative magnitudes, and patterns among sites and constituents. In this study, the TSM is considered to be a useful tool for simplifying the environmental complexity in the upper Clark Fork Basin to provide a large-scale evaluation of general temporal changes in FACs and constituent transport independent from streamflow variability. Thus, the TSM best-fit trend lines are considered to provide important information beyond the strict statistical characteristics of the trend results (in terms of *p*-values and levels of significance) because they aid in comparing and summarizing large-scale patterns among the sampling sites. Factors affecting temporal variability in water quality in the upper Clark Fork Basin are complex. Much information on changes in water quality is presented herein, but it is beyond the scope of this report to provide detailed explanations for all of the changes or to link specific trends with specific remediation activities.

Table 6. Summary of flow-adjusted trend results for selected sampling sites and constituents, water years 1996–2015.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. Gray shading indicates a statistically significant (*p*-value less than 0.01) trend for the trend period before the shaded value. *p*-value, statistical probability level; µS/cm, microsiemen per centimeter at 25 degrees Celsius; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, flow-adjusted units of measurement	Fitted trend values					Percent change from start of period 1 through end of period 4[1]
	Start of water year 1996 (start of period 1)	Start of water year 2001 (start of period 2)	Start of water year 2006 (start of period 3)	Start of water year 2011 (start of period 4)	End of water year 2015 (end of period 4)	
Silver Bow Creek at Warm Springs, Montana (sampling site 8, fig. 1, table 1)						
Specific conductance, µS/cm	521	514	501	513	446	-14
Copper, filtered, µg/L	8.9	4.6	4.1	3.8	2.9	-67
Copper, unfiltered-recoverable, µg/L	15	9.3	7.9	7.0	5.0	-67
Zinc, unfiltered-recoverable, µg/L	35	16	8.4	9.8	6.1	-83
Arsenic, filtered, µg/L	19	19	20	21	17	-11
Arsenic, unfiltered-recoverable, µg/L	22	22	23	23	19	-14
Suspended sediment, mg/L	5.3	6.3	4.6	2.7	3.1	-42
Clark Fork near Galen, Montana (sampling site 11, fig. 1, table 1)						
Specific conductance, µS/cm	447	454	415	443	388	-13
Copper, filtered, µg/L	7.6	4.2	4.0	3.3	3.4	-55
Copper, unfiltered-recoverable, µg/L	15	11	11	11	8.1	-46
Zinc, unfiltered-recoverable, µg/L	30	13	9.0	12	7.1	-76
Arsenic, filtered, µg/L	12	11	13	10	11	-8
Arsenic, unfiltered-recoverable, µg/L	15	14	15	12	14	-7
Suspended sediment, mg/L	5.2	5.8	4.7	5.1	3.8	-27
Clark Fork at Deer Lodge, Montana (sampling site 14, fig. 1, table 1)						
Specific conductance, µS/cm	479	482	463	454	456	-5
Copper, filtered, µg/L	6.9	5.8	6.1	5.4	5.8	-16
Copper, unfiltered-recoverable, µg/L	30	23	24	25	23	-23
Zinc, unfiltered-recoverable, µg/L	39	24	24	22	19	-51
Arsenic, filtered, µg/L	11	11	13	11	11	0
Arsenic, unfiltered-recoverable, µg/L	16	14	15	14	14	-13
Suspended sediment, mg/L	18	15	14	15	12	-33
Clark Fork at Goldcreek, Montana (sampling site 16, fig. 1, table 1)						
Specific conductance, µS/cm	425	418	406	398	398	-6
Copper, filtered, µg/L	4.8	3.8	4.3	3.8	3.9	-19
Copper, unfiltered-recoverable, µg/L	19	19	15	14	15	-21
Zinc, unfiltered-recoverable, µg/L	27	20	13	15	13	-52
Arsenic, filtered, µg/L	9.4	8.2	8.8	8.6	8.2	-13
Arsenic, unfiltered-recoverable, µg/L	12	10	10	10	9.7	-19
Suspended sediment, mg/L	15	17	8.3	13	11	-27

Table 6. Summary of flow-adjusted trend results for selected sampling sites and constituents, water years 1996–2015.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. Gray shading indicates a statistically significant (*p*-value less than 0.01) trend for the trend period before the shaded value. *p*-value, statistical probability level; µS/cm, microsiemen per centimeter at 25 degrees Celsius; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, flow-adjusted units of measurement	Fitted trend values					Percent change from start of period 1 through end of period 4[1]
	Start of water year 1996 (start of period 1)	Start of water year 2001 (start of period 2)	Start of water year 2006 (start of period 3)	Start of water year 2011 (start of period 4)	End of water year 2015 (end of period 4)	
Clark Fork near Drummond, Montana (sampling site 18, fig. 1, table 1)						
Specific conductance, µS/cm	461	459	449	434	461	0
Copper, filtered, µg/L	3.9	3.9	4.3	3.3	3.7	-5
Copper, unfiltered-recoverable, µg/L	17	15	14	13	12	-29
Zinc, unfiltered-recoverable, µg/L	36	19	15	17	13	-64
Arsenic, filtered, µg/L	9.6	9.0	9.4	8.4	8.6	-10
Arsenic, unfiltered-recoverable, µg/L	12	10	11	10	10	-17
Suspended sediment, mg/L	21	16	13	16	13	-38
Clark Fork at Turah Bridge near Bonner, Montana (sampling site 20, fig. 1, table 1)						
Specific conductance, µS/cm	347	330	324	334	327	-6
Copper, filtered, µg/L	3.3	2.5	2.8	2.6	2.1	-36
Copper, unfiltered-recoverable, µg/L	10	9.0	8.3	8.2	7.9	-21
Zinc, unfiltered-recoverable, µg/L	21	13	9.2	14	9.7	-54
Arsenic, filtered, µg/L	5.4	5.1	5.4	5.5	4.7	-13
Arsenic, unfiltered-recoverable, µg/L	6.8	6.1	6.1	6.6	5.6	-18
Suspended sediment, mg/L	13	12	8.8	12	9.5	-27

[1]Shading represents qualitative observations on overall trend magnitudes (percent change from start of water year 1996 to end of water year 2015) as follows: no shading—minor (the absolute value was less than about 20 percent); green shading—small (the absolute value was in the range of about 20–40 percent; tan shading—moderate (the absolute value was in the range of about 40–60 percent; and purple shading—large (the absolute value was greater than about 60 percent).

Table 7. Summary of flow-adjusted trend results for Clark Fork above Missoula, Montana (sampling site 22), for selected constituents, water years 1996–2015.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. Gray shading indicates a statistically significant (*p*-value less than 0.01) trend for the trend period before the shaded value. *p*-value, statistical probability level; µS/cm, microsiemen per centimeter at 25 degrees Celsius; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, flow-adjusted units of measurement	Fitted trend values: Start of water year 1996 (start of period 1)	Start of water year 2001 (start of period 2)	Start of water year 2006 (start of period 3A)	March 28, 2008 (start of period 3B)	Start of water year 2011 (start of period 4)	End of water year 2015 (end of period 4)	Percent change from start of period 1 through end of period 4[1]
Clark Fork above Missoula, Montana (sampling site 22, fig. 1, table 1)							
Specific conductance, µS/cm	277	275	270	273	283	265	-4
Copper, filtered, µg/L	2.3	1.7	2.1	2.4	1.9	1.4	-39
Copper, unfiltered-recoverable, µg/L	6.4	4.9	6.9	15	6.3	3.0	-53
Zinc, unfiltered-recoverable, µg/L	14	7.2	10	30	10	5.0	-64
Arsenic, filtered, µg/L	3.3	2.8	3.2	3.6	3.4	2.6	-21
Arsenic, unfiltered-recoverable, µg/L	4.2	3.3	3.9	4.8	4.0	3.0	-29
Suspended sediment, mg/L	7.7	7.4	9.2	25	9.9	6.0	-22

[1]Shading represents qualitative observations on overall trend magnitudes (percent change from start of water year 1996 to end of water year 2015) as follows: no shading—minor (the absolute value was less than about 20 percent); green shading—small (the absolute value was in the range of about 20–40 percent; tan shading—moderate (the absolute value was in the range of about 40–60 percent; and purple shading—large (the absolute value was greater than about 60 percent).

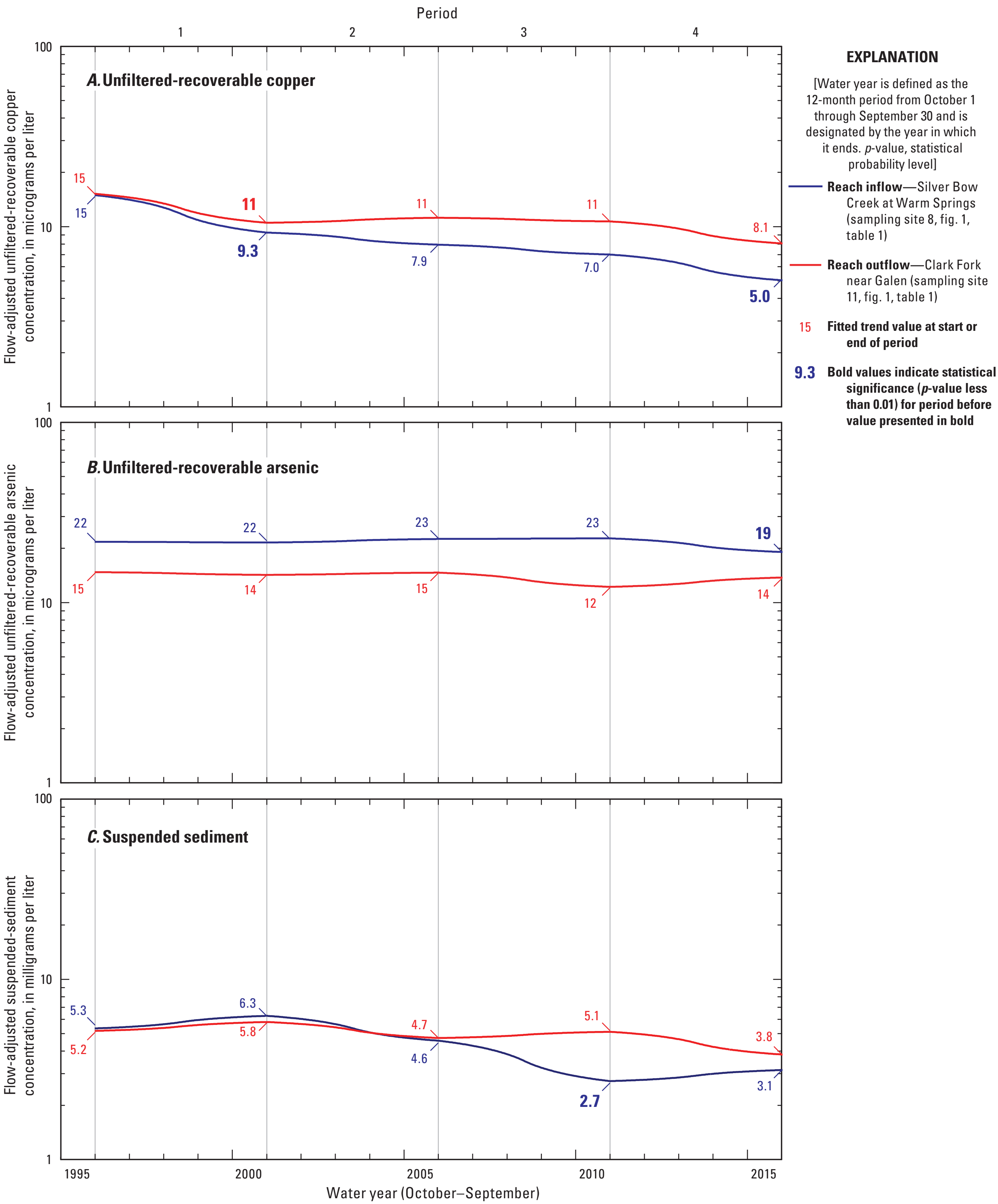


Figure 5. Flow-adjusted fitted trends for selected constituents for sampling sites in reach 4, extending from Silver Bow Creek at Warm Springs, Montana (sampling site 8), to Clark Fork near Galen, Montana (sampling site 11), water years 1996–2015.

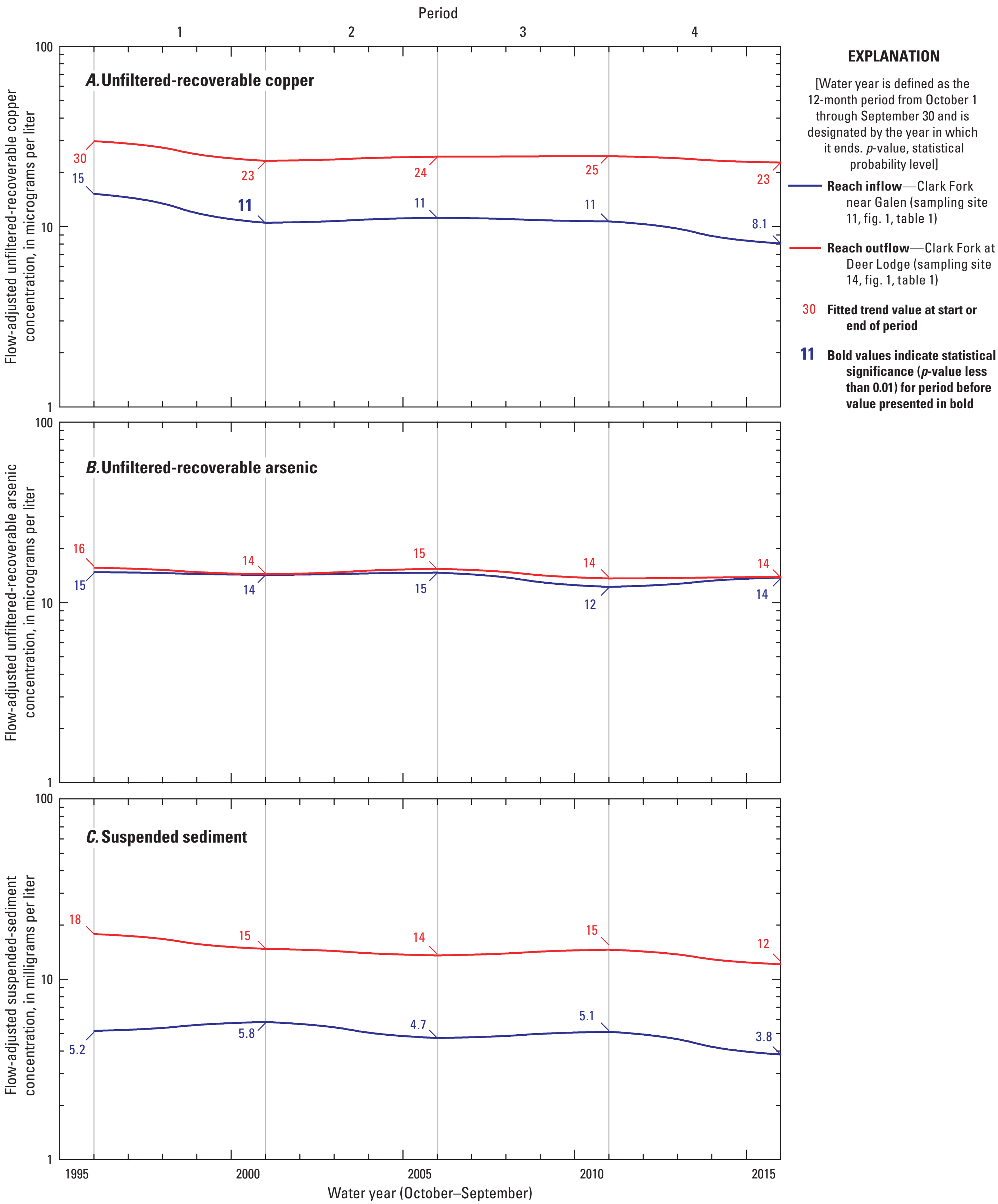


Figure 6. Flow-adjusted fitted trends for selected constituents for sampling sites in reach 5, extending from Clark Fork near Galen, Montana (sampling site 11), to Clark Fork at Deer Lodge, Montana (sampling site 14), water years 1996–2015.

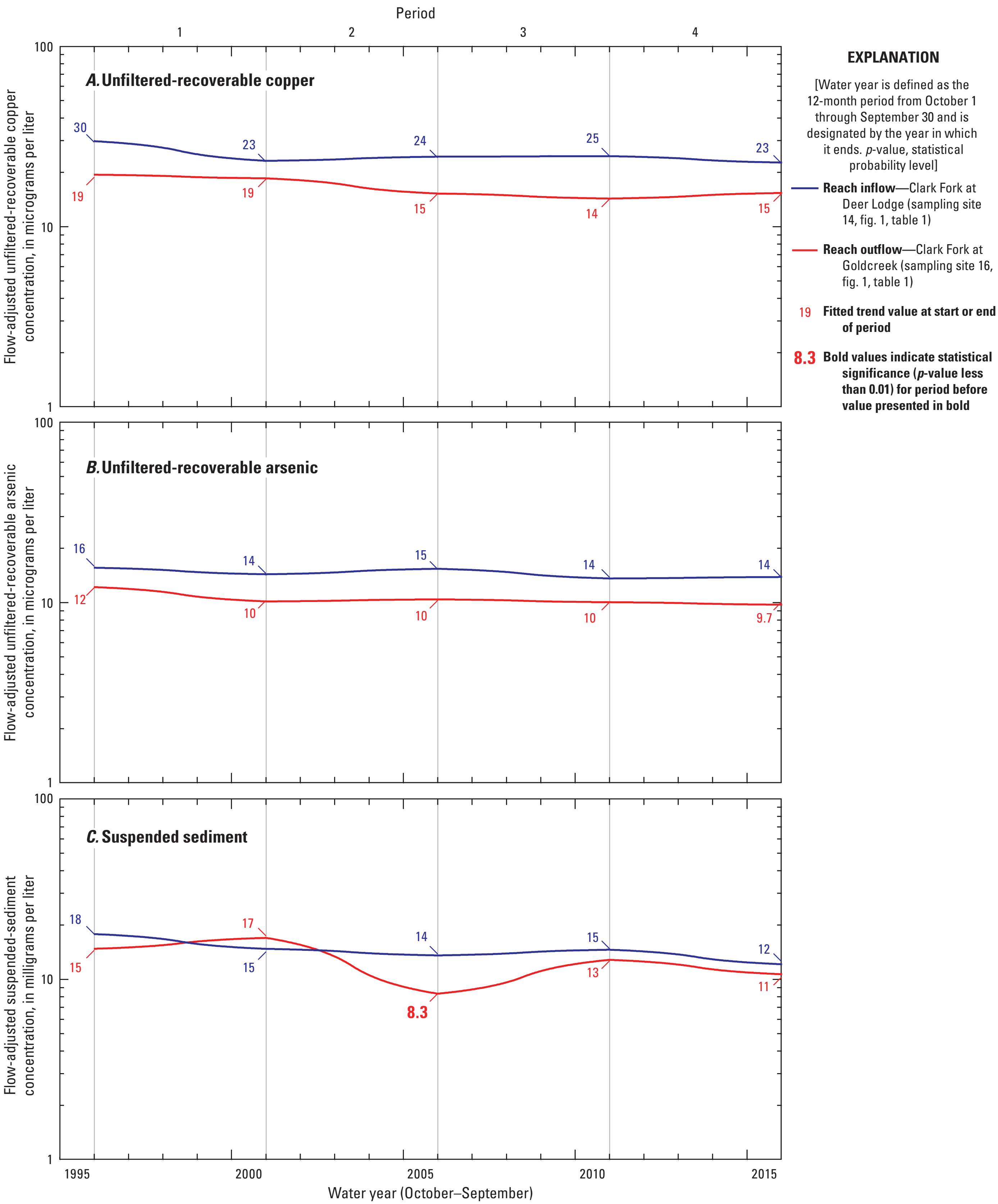


Figure 7. Flow-adjusted fitted trends for selected constituents for sampling sites in reach 6, extending from Clark Fork at Deer Lodge, Montana (sampling site 14), to Clark Fork at Goldcreek, Montana (sampling site 16), water years 1996–2015.

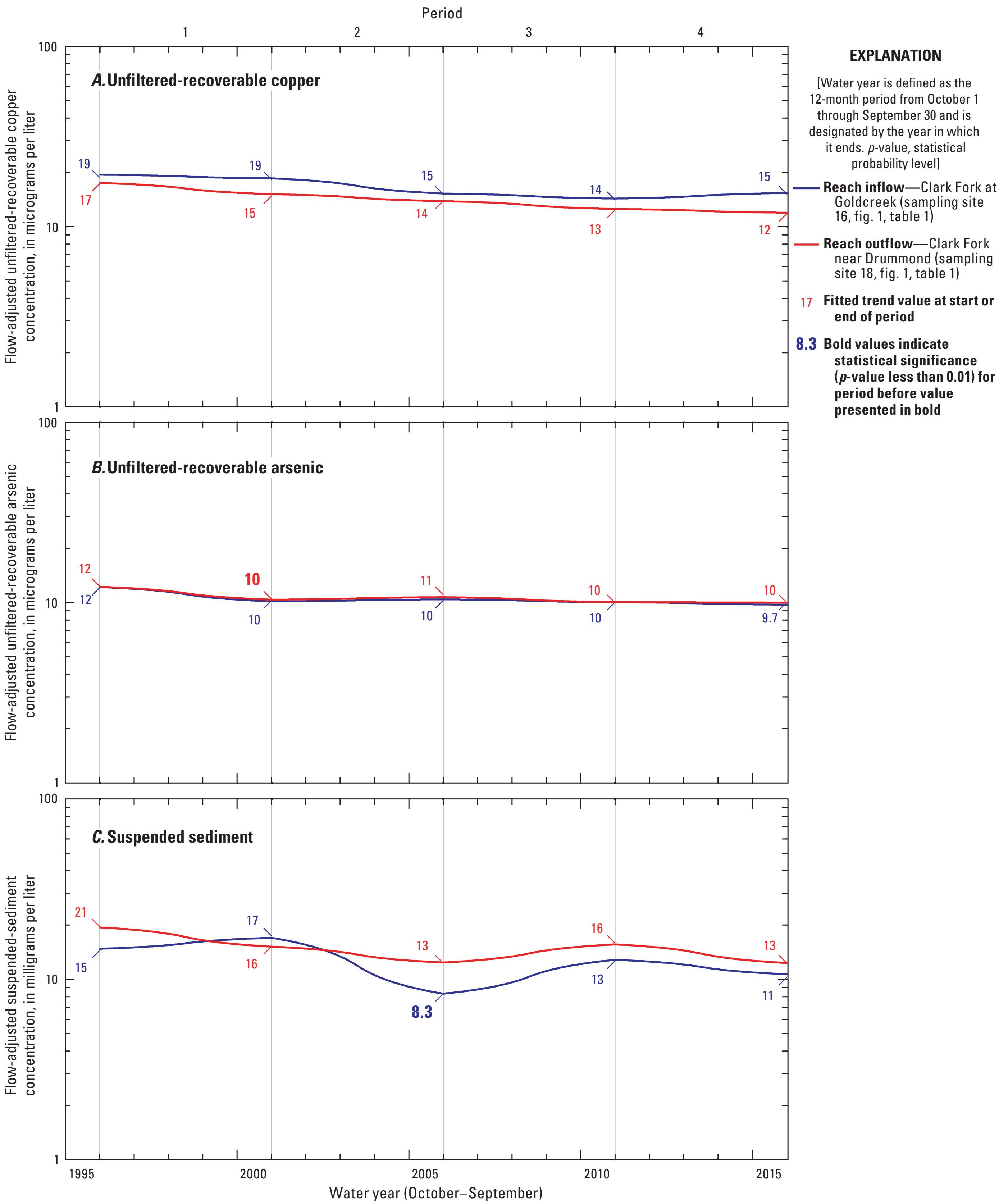


Figure 8. Flow-adjusted fitted trends for selected constituents for sampling sites in reach 7, extending from Clark Fork at Goldcreek, Montana (sampling site 16), to Clark Fork near Drummond, Montana (sampling site 18), water years 1996–2015.

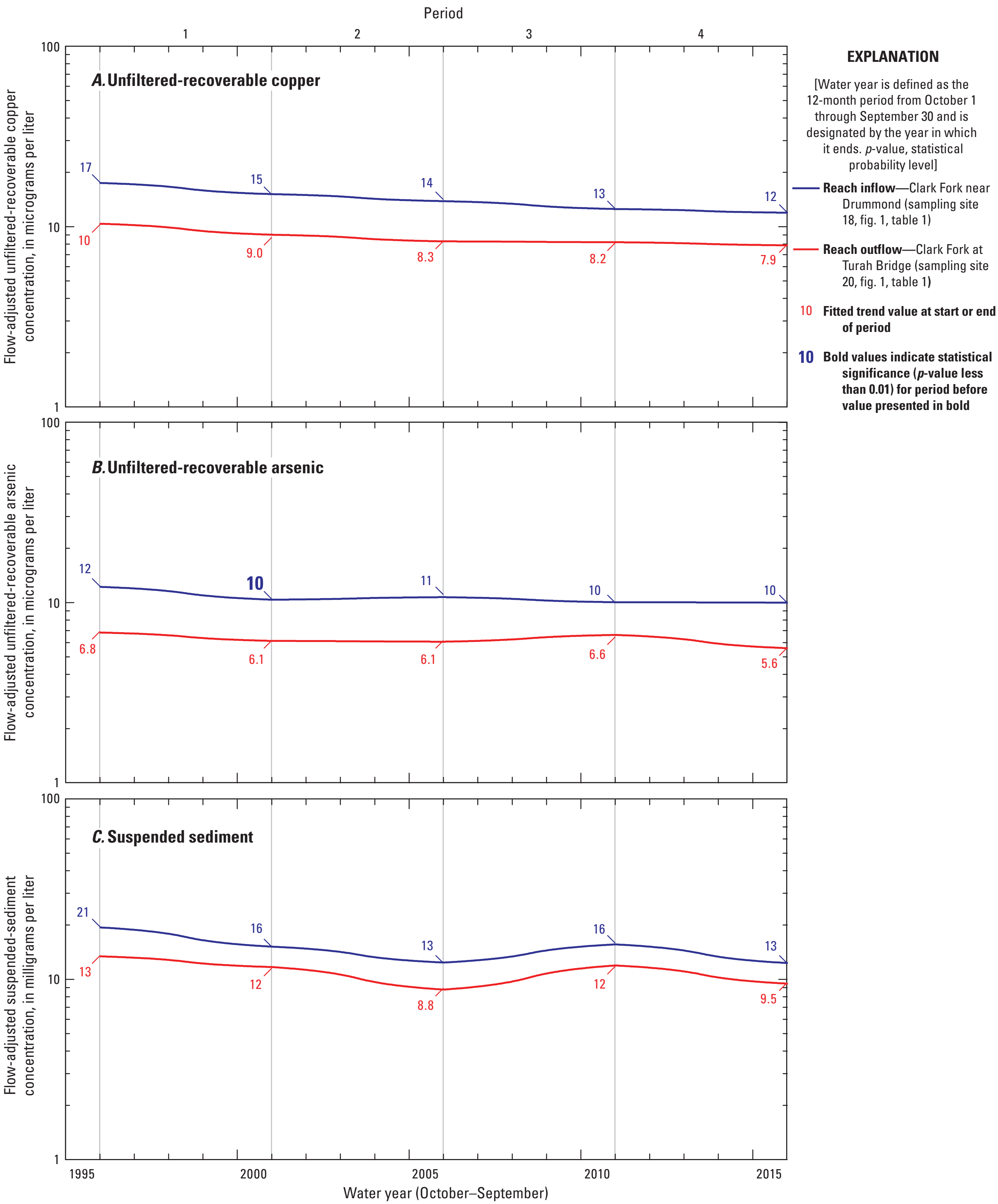


Figure 9. Flow-adjusted fitted trends for selected constituents for sampling sites in reach 8, extending from Clark Fork near Drummond, Montana (sampling site 18), to Clark Fork at Turah Bridge near Bonner, Montana (sampling site 20), water years 1996–2015.

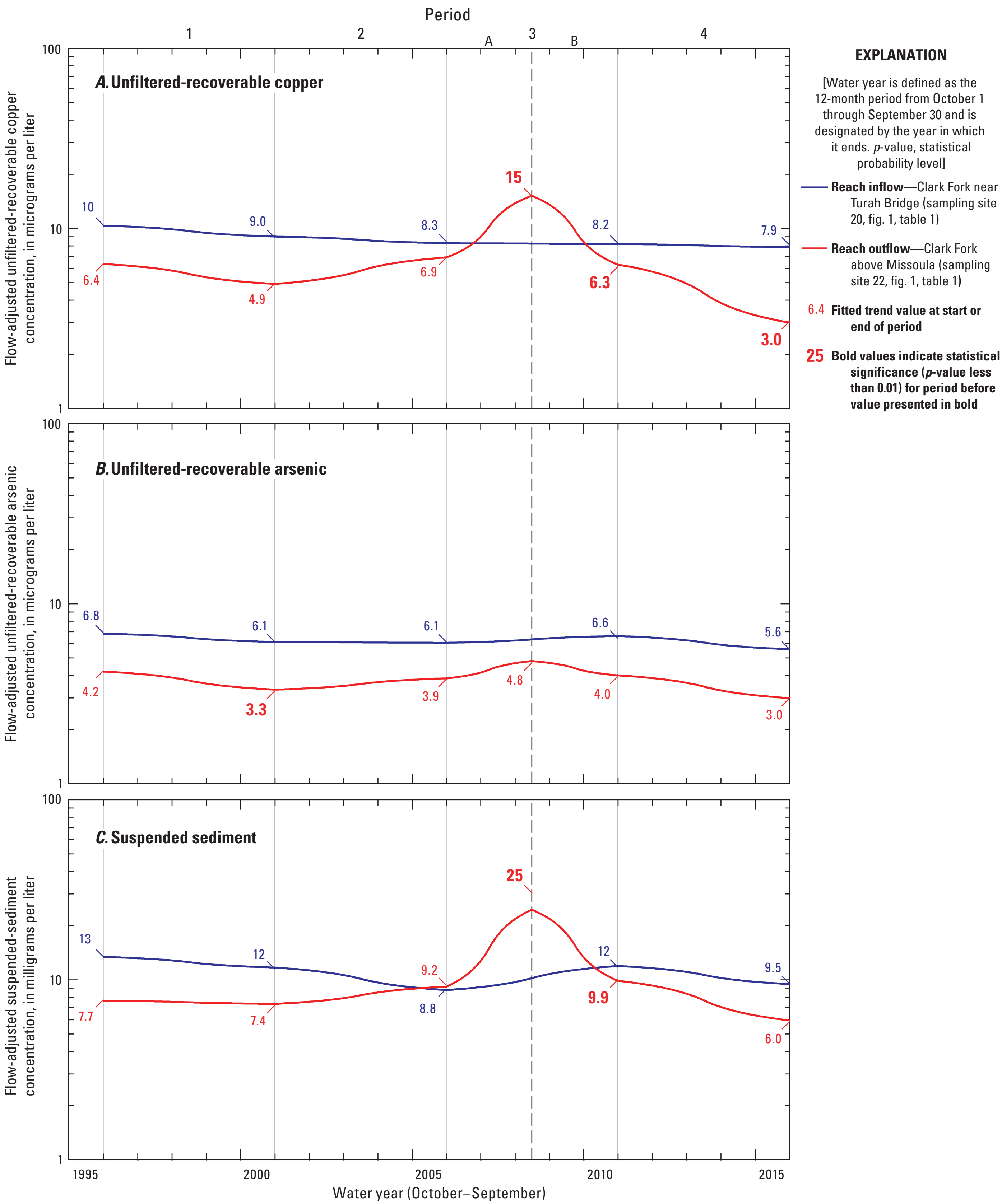


Figure 10. Flow-adjusted fitted trends for selected constituents for sampling sites in reach 9, extending from Clark Fork at Turah Bridge near Bonner, Montana (sampling site 20), to Clark Fork above Missoula, Montana (sampling site 22), water years 1996–2015.

Copper

Trend results indicate that FACs of unfiltered-recoverable copper decreased at the sampling sites from the start of period 1 through the end of period 4 (tables 6 and 7); the decreases ranged from large for one sampling site (Silver Bow Creek at Warm Springs [sampling site 8]) to moderate for two sampling sites (Clark Fork near Galen [sampling site 11] and Clark Fork above Missoula [sampling site 22]) to small for four sampling sites (Clark Fork at Deer Lodge [sampling site 14], Clark Fork at Goldcreek [sampling site 16], Clark Fork near Drummond [sampling site 18], and Clark Fork at Turah Bridge [sampling site 20]). For period 4 (water years 2011–15), the most notable changes indicated for the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin were statistically significant decreases in FACs of unfiltered-recoverable copper for sampling sites 8 and 22. For all other sampling sites, the period 4 changes in FACs of unfiltered-recoverable copper were not statistically significant.

Arsenic

Trend results indicate that FACs of unfiltered-recoverable arsenic decreased at the sampling sites from the start of period 1 through the end of period 4 (tables 6 and 7); the decreases ranged from minor for six sampling sites (sampling sites 8–20) to small for one sampling site (sampling site 22). For period 4 (water years 2011–15), the most notable changes indicated for the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin were statistically significant decreases in FACs of unfiltered-recoverable arsenic for sampling site 8 and near statistically significant decreases for sampling site 22; the *p*-value (0.012) for the period 4 decrease for sampling site 22 is not statistically significant but is only slightly larger than the selected alpha level (0.01 in this report). For all other sampling sites, the period 4 changes in FACs of unfiltered-recoverable arsenic were not statistically significant.

Suspended Sediment

Trend results indicate that FACs of suspended sediment decreased at the sampling sites from the start of period 1 through the end of period 4 (tables 6 and 7); the decreases ranged from moderate for one sampling site (sampling site 8) to small for six sampling sites (sampling sites 11–22). For period 4 (water years 2011–15), the changes in FACs of suspended sediment were not statistically significant for any sampling sites.

Overview of Water-Quality Trend Results

The most notable changes in water quality in period 4 were indicated for Silver Bow Creek at Warm Springs (sampling site 8; reach 4 inflow) and Clark Fork above Missoula (sampling 22; reach 9 outflow). Trend results for sampling site 8 indicated more substantial changes than most other sampling sites; the decreases in specific conductance, unfiltered-recoverable copper, unfiltered-recoverable zinc, and unfiltered-recoverable arsenic were statistically significant (fig. 5 and 3–1; tables 6 and 3–1). The most extensive remediation activities in the upper Clark Fork Basin have been conducted in the Silver Bow Creek Basin upstream from the reach 4 inflow (sampling site 8). Sando and others (2014) noted that among the most notable changes indicated in the upper Clark Fork Basin during water years 1996–2010 were moderate to large decreases in FACs and loads of copper and suspended sediment in Silver Bow Creek upstream from Warm Springs. The period 4 (water years 2011–15) statistically significant decreases in FACs of unfiltered-recoverable copper and zinc provide indication that FACs of metallic contaminants continued to substantially decline at sampling site 8.

The removal of the former Milltown Dam, which was located between Clark Fork at Turah Bridge (sampling site 20; reach 9 inflow) and Clark Fork above Missoula (sampling site 22; reach 9 outflow), in 2008 was an important remediation activity in the upper Clark Fork Basin and strongly affected water-quality trends and transport characteristics within reach 9. As such, detailed discussion of trends is presented for reach 9. During periods 1 and 2, the former Milltown Dam was in place, and large amounts of contaminated sediments were retained in the former Milltown Reservoir in reach 9; however, the contaminated sediments largely were unavailable for mobilization and transport because of backwater effects of the former Milltown Dam (Sando and Lambing, 2011). Remediation activities preparing for the removal of the former Milltown Dam started in period 2 but were focused early in period 3 and included physical removal of large amounts of contaminated sediments; however, substantial amounts of contaminated sediments still remained in the Clark Fork channel and flood plain in reach 9. With the removal of the former Milltown Dam in 2008, the remaining contaminated sediments in reach 9 became more available for mobilization and transport than before the dam removal. Because of the substantial effect of the intentional breach of Milltown Dam on March 28, 2008, for sampling site 22, period 3 was subdivided into period 3A (October 1, 2005–March 27, 2008) and period 3B (March 28, 2008–September 30, 2010).

A statistically significant increase in FACs of unfiltered-recoverable copper is indicated for period 3A for sampling site 22 (117 percent, from 6.9 to 15 µg/L; table 7). The temporary increase in FACs is associated with activities that prepared for the removal of the Milltown Dam, including construction of roads and facilities, reservoir level drawdowns, and physical removal of large amounts of contaminated sediments, which likely increased mobilization of sediments enriched in trace elements (Sando and Lambing, 2011). After the intentional breach, statistically significant decreases were indicated for unfiltered-recoverable copper for period 3B (-58 percent, from 15 to 6.3 µg/L) and period 4 (-52 percent, from 6.3 to 3.0 µg/L). For unfiltered-recoverable arsenic, an increase in FACs is indicated for period 3A (23 percent, from 3.9 to 4.8 µg/L). After the intentional breach, a decrease is indicated for unfiltered-recoverable arsenic for period 3B (-17 percent, from 4.8 to 4.0 µg/L) and a near statistically significant decrease is indicated for period 4 (-25 percent, from 4.0 to 3.0 µg/L; *p*-value of 0.012). For suspended sediment, a statistically significant increase is indicated for period 3A (172 percent, from 9.2 to 25 mg/L). After the intentional breach, a statistically significant decrease for suspended sediment is indicated for period 3B (-60 percent, from 25 to 9.9 mg/L), and a decrease is indicated for period 4 (-39 percent, from 9.9 to 6.0 mg/L). For period 4 (water years 2011–15), trend results for the reach 9 outflow (sampling site 22) indicate more substantial changes than most other sampling sites; decreases in unfiltered-recoverable copper, unfiltered-recoverable zinc, and filtered arsenic were statistically significant. The *p*-value (0.012) for the period 4 decrease in FACs of unfiltered-recoverable arsenic for sampling site 22 is not statistically significant but is only slightly larger than the selected alpha level (0.01 in this report).

The somewhat high streamflow conditions of period 4 promoted mobilization of trace-element contaminants from the former Milltown Reservoir, thus decreasing within-reach source materials and resulting in lower FACs. The substantial decreases in FACs of unfiltered-recoverable copper for period 3B continued in period 4. Comparison of the period 4 fitted trends for unfiltered-recoverable copper between the reach 9 inflow (sampling site 20) and the reach 9 outflow (sampling site 22) indicates large deviation from the start of to the end of period 4 (fig. 10*A*) and provides evidence of continued effects of the removal of the former Milltown Dam. Deviations in fitted trends between the period 4 reach inflow and reach outflow also are apparent for unfiltered-recoverable arsenic (fig. 10*B*) and suspended sediment (fig. 10*C*); however, the deviations are not as strong for those constituents as for unfiltered-recoverable copper.

Constituent-Transport Analysis Results

Estimated normalized loads are presented in the framework of a transport analysis to assess the temporal trends in FACs in the context of sources and transport. Drainage area and streamflow information relevant to the transport analysis are presented in table 8. Balance calculations for the transport analysis (that is, differences between reach inflows and reach outflows) are presented in tables 4–1 through 4–6 for reaches 4–9, respectively, in appendix 4. The transport balance calculations indicate within-reach changes in estimated normalized loads and allow assessment of temporal changes in relative contributions from upstream source areas to loads transported past each reach outflow.

Hydrologic characteristics of the source areas (geometric mean streamflow; table 8) and balance results for the transport analysis are illustrated by using pie charts that show source-area information and load contributions to reach outflow. Pie charts illustrating temporal patterns in estimated normalized loads for all data-summary reaches are presented in figures 11–13 for unfiltered-recoverable copper, unfiltered-recoverable arsenic, and suspended sediment, respectively. The pie charts provide a side-by-side graphical summary for evaluating spatial and temporal variability in constituent transport relative to streamflow contributions in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin. The estimated normalized loads (hereinafter referred to as “loads”) do not represent actual magnitudes of total mass transport, but rather provide information on relative temporal changes in constituent transport characteristics in the upper Clark Fork Basin quantified with respect to near-median conditions.

In figures 11–13, geometric mean streamflows (water years 1996–2015) for each reach are shown across the top of each figure, with the size (area) of each pie chart being proportional to the geometric mean streamflow for Clark Fork above Missoula (sampling site 22; reach 9 outflow). Pie charts that illustrate the constituent-transport analysis results for each reach for periods 1–4 are shown below the pie charts representing geometric mean streamflows. Pie charts illustrating loads are sized proportionally to the period 1 reach 9 outflow load. The period 1 reach 9 outflow load was selected as an index for sizing the pie charts because it represents the total load transported from the Milltown Reservoir/Clark Fork River Superfund Site somewhat near the start of remediation activities. As such, the period 1 reach 9 outflow load is a useful index in evaluating effects of remediation in the upper Clark Fork Basin.

Figure 11 presents pie charts representing loads for unfiltered-recoverable copper and serves as an example for explaining the presentation of the constituent-transport analysis results. The size (area) of each loads pie chart represents the total outflow from the reach, with colored areas indicating relative contributions from each of the two source areas; that is, (1) the reach inflow and (2) the intervening drainage between the reach inflow and outflow (or within-reach sources). The left-hand column of the load pie charts presents results for reach 4 for periods 1–4. The period 1 load transported past the reach 4 outflow (sampling site 11) is 3.7 kilograms per day (kg/d), which is 13 percent of the period 1 load transported past the reach 9 outflow (29 kg/d at sampling site 22 shown in right-hand column); thus, the size of the period 1 reach 4 pie chart is 13 percent of the size of the period 1 reach 9 pie chart. The blue-colored part of the period 1 reach 4 pie chart represents the load (1.9 kg/d) transported past the reach 4 inflow (sampling site 8). The orange-colored part of the period 1 reach 4 pie chart represents the total within-reach change in load (that is, net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain). The total within-reach change in load (1.8 kg/d) was calculated by subtracting the reach inflow (1.9 kg/d) from the reach outflow (3.7 kg/d). In figure 11, results for reach 9 are not shown for period 3 because of effects of the removal of the former

Table 8. Drainage area and streamflow information relevant to the transport analysis for data-summary reaches in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 1996–2015.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft^3/s, cubic foot per second]

Abbreviated sampling site name (table 1) and number or summation category	Drainage area, in square miles	Geometric mean streamflow, water years 1996–2015, in ft^3/s
Reach 4 [extending about 2 river miles from Silver Bow Creek at Warm Springs (sampling site 8, fig. 1, table 1) to Clark Fork near Galen (sampling site 11, fig. 1, table 1)]		
Inflow		
Silver Bow Creek at Warm Springs (sampling site 8)	473	64
Outflow		
Clark Fork near Galen (sampling site 11)	651	118
Within-reach change—outflow (sampling site 11) minus inflow (sampling site 8) (contributions from all within-reach sources, including groundwater inflow and tributaries)	178	54
Reach 5 [extending about 21 river miles from Clark Fork near Galen (sampling site 11, fig. 1, table 1) to Clark Fork at Deer Lodge (sampling site 14, fig. 1, table 1)]		
Inflow		
Clark Fork near Galen (sampling site 11)	651	118
Outflow		
Clark Fork at Deer Lodge (sampling site 14)	995	208
Within-reach change—outflow (sampling site 14) minus inflow (sampling site 11) (contributions from all within-reach sources, including groundwater inflow and tributaries)	344	90
Reach 6 [extending about 26 river miles from Clark Fork at Deer Lodge (sampling site 14, fig. 1, table 1) to Clark Fork at Goldcreek (sampling site 16, fig. 1, table 1)]		
Inflow		
Clark Fork at Deer Lodge (sampling site 14)	995	208
Outflow		
Clark Fork at Goldcreek (sampling site 16)	1,704	406
Within-reach change—outflow (sampling site 16) minus inflow (sampling site 14) (contributions from all within-reach sources, including groundwater inflow and tributaries)	709	198

Milltown Dam and difficulties in presenting those results in conjunction with results for other reaches.

Constituent-transport analysis results are described for copper, arsenic, and suspended sediment in the following subsections. Observations are made comparing the relative proportions of within-reach contributions of constituent loads and within-reach contributions of streamflow. Those proportional comparisons indicate the importance of a given reach as a source of constituent loading to Silver Bow Creek or the Clark Fork. If the contribution of a constituent from within a reach is proportionally much larger than the contribution of streamflow from within a reach, the given reach is indicated to be an important disproportionate source of constituent loading. Conversely, if the contribution of a constituent from within a reach is proportionally smaller than or similar to the contribution of streamflow from within a reach, the given reach is not indicated to be an important disproportionate source of constituent loading and generally acts as a flow-through reach.

Table 8. Drainage area and streamflow information relevant to the transport analysis for data-summary reaches in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 1996–2015.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. ft^3/s, cubic foot per second]

Abbreviated sampling site name (table 1) and number or summation category	Drainage area, in square miles	Geometric mean streamflow, water years 1996–2015, in ft^3/s
Reach 7 [extending about 31 river miles from Clark Fork at Goldcreek (sampling site 16, fig. 1, table 1) to Clark Fork near Drummond (sampling site 18, fig. 1, table 1)]		
Inflow		
Clark Fork at Goldcreek (sampling site 16)	1,704	406
Outflow		
Clark Fork near Drummond (sampling site 18)	2,501	589
Within-reach change—outflow (sampling site 18) minus inflow (sampling site 16) (contributions from all within-reach sources, including groundwater inflow and tributaries)	797	183
Reach 8 [extending about 34 river miles from Clark Fork near Drummond (sampling site 18, fig. 1, table 1) to Clark Fork at Turah Bridge (sampling site 20, fig. 1, table 1)]		
Inflow		
Clark Fork near Drummond (sampling site 18)	2,501	589
Outflow		
Clark Fork at Turah Bridge (sampling site 20)	3,641	1,060
Within-reach change—outflow (sampling site 20) minus inflow (sampling site 18) (contributions from all within-reach sources, including groundwater inflow and tributaries)	1,140	470
Reach 9 [extending about 9 river miles from Clark Fork at Turah Bridge (sampling site 20, fig. 1, table 1) to Clark Fork above Missoula (sampling site 22, fig. 1, table 1)]		
Inflow		
Clark Fork at Turah Bridge (sampling site 20)	3,641	1,060
Outflow		
Clark Fork above Missoula (sampling site 22)	5,999	2,100
Within-reach change—outflow (sampling site 22) minus inflow (sampling site 20) (contributions from all within-reach sources, including groundwater inflow and tributaries)	2,358	1,040

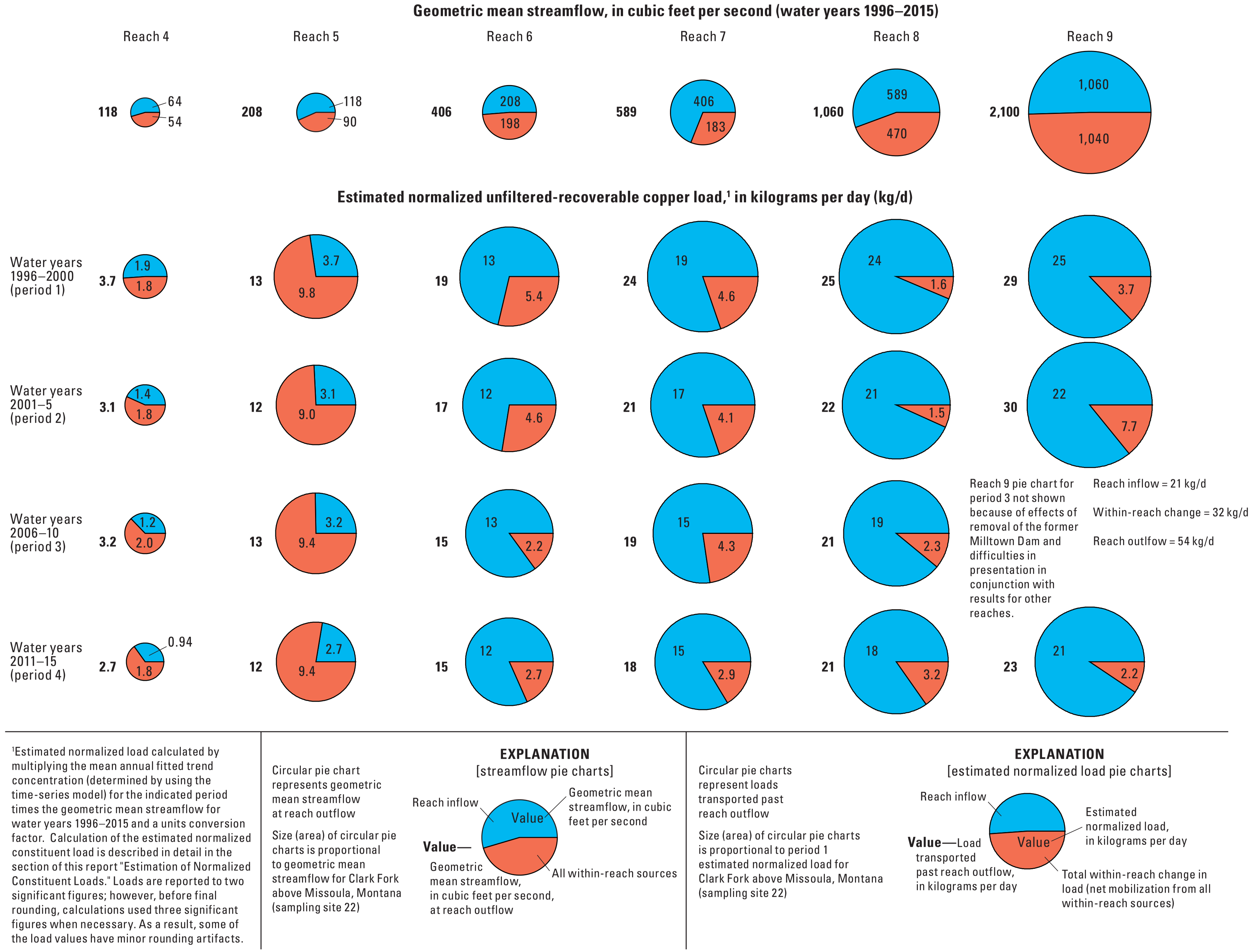
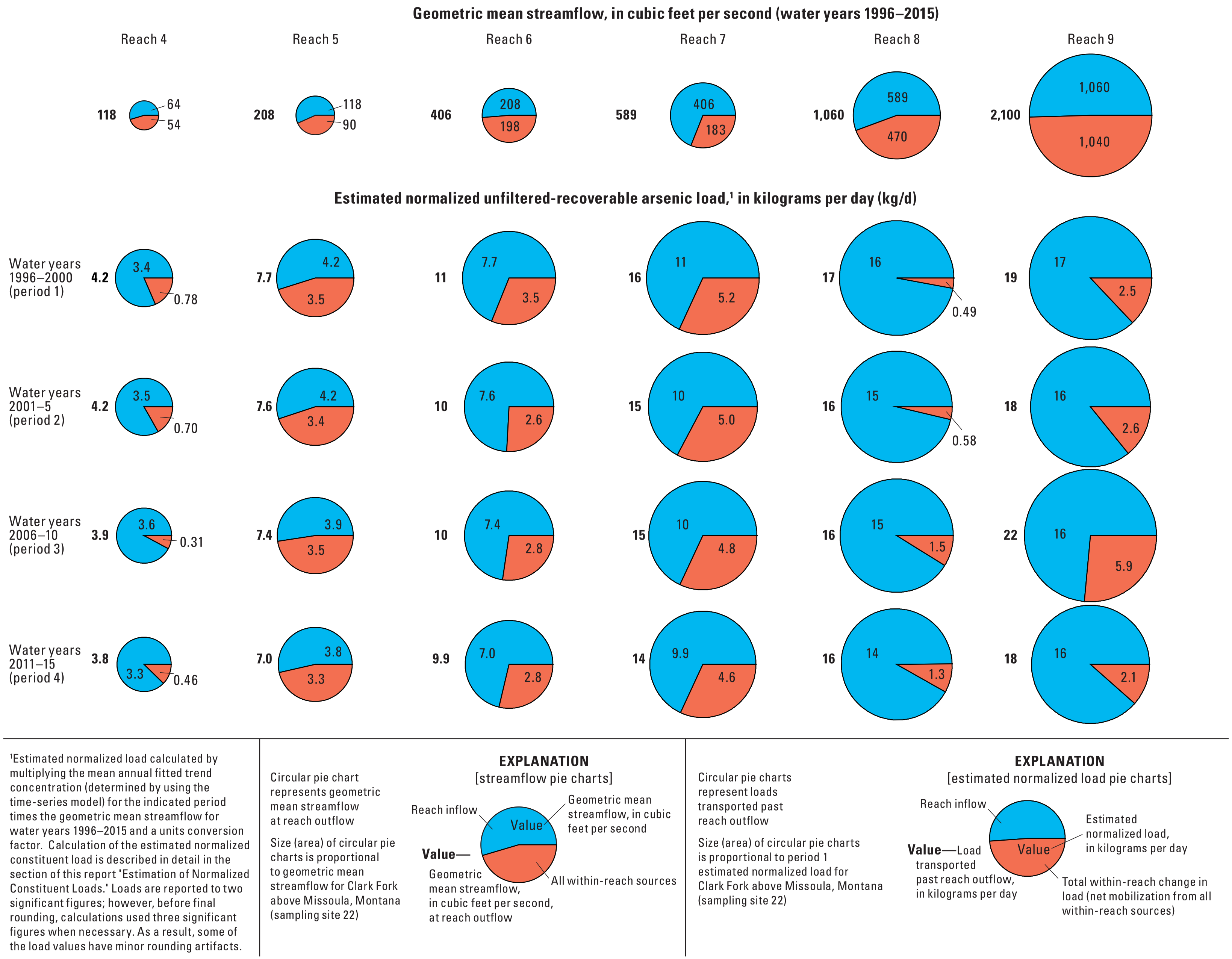


Figure 11. Pie charts representing geometric mean streamflow and estimated normalized unfiltered-recoverable copper loads contributed from reach inflow and within-reach sources for data-summary reaches for selected periods.



[1]Estimated normalized load calculated by multiplying the mean annual fitted trend concentration (determined by using the time-series model) for the indicated period times the geometric mean streamflow for water years 1996–2015 and a units conversion factor. Calculation of the estimated normalized constituent load is described in detail in the section of this report "Estimation of Normalized Constituent Loads." Loads are reported to two significant figures; however, before final rounding, calculations used three significant figures when necessary. As a result, some of the load values have minor rounding artifacts.

Figure 12. Pie charts representing geometric mean streamflow and estimated normalized unfiltered-recoverable arsenic loads contributed from reach inflow and within-reach sources for data-summary reaches for selected periods.

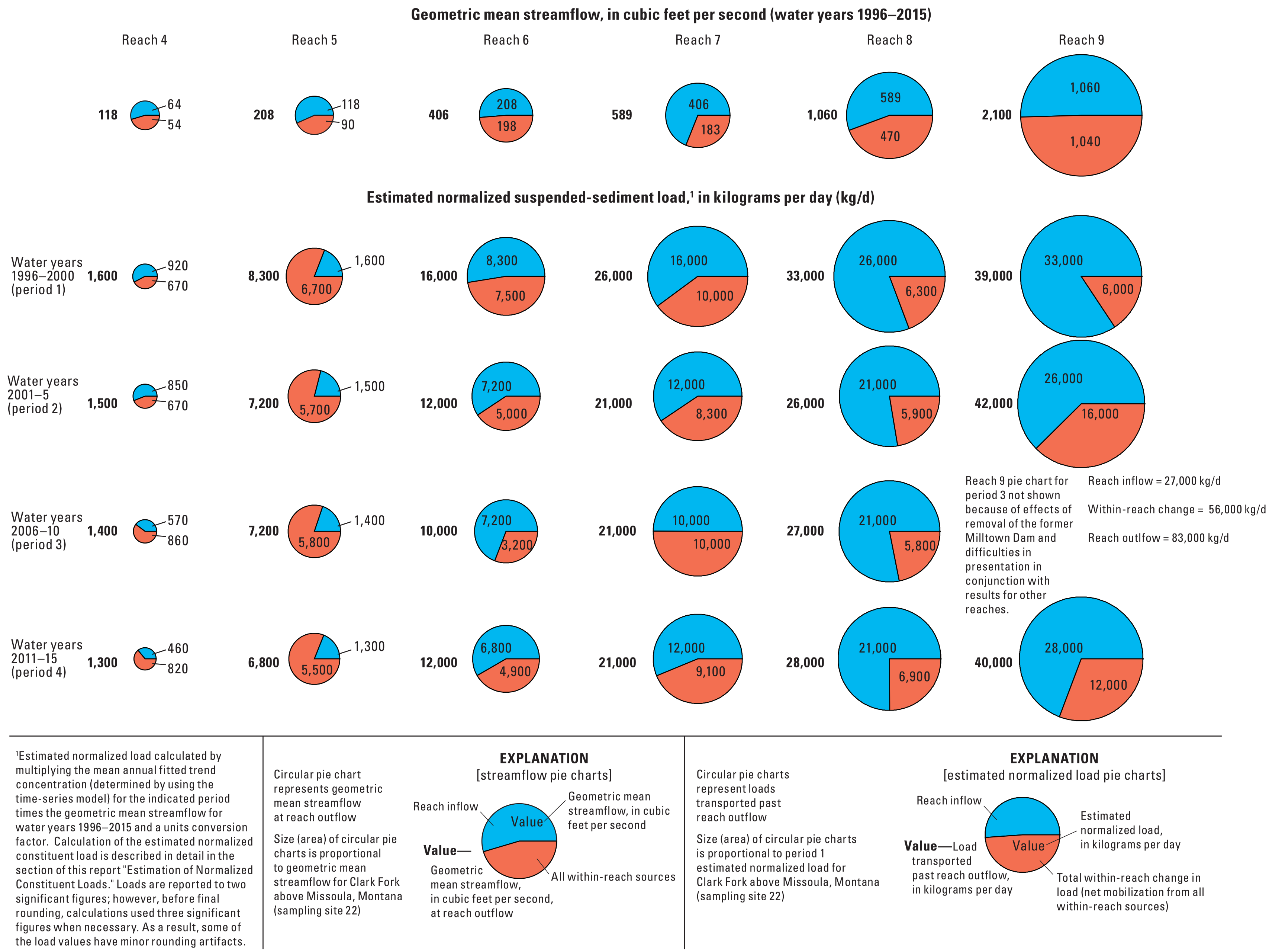


Figure 13. Pie charts representing geometric mean streamflow and estimated normalized suspended-sediment loads contributed from reach inflow and within-reach sources for data-summary reaches for selected periods.

Copper

The transport-analysis results indicate that outflow loads of unfiltered-recoverable copper decreased from the center of period 1 through the center of period 4 for all reaches (fig. 11). The largest decrease was for the reach 4 outflow load (about -27 percent, from 3.7 to 2.7 kg/d). The decrease in the reach 4 outflow load (sampling site 11) largely was because of a substantial decrease (-50 percent, from 1.9 to 0.94 kg/d) in the reach 4 inflow load (sampling site 8), with little change indicated for within-reach sources. The smallest decrease was for the reach 5 outflow load (about -8 percent from 13 to 12 kg/d). Decreases in outflow loads for the other reaches (reaches 6–9) ranged from about -16 to -25 percent.

Contributions of unfiltered-recoverable copper from reach 4 sources were proportionally similar to or slightly larger than streamflow contributions from within reach 4 (fig. 11, tables 8 and 4–1) for all periods, and thus reach 4 is somewhat indicated to be a disproportionate source of copper loading. However, the period 4 net mobilization from sources within reach 4 (1.8 kg/d) was only about 8 percent of the period 4 reach 9 outflow load (Clark Fork above Missoula, sampling site 22; 23 kg/d). Contributions of unfiltered-recoverable copper from reach 5 sources were proportionally much larger than streamflow contributions from within reach 5 for all periods; the period 4 net mobilization from sources within reach 5 (9.4 kg/d) accounted for a substantial part (about 41 percent) of the period 4 reach 9 outflow load. Thus, reach 5 is indicated to be an important disproportionate source of copper loading. Contributions of unfiltered-recoverable copper from sources within the other reaches (reaches 6–9) were proportionally smaller than the within-reach streamflow contributions.

The removal of the former Milltown Dam in 2008 warrants more detailed discussion of transport analysis results for reach 9. The segregation of period 3 into periods 3A and 3B for the reach 9 outflow (sampling site 22) is not directly incorporated into the transport analysis for reach 9; thus, the transport-analysis balance calculations for period 3 reflect the net changes in transport characteristics before and after the removal of the former Milltown Dam. For unfiltered-recoverable copper (fig. 11), the reach 9 outflow load (sampling site 22) decreased by about 21 percent from the center of period 1 (29 kg/d) to the center of period 4 (23 kg/d). Net mobilization from sources within reach 9 increased between periods 1 and 2 and also between periods 2 and 3 (fig. 11). Net mobilization from sources within reach 9 substantially decreased between periods 3 and 4. Net mobilization from sources within reach 9 were proportionally larger than streamflow contributions from within reach 9 for period 3 but were proportionally smaller than streamflow contributions for the other periods. Net mobilization from sources within reach 9 were smaller for period 4 (2.2 kg/d) than for period 1 (3.7 kg/d).

Arsenic

The transport-analysis results indicate that outflow loads of unfiltered-recoverable arsenic decreased from the center of period 1 through the center of period 4 for all reaches (fig. 12). Decreases in outflow loads for the reaches ranged from about -5 to -12 percent. Temporal decreases in unfiltered-recoverable arsenic were smaller than copper and suspended sediment, which probably reflects the dispersion and solubility characteristics of arsenic.

At the upstream end of the Milltown Reservoir/Clark Fork River Superfund site, the reach 4 inflow load is a disproportionate source of arsenic loading, with the inflow load being proportionally larger than the streamflow (fig. 12, tables 8 and 4–1). Contributions of unfiltered-recoverable arsenic from reach 4 sources were proportionally smaller than streamflow contributions from within reach 4 for all periods. Downstream from reach 4, contributions of unfiltered-recoverable arsenic from sources within reaches 5 and 7 were proportionally similar to within-reach streamflow contributions. Contributions of unfiltered-recoverable arsenic from sources within the other reaches (reaches 6, 8, and 9) were proportionally smaller than the within-reach streamflow contributions.

For unfiltered-recoverable arsenic (fig. 12), the reach 9 outflow load (sampling site 22) decreased by about 5 percent from the center of period 1 (19 kg/d) to the center of period 4 (18 kg/d). Net mobilization from sources within reach 9 increased between periods 2 and 3 (fig. 12). Net mobilization from sources within reach 9 substantially decreased between periods 3 and 4. Contributions of unfiltered-recoverable arsenic from reach 9 sources were proportionally smaller than streamflow contributions from within reach 9 for all periods. Net mobilization from sources within reach 9 were slightly smaller for period 4 (2.1 kg/d) than for period 1 (2.5 kg/d).

Suspended Sediment

The transport-analysis results indicate that outflow loads of suspended sediment decreased from the center of period 1 through the center of period 4 for reaches 4–8 but slightly increased for reach 9 (fig. 13). Decreases in outflow loads for reaches 6–8 ranged from about -15 to -25 percent.

Contributions of suspended sediment from reach 4 sources were proportionally similar to or slightly larger than streamflow contributions from within reach 4 (fig. 13, tables 8 and 4–1) for all periods, and thus, reach 4 is somewhat indicated to be a disproportionate source of suspended-sediment loading. However, the period 4 net mobilization from sources within reach 4 (820 kg/d) was only about 2 percent of the period 4 reach 9 outflow load (Clark Fork above Missoula, sampling site 22; 40,000 kg/d). Contributions of suspended sediment from reach 5 sources were proportionally much larger than streamflow contributions from within reach 5; the period 4 net mobilization from sources within reach 5 (5,500 kg/d) accounted for about 14 percent of the period 4 reach 9 outflow load. Thus, reach 5 is indicated to be a disproportionate source of suspended-sediment loading. Downstream from reach 5, contributions of sediment from sources within reach 7 were proportionally similar to within-reach streamflow contributions; the period 4 net mobilization from sources within reach 7 (9,100 kg/d) accounted for about 23 percent of the period 4 reach 9 outflow load. Contributions of suspended sediment from sources within the other reaches (reaches 6, 8, and 9) were proportionally smaller than the within-reach streamflow contributions.

For suspended sediment (fig. 13), the reach 9 outflow load (sampling site 22) increased by about 3 percent from the center of period 1 (39,000 kg/d) to the center of period 4 (40,000 kg/d). Net mobilization from sources within reach 9 increased between periods 1 and 2 and also between periods 2 and 3 (fig. 13). Net mobilization from sources within reach 9 substantially decreased between periods 3 and 4. Net mobilization from sources within reach 9 was proportionally larger than streamflow contributions from within reach 9 for period 3 but was proportionally smaller than streamflow contributions for the other periods. Net mobilization from sources within reach 9 were larger for period 4 (12,000 kg/d) than for period 1 (6,000 kg/d). The increase in net mobilization of suspended sediment from sources within reach 9 between periods 1 and 4 is in contrast to decreases in net mobilization of unfiltered-recoverable copper and arsenic between periods 1 and 4. A possible explanation for this pattern might relate to flood-plain disturbance and placement of uncontaminated fill in the flood plain associated with remediation activities. The artificially installed uncontaminated fill might be more available for mobilization than sediment within the former Milltown Reservoir during period 1.

Overview of Constituent-Transport Analysis Results

At the upstream end of the Milltown Reservoir/Clark Fork River Superfund site, the reach 4 inflow had substantial decreases from the center of period 1 to the center of period 4 in unfiltered-recoverable copper and suspended-sediment loads (about -50 percent for both constituents), but the reach 4 inflow accounts for small parts of the streamflow (about 3 percent), unfiltered-recoverable copper load (about 4 percent), and suspended-sediment load (about 1 percent) of the reach 9 outflow in period 4 (figs. 11 and 13). The reach 4 inflow is a disproportionate source of unfiltered-recoverable arsenic and accounts for about 18 percent of the reach 9 outflow load in period 4 (fig. 12). Some downstream reaches (including reaches 5 and 7) have within-reach contributions of unfiltered-recoverable arsenic that are proportionally similar to streamflow contributions and also substantially contribute to the reach 9 outflow load. For all reaches, temporal changes for unfiltered-recoverable arsenic loads are smaller than for unfiltered-recoverable copper and suspended-sediment loads.

Reach 5 is a large source of unfiltered-recoverable copper and suspended sediment, which strongly affects downstream transport of those constituents (figs. 11 and 13). Mobilization of unfiltered-recoverable copper and suspended sediment from flood-plain tailings and the streambed of the Clark Fork and its tributaries within reach 5 results in a contribution of those constituents from within reach 5 that is proportionally much larger than the contribution of streamflow from within reach 5. In reach 5, unfiltered-recoverable copper loads in the Clark Fork increased by a factor of about 4 and suspended-sediment loads increased by a factor of about 5, whereas streamflow increased by a factor of slightly less than 2 (fig. 11). For period 4 (water years 2011–15), unfiltered-recoverable copper and suspended-sediment loads sourced from within reach 5 accounted for about 41 and 14 percent, respectively, of the loads at Clark Fork above Missoula (sampling site 22), whereas streamflow sourced from within the reach accounted for about 4 percent of the streamflow at sampling site 22. During water years 1996–2015, decreases in unfiltered-recoverable copper and suspended-sediment loads (fig. 11 and 13) for the reach 5 outflow and for sources within reach 5 generally were proportionally smaller than for most other reaches.

For the reaches downstream from reach 5 (reaches 6–8), contributions of copper loads sourced from within the reaches were proportionally smaller than contributions of streamflow sourced from within the reaches (fig. 11); thus, the lower reaches contributed proportionally much less than reach 5 to unfiltered-recoverable copper loading in the Clark Fork. Although substantial decreases in unfiltered-recoverable copper and suspended-sediment loads were indicated for the reach 4 inflow (sampling site 8), those substantial decreases were not translated to the downstream reaches (reaches 5–8). The effect of reach 5 as a large source of unfiltered-recoverable copper and suspended sediment, in combination with little temporal change in those constituents for the reach 5 outflow, contributes to this pattern.

For unfiltered-recoverable copper, unfiltered-recoverable arsenic, and suspended sediment, contributions from within reach 8 generally increased between periods 2 and 4; this pattern is in contrast to patterns for most other reaches. A possible explanation for this pattern might relate to effects of the removal of the former Milltown Dam during period 3. Before the removal of the former Milltown Dam, backwater effects of the dam during high-flow conditions might have extended far enough upstream to affect the hydraulic gradient at the reach 8 outflow (sampling site 20) and also affect the transport of materials from reach 8. After the removal of the former Milltown Dam, the hydraulic gradient at sampling site 20 might have steepened and promoted transport of materials from reach 8 during high streamflow conditions.

With the removal of the former Milltown Dam in 2008, substantial amounts of contaminated sediments that remained in the Clark Fork channel and flood plain in reach 9 became more available for mobilization and transport than before the dam removal. Net mobilization of unfiltered-recoverable copper, unfiltered-recoverable arsenic, and suspended sediment from sources within reach 9 substantially decreased between periods 3 and 4. Net mobilization of unfiltered-recoverable copper and arsenic from sources within reach 9 is smaller for period 4 than for period 1 when the former Milltown Dam was in place, providing evidence that contaminant source materials have been substantially reduced in reach 9. However, net mobilization of suspended sediment from sources within reach 9 were slightly larger for period 4 than for period 1. A possible explanation for this pattern might relate to flood-plain disturbance and placement of uncontaminated fill in the flood plain associated with remediation activities. The artificially installed uncontaminated fill might be more available for mobilization than sediment within the former Milltown Reservoir during period 1.

Summary and Conclusions

This report characterizes temporal trends in flow-adjusted concentrations (filtered and unfiltered) of mining-related contaminants and assesses those trends in the context of source areas and transport of those contaminants through the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin in Montana. The Milltown Reservoir/Clark Fork River Superfund Site extends about 123 river miles from the outlet of Warm Springs Ponds on Silver Bow Creek to the outlet of the former Milltown Reservoir near Missoula. Trend analysis was done on specific conductance, selected trace elements (arsenic, copper, and zinc), and suspended sediment by using a joint time-series model (TSM) for concentration and streamflow for seven sampling sites for water years 1996–2015. The most upstream site included in trend analysis is Silver Bow Creek at Warm Springs, Montana (sampling site 8), and the most downstream site is Clark Fork above Missoula, Montana (sampling site 22), which is just downstream from the former Milltown Dam.

During the extended history of mining in the upper Clark Fork Basin in Montana, large amounts of waste materials enriched with metallic contaminants (cadmium, copper, lead, and zinc) and the metalloid trace element arsenic were generated from mining operations near Butte, and the milling and smelting operations near Anaconda. Extensive deposition of mining wastes in the Silver Bow Creek and Clark Fork channels and flood plains had substantial effects on water quality. Federal Superfund remediation activities in the upper Clark Fork Basin began in 1983 and have included substantial remediation near Butte and removal of the former Milltown Dam.

Water-quality data collection by the U.S. Geological Survey (USGS) in the upper Clark Fork Basin began during 1985–88 with the establishment of a small long-term monitoring program that has expanded through time and continued through present (2016). A previous study analyzed the monitoring data and characterized flow-adjusted trends in mining-related contaminants for 22 sampling sites in the upper Clark Fork Basin for water years 1996–2010 (water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends). An update of flow-adjusted water-quality trends for the monitoring data was needed for seven sampling sites to provide timely information for the 2016 5-year review for the Milltown Reservoir/Clark Fork River Superfund Site.

The TSM was used to detect trends in flow-adjusted concentrations (FACs). The intent of flow-adjustment is to identify and remove streamflow-related variability in concentration and thereby enhance the capability to detect trends independent from effects of climatic variability. To provide temporal resolution of changes in water quality, trend analysis was conducted on four sequential 5-year periods: period 1 (water years 1996–2000), period 2 (water years 2001–5), period 3 (water years 2006–10), and period 4 (water years 2011–15). Because of the substantial effect of the intentional breach of Milltown Dam on March 28, 2008, for Clark Fork above Missoula (sampling site 22), period 3 was subdivided into period 3A (October 1, 2005–March 27, 2008) and period 3B (March 28, 2008–September 30, 2010). The TSM was applied as consistently as possible among sampling sites and is considered to be a useful tool for simplifying the environmental complexity in the upper Clark Fork Basin to provide a large-scale evaluation of general temporal changes in constituent transport independent from streamflow variability.

In conjunction with the trend analysis, estimated normalized constituent loads were calculated and presented in the framework of a constituent-transport analysis to assess the temporal trends in FACs in the context of sources and transport. The transport analysis allows assessment of temporal changes in relative contributions from upstream source areas to loads transported past each reach outflow.

Trend results are presented for all constituents investigated; however, emphasis is placed on copper, arsenic, and suspended sediment. Trend results were considered statistically significant when the statistical probability level (p-value) was less than 0.01.

Trend results indicate that FACs of unfiltered-recoverable copper decreased at the sampling sites from the start of period 1 through the end of period 4; the decreases ranged from large for one sampling site (Silver Bow Creek at Warm Springs [sampling site 8]) to moderate for two sampling sites (Clark Fork near Galen, Montana [sampling site 11] and Clark Fork above Missoula [sampling site 22]) to small for four sampling sites (Clark Fork at Deer Lodge, Montana [sampling site 14], Clark Fork at Goldcreek, Montana [sampling site 16], Clark Fork near Drummond, Montana [sampling site 18], and Clark Fork at Turah Bridge near Bonner, Montana [sampling site 20]). For period 4 (water years 2011–15), the most notable changes indicated for the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin were statistically significant decreases in FACs and loads of unfiltered-recoverable copper for sampling sites 8 and 22. For all other sampling sites, the period 4 changes in FACs of unfiltered-recoverable copper were not statistically significant.

Trend results indicate that FACs of unfiltered-recoverable arsenic decreased at the sampling sites from the start of period 1 through the end of period 4; the decreases ranged from minor (sampling sites 8–20) to small (sampling site 22). For period 4 (water years 2011–15), the most notable changes indicated for the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin were statistically significant decreases in FACs and loads of unfiltered-recoverable arsenic for sampling site 8 and near statistically significant decreases (p-value of 0.012) for sampling site 22. For all other sampling sites, the period 4 changes in FACs of unfiltered-recoverable arsenic were not statistically significant.

Trend results indicate that FACs of suspended sediment decreased at the sampling sites from the start of period 1 through the end of period 4; the decreases ranged from moderate (sampling site 8) to small (sampling sites 11–22). For period 4 (water years 2011–15), the changes in FACs of suspended sediment were not statistically significant for any sampling sites.

The reach of the Clark Fork from Galen to Deer Lodge is a large source of metallic contaminants and suspended sediment, which strongly affects downstream transport of those constituents. Mobilization of unfiltered-recoverable copper and suspended sediment from flood-plain tailings and the streambed of the Clark Fork and its tributaries within the reach results in a contribution of those constituents that is proportionally much larger than the contribution of streamflow from within the reach. Within the reach, unfiltered-recoverable copper loads increased by a factor of about 4 and suspended-sediment loads increased by a factor of about 5, whereas streamflow increased by a factor of slightly less than 2. For period 4 (water years 2011–15), unfiltered-recoverable copper and suspended-sediment loads sourced from within the reach accounted for about 41 and 14 percent, respectively, of the loads at Clark Fork above Missoula (sampling site 22), whereas streamflow sourced from within the reach accounted for about 4 percent of the streamflow at sampling site 22. During water years 1996–2015, decreases in FACs and loads of unfiltered-recoverable copper and suspended sediment for the reach generally were proportionally smaller than those for most other reaches.

Unfiltered-recoverable copper loads sourced within the reaches of the Clark Fork between Deer Lodge and Turah Bridge near Bonner were proportionally smaller than contributions of streamflow sourced from within the reaches; these reaches contributed proportionally much less to copper loading in the Clark Fork than the reach between Galen and Deer Lodge. Although substantial decreases in FACs and loads of unfiltered-recoverable copper and suspended sediment were indicated for Silver Bow Creek at Warm Springs (sampling site 8), those substantial decreases were not translated to downstream reaches between Deer Lodge and Turah Bridge near Bonner. The effect of the reach of the Clark Fork from Galen to Deer Lodge as a large source of copper and suspended sediment, in combination with little temporal change in those constituents for the reach, contributes to this pattern.

With the removal of the former Milltown Dam in 2008, substantial amounts of contaminated sediments that remained in the Clark Fork channel and flood plain in reach 9 became more available for mobilization and transport than before the dam removal. After the removal of the former Milltown Dam, the Clark Fork above Missoula (sampling site 22) had statistically significant decreases in FACs of unfiltered-recoverable copper in period 3B (March 28, 2008, through water year 2010) that continued in period 4 (water years 2011–15). Also, decreases in FACs of unfiltered-recoverable arsenic and suspended sediment were indicated for period 4 at this site. The decrease in FACs of unfiltered-recoverable copper for sampling site 22 during period 4 was proportionally much larger than the decrease for the Clark Fork at Turah Bridge near Bonner (sampling site 20). Net mobilization of unfiltered-recoverable copper, unfiltered-recoverable arsenic, and suspended sediment from sources within reach 9 substantially decreased between periods 3 and 4. Net mobilization of unfiltered-recoverable copper and arsenic from sources within reach 9 were smaller for period 4 than for period 1 when the former Milltown Dam was in place, providing evidence that contaminant source materials have been substantially reduced in reach 9. However, net mobilization of suspended sediment from sources within reach 9 were slightly larger for period 4 than for period 1. A possible explanation for this pattern might relate to flood-plain disturbance and placement of uncontaminated fill in the flood plain associated with remediation activities. The artificially installed uncontaminated fill might be more available for mobilization than sediment within the former Milltown Reservoir during period 1.

References

Andrews, E.D., 1987, Longitudinal dispersion of trace metals in the Clark Fork River, Montana, *in* Averett, R.C., and McKnight, D.M., eds., The chemical quality of water and the hydrologic cycle: Chelsea, Mich., Lewis Publishers, Inc., p. 1–13.

CDM, 2005, Second five year review report for Silver Bow Creek/Butte Area Superfund Site: CDM, Helena, Montana, 217 p.

Chanat, J.G., Rice, K.C., and Hornberger, G.M, 2002, Consistency of patterns in concentration-discharge plots: Water Resources Research, v. 38, 10 p.

Chatham, J.R., 2012, Chemical cycling and nutrient loading at Warm Springs Ponds (MT): LaPalma, Calif., Atlantic Richfield Company, 96 p.

Cleveland, W.S., 1985, The elements of graphing data: Monterey, Calif., Wadsworth Books, 323 p.

Cleveland, W.S., and McGill, Robert, 1984, The many faces of a scatterplot: Journal of the American Statistical Association, v. 79, p. 807–822.

Cohn, T.A., 1988, Adjusted maximum likelihood estimation of the moments of lognormal populations from type 1 censored samples: U.S. Geological Survey Open-File Report 88–350, 34 p.

Colby, B.R., 1956, Relationship of sediment discharge to streamflow: U.S. Geological Survey Open-File Report 56–27, 170 p.

Dodge, K.A., Hornberger, M.I., and Dyke, J.L., 2015, Water-quality, bed-sediment, and biological data (October 2013 through September 2014) and statistical summaries of data for streams in the Clark Fork Basin, Montana: U.S. Geological Survey Open-File Report 2015–1223, 125 p., accessed February 1, 2016, at https://pubs.er.usgs.gov/publication/ofr20151223.

Fishman, M.J., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.

Freeman, H.C., 1900, A brief history of Butte, Montana—The world's greatest mining company: Chicago, Ill., Henry O. Shepard Company, 128 p.

Gammons, C.H., Metesh, J.J., and Duaime, T.E., 2006, An overview of the mining history and geology of Butte, Montana: Mine Water and the Environment, v. 25, p. 70–75, accessed November 19, 2012, at http://dx.doi.org/10.1007/s10230-006-0113-7.

Garbarino, J.R., Kanagy, L.K., and Cree, M.E., 2006, Determination of elements in natural-water, biota, sediment, and soil samples using collision/reaction cell inductively coupled plasma-mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. 1B, 88 p.

Garbarino, J.R., and Struzeski, T.M., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of elements in whole-water digests using inductively coupled plasma-optical emission spectrometry and inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 98–165, 101 p.

Helsel, D.R., 2005, Nondetects and data analysis—Statistics for censored environmental data: New York, John Wiley and Sons, 250 p.

Helsel, D.R., and Hirsch, R.M., 2002, Statistical methods in water resources: Techniques of Water-Resources Investigations of the United States Geological Survey, book 4, chap. A3, 510 p.

Lambing, J.H., 1998, Estimated 1996–97 and long-term average annual loads for suspended sediment and selected trace metals in streamflow of the upper Clark Fork Basin from Warm Springs to Missoula, Montana: U.S. Geological Survey Water-Resources Investigations Report 98–4137, 35 p., accessed November 19, 2012, at http://pubs.er.usgs.gov/publication/wri984137.

Montana Department of Environmental Quality, 2012, DEQ-7 Montana numeric water quality standards: Helena, Montana, Water Quality Planning Bureau, Water Quality Standards Section, 76 p.

Montana Department of Environmental Quality, 2016, Clark Fork River Operable Unit: Montana Department of Environmental Quality Web page, accessed May 24, 2016, at https://deq.mt.gov/Land/fedsuperfund/cfr.

Nimick, D.A., Gammons, C.H., Cleasby, T.E., Madison, J.P., Skaar, Don, and Brick, C.M., 2003, Diel cycles in dissolved metal concentrations in streams—Occurrence and possible causes: Water Resources Research, v. 39, 17 p.

Nimick, D.A., Gammons, C.H., and Parker, S.R., 2011, Diel biogeochemical processes and their effect on the aqueous chemistry of streams—A review: Chemical Geology, v. 283, p. 3–17.

Sando, S.K., and Lambing, J.H., 2011, Estimated loads of suspended sediment and selected trace elements transported through the Clark Fork Basin, Montana, in selected periods before and after the breach of Milltown Dam (water years 1985–2009): U.S. Geological Survey Scientific Investigations Report 2011–5030, 64 p., accessed November 19, 2012, at http://pubs.usgs.gov/sir/2011/5030.

Sando, S.K., Vecchia, A.V., Lorenz, D.L., and Barnhart, E.P, 2014, Water-quality trends for selected sampling sites in the upper Clark Fork Basin, Montana, water years 1996–2010: U.S. Geological Survey Scientific Investigations Report 2013–5217, 162 p., with appendixes.

Smith, J.D., Lambing, J.H., Nimick, D.A., Parrett, Charles, Ramey, Michael, and Schafer, William, 1998, Geomorphology, flood-plain tailings, and metal transport in the upper Clark Fork Valley, Montana: U.S. Geological Survey Water-Resources Investigations Report 98–4170, 56 p., accessed November 19, 2012, at http://pubs.er.usgs.gov/publication/wri984170.

Stumm, Werner, and Morgan, J.J., 1970, Aquatic chemistry—An introduction emphasizing chemical equilibria in natural water: New York, John Wiley and Sons, 583 p.

Tasker, G.D., 1978, Relation between standard errors in log units and standard errors in percent: U.S. Geological Survey Water Resources Division Bulletin, January–March 1978, p. 86–87.

Taylor, J.K., 1987, Quality assurance of chemical measurements: Chelsea, Mich., Lewis Publishers, 328 p.

U.S. Environmental Protection Agency, 2000, Five-year review report, Silver Bow Creek/Butte Area Superfund Site with emphasis on the Warm Springs Ponds performance review: Helena, Montana, U.S. Environmental Protection Agency, Region 8, 266 p.

U.S. Environmental Protection Agency, 2004, Milltown Reservoir Sediments Operable Unit of the Milltown Reservoir/Clark Fork River Superfund Site—Record of decision, part 2: U.S. Environmental Protection Agency Decision Summary, 141 p.

U.S. Environmental Protection Agency, 2005, Second five-year review report, Silver Bow Creek/Butte Area Superfund Site: Helena, Montana, U.S. Environmental Protection Agency, Region 8, 217 p.

U.S. Environmental Protection Agency, 2010, Five-year review report, Anaconda Smelter National Priority List Site, Deer Lodge County, Montana: Helena, Montana, U.S. Environmental Protection Agency, Region 8, 104 p.

U.S. Geological Survey, 2015, National Water Information System (NWISWeb): U.S. Geological Survey database, accessed November 1, 2015, at http://waterdata.usgs.gov/nwis.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, 2 v. [variously paged]. [Also available at http://pubs.water.usgs.gov/twri9A. Chapters originally were published from 1997–1999; updates and revisions are ongoing and are summarized at http://water.usgs.gov/owq/FieldManual/mastererrata.html.]

Vecchia, A.V., 2003, Water-quality trend analysis and sampling design for streams in North Dakota: U.S. Geological Survey Water-Resources Investigations Report 03–4094, 79 p.

Vecchia, A.V., 2005, Water-quality trend analysis and sampling design for streams in the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1970–2001: U.S. Geological Survey Scientific Investigations Report 2005–5224, 60 p.

Appendixes

Appendix 1—Summary Information Relating to Quality-Control Data

Summary information is presented relating to quality-control data. Results for quality-control equipment blank and replicate samples collected during water years 1993–2015 are summarized in table 1–1. Spike recoveries for laboratory-spiked deionized-water blank samples collected during water years 1993–2015 are presented in table 1–2. Spike recoveries for laboratory-spiked stream-water blank samples collected during water years 1993–2015 are presented in table 1–3. For reference, aquatic-life standards (based on median hardness for water years 2011–15, Montana Department of Environmental Quality, 2012) are presented in table 1–4.

Evaluation of long-term spike-recovery data is particularly relevant to the long-term trend analysis. Spike-recoveries during water years 1993–2015 for laboratory-spiked deionized-water blank samples (table 1–2 and fig. 1–1) and laboratory-spiked stream-water samples (table 1–3 and fig. 1–2) indicate generally consistent recoveries over time, typically varying within plus or minus 10 percent of 100 percent recovery. However, before about water year 2000, spike recoveries for unfiltered-recoverable copper in spiked stream-water samples generally were near 100 percent (mean annual spike recovery for water years 1993–99 of 99.1 percent), whereas after about water year 2000, spike recoveries mostly were less than 100 percent (mean annual spike recovery for water years 2000–15 of 94.3 percent). Changes in spike recoveries in about water year 2000 probably were related to a change in about water year 2000 by the U.S. Geological Survey National Water Quality Laboratory from analysis of most metallic elements by graphite furnace atomic absorption spectrophotometry (Fishman, 1993) to inductively coupled plasma-mass spectrometry (Garbarino and Struzeski, 1998; Garbarino and others, 2006). The potential effects of temporal changes in spike recoveries on trend results were evaluated in exploratory analyses, as described in appendix 2.

Table 1–1. Summary information relating to quality-control samples (field equipment blank and replicate samples) collected at sampling sites in the upper Clark Fork Basin, Montana, water years 1993–2015.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. LRL, laboratory reporting level; SRL, study reporting level; RSD, relative standard deviation; µS/cm, microsiemen per centimeter at 25 degrees Celsius; NA, not applicable; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent or property, units of measurement	Summary information for field blank samples							Summary information for field replicate samples	
	Number of field blank samples	Number of field blank samples with detected concentrations greater than the LRL at the time of analysis	Percentage of field blank samples with detected concentrations greater than the LRL at the time of analysis	Maximum detected concentration for field blank samples	Median concentration in field blank samples with detected concentrations greater than the LRL at the time of analysis	SRL used in application of the time-series model	Percentage of detections in blank samples at concentrations greater than the SRL used in the application of the time-series model	Number of field replicate pairs	RSD,[1] in percent
Specific conductance, µS/cm	NA	NA	NA	NA	NA	NA	NA	162	0.1
Cadmium, filtered, µg/L	193	5	2.6	0.337	0.071	NA	NA	179	13.4
Cadmium, unfiltered-recoverable, µg/L	189	1	0.5	0.010	0.010	NA	NA	180	4.5
Copper, filtered,[2] µg/L	192	15	7.8	3.6	0.50	1.0	1.0	182	12.4
Copper, unfiltered-recoverable,[2] mg/L	189	11	5.8	3.0	1.0	1.0	2.1	180	9.0
Iron, filtered, µg/L	189	4	2.1	5.9	4.8	NA	NA	171	9.8
Iron, unfiltered-recoverable, µg/L	185	10	5.4	35.6	7.0	NA	NA	178	5.5
Lead, filtered, µg/L	193	6	3.1	0.600	0.101	NA	NA	178	11.0
Lead, unfiltered-recoverable, µg/L	189	10	5.3	0.16	0.05	NA	NA	180	16.3
Manganese, filtered, µg/L	188	22	11.7	0.62	0.36	NA	NA	183	5.7
Manganese, unfiltered-recoverable, µg/L	185	10	5.4	0.3	0.2	NA	NA	180	5.8
Zinc, filtered, µg/L	191	39	20.4	6.2	0.9	NA	NA	181	9.6
Zinc, unfiltered-recoverable,[2] µg/L	187	20	10.7	3.4	1.4	2.0	2.7	181	9.0
Arsenic, filtered,[2] µg/L	193	1	0.5	0.1	0.1	1.0	0.0	182	5.4
Arsenic, unfiltered-recoverable,[2] µg/L	189	3	1.6	0.1	0.1	1.0	0.0	181	6.8
Suspended sediment,[2] mg/L	NA	NA	NA	NA	NA	1	NA	170	9.1

[1]*RSD* is calculated according to the following equation (Taylor, 1987):

$$RSD = \frac{S}{\overline{X}} \times 100,$$

where

RSD is the relative standard deviation;

S is the standard deviation; and

$\overline{X}$ is the mean concentration for all replicate analyses.

[2]Property or constituent was analyzed for temporal trends.

Table 1–2. Summary information relating to quality-control samples (laboratory-spiked deionized-water blank samples) collected at sampling sites in the upper Clark Fork Basin, Montana, water years 1993–2015.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. F, filtered; UFR, unfiltered-recoverable]

Water year	Cadmium, F	Cadmium, UFR	Copper, F	Copper, UFR	Iron, F	Iron, UFR	Lead, F	Lead, UFR	Manganese, F	Manganese, UFR	Zinc, F	Zinc, UFR	Arsenic, F	Arsenic, UFR
Mean spike recovery, in percent (values in parentheses indicate 95 percent confidence intervals)														
1993	93.4 (85.9, 101)	97 (93.5, 101)	99.5 (95.9, 103)	101.7 (94.4, 109)	94 (90.0, 98.0)	103.3 (92.4, 114)	105.8 (99.5, 112)	100.5 (95.2, 106)	96.9 (96.3, 97.5)	95.6 (82.2, 109)	106.5 (99.7, 113)	96.3 (94.1, 98.5)	94 (89.6, 98.4)	102.6 (95.8, 109)
1994	97.5 (89.1, 106)	98.8 (90.6, 107)	101.1 (98.4, 104)	99.7 (94.3, 105)	100 (93.0, 107)	94.6 (84.2, 105)	100.5 (98.5, 102)	99.1 (94.3, 104)	95.7 (90.8, 100)	101.5 (96.2, 107)	106.5 (95.8, 117)	102.6 (91.5, 114)	100.6 (95.6, 106)	109.3 (104, 114)
1995	100 (97.3, 103)	101.3 (97.5, 105)	102.7 (101, 105)	97.6 (92.3, 103)	102.2 (97.8, 107)	93.8 (87.9, 99.7)	102.3 (97.7, 107)	100.8 (96.6, 105)	96.5 (92.0, 101)	98.5 (93.1, 104)	102.3 (97.1, 108)	101.5 (97.1, 106)	103.9 (99.1, 109)	106.8 (103, 110)
1996	95.3 (92.2, 98.4)	82.3 (79.7, 84.9)	99.2 (91.4, 107)	99.6 (93.5, 106)	89.8 (76.0, 104)	90.8 (70.9, 111)	100.5 (93.3, 108)	97.4 (80.2, 115)	89.2 (77.9, 100)	96.5 (91.6, 101)	96.1 (84.3, 108)	87.8 (82.8, 92.8)	89.7 (77.1, 102)	104.1 (101, 107)
1997	98.5 (92.1, 105)	85.7 (77.7, 93.7)	101.1 (86.2, 116)	106.4 (82.0, 131)	94.7 (78.5, 111)	96.1 (80.2, 112)	101 (93.4, 109)	101.1 (88.9, 113)	90.3 (82.7, 97.9)	99.3 (95.8, 103)	97.9 (78.1, 118)	92.7 (86.4, 99.0)	93.9 (87.8, 100)	106.1 (104, 108)
1998	104 (93.8, 114)	97.4 (87.0, 108)	100.4 (93.4, 107)	103.4 (98.8, 108)	101.8 (90.7, 113)	95.7 (89.9, 102)	100.2 (91.8, 109)	104.8 (88.8, 121)	102.8 (94.4, 111)	99 (92.1, 106)	95.2 (85.9, 104)	101.3 (86.9, 116)	91.5 (87.3, 95.7)	105.4 (99.2, 112)
1999	100.9 (92.6, 109)	103.4 (99.9, 107)	107.5 (99.5, 116)	105 (102, 108)	97.7 (94.3, 101)	96.5 (90.0, 103)	97.4 (87.9, 107)	96.2 (85.2, 107)	96 (91.8, 100)	95.9 (86.3, 106)	96.9 (92.9, 101)	93.3 (88.9, 97.7)	108.9 (95.4, 122)	102.9 (97.8, 108)
2000	103.8 (97.3, 110)	105 (96.0, 114)	104 (96.0, 112)	100.3 (92.4, 108)	97.4 (92.3, 102)	100.6 (89.2, 112)	98.3 (88.9, 108)	102.6 (97.3, 108)	100.8 (93.3, 108)	103.2 (96.8, 110)	107.8 (95.8, 120)	102.6 (90.0, 115)	101.6 (95.3, 108)	101.4 (95.1, 108)
2001	102.9 (98.9, 107)	107.9 (101, 115)	105.2 (98.6, 112)	96.8 (93.7, 99.9)	101.3 (95.5, 107)	98.3 (86.7, 110)	97.3 (91.9, 103)	96.4 (93.7, 99.1)	101.9 (79.0, 125)	103.7 (89.9, 118)	102 (87.9, 116)	99.1 (82.7, 116)	99.2 (92.3, 106)	97.7 (86.6, 109)
2002	101.1 (98.8, 103)	97.6 (96.3, 98.9)	99.4 (95.0, 104)	98.8 (96.7, 101)	95.1 (89.3, 101)	102.3 (93.0, 112)	98.5 (89.9, 107)	96.9 (90.5, 103)	98.5 (95.4, 102)	96.5 (88.8, 104)	103.9 (94.4, 113)	98.3 (91.8, 105)	105.1 (95.8, 114)	97.9 (93.0, 103)
2003	98.6 (92.6, 105)	97.5 (94.1, 101)	100.4 (93.0, 108)	97.6 (93.2, 102)	101.6 (96.4, 107)	93.1 (87.4, 8.8)	97.2 (92.3, 102)	96 (93.9, 98.1)	95.8 (90.7, 101)	96.6 (79.7, 114)	101.4 (89.8, 113)	99.1 (93.2, 105)	87.9 (71.3, 104)	96.6 (78.5, 115)
2004	97.4 (95.6, 99.2)	100 (98.6, 101)	98.9 (92.7, 105)	99.6 (95.4, 104)	101 (96.3, 106)	96.1 (88.8, 103)	96 (91.9, 100)	98.9 (97.3, 100)	99.1 (92.3, 106)	98.6 (90.6, 107)	102 (91.7, 112)	100 (96.3, 104)	101 (75, 127)	102 (93.6, 110)
2005	102 (97.3, 106)	97.5 (88.1, 107)	102 (97.4, 107)	97.6 (88.4, 107)	97.6 (90.5, 105)	100 (95.2, 105)	101 (95.5, 106)	104 (99.4, 108)	93.8 (82.2, 105)	102 (86.4, 117)	102 (88.3, 116)	96.1 (83.5, 109)	97.4 (95.5, 99.3)	101 (90.7, 111)
2006	100 (92.6, 107)	98.9 (94.1, 104)	102 (97.7, 107)	98.7 (93.8, 104)	106 (101, 112)	103 (95.4, 111)	99 (89.3, 109)	98 (91.2, 105)	97 (90.7, 103)	105 (95.3, 115)	105 (95.4, 115)	94.9 (90.1, 100)	95.2 (89.2, 101)	98.5 (94.7, 102)
2007	107 (103, 112)	103 (94.4, 111)	105 (99.2, 111)	98.4 (86.9, 110)	99.9 (92.1, 108)	104 (98.5, 110)	99.6 (93.9, 105)	103 (100, 106)	107 (99.9, 114)	107 (97.0, 116)	107 (102, 113)	103 (96.5, 110)	105 (96.6, 114)	102 (95.2, 109)
2008	102 (88.2, 116)	101 (91.9, 110)	105 (88, 121)	97.9 (87.2, 109)	103 (95.9, 110)	101 (96.5, 106)	101 (89, 112)	101 (98, 105)	102 (92.9, 111)	102 (92.5, 112)	99.8 (87.9, 112)	103 (96, 111)	103 (89.2, 117)	102 (93.9, 110)
2009	102 (97.4, 107)	97.2 (93.6, 101)	102 (92.0, 113)	96 (94.0, 97.0)	102 (91.4, 112)	104 (78.8, 130)	102 (96.0, 107)	98.4 (96.1, 101)	105 (103, 106)	99.7 (94.6, 105)	111 (104, 118)	93.3 (88.5, 98.1)	101 (92.3, 110)	97 (94.9, 99.1)
2010	106 (94.9, 117)	100 (88.4, 112)	97.2 (84.9, 109)	98.6 (84.0, 113)	108 (101, 115)	102 (95.8, 108)	102 (91.5, 113)	102 (91.0, 113)	103 (95.2, 111)	105 (97.2, 112)	113 (94.7, 132)	101 (89.6, 113)	105 (96.7, 113)	102 (89.7, 114)

Table 1–2. Summary information relating to quality-control samples (laboratory-spiked deionized-water blank samples) collected at sampling sites in the upper Clark Fork Basin, Montana, water years 1993–2015.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. F, filtered; UFR, unfiltered-recoverable]

Water year	Cadmium, F	Cadmium, UFR	Copper, F	Copper, UFR	Iron, F	Iron, UFR	Lead, F	Lead, UFR	Manganese, F	Manganese, UFR	Zinc, F	Zinc, UFR	Arsenic, F	Arsenic, UFR
Mean spike recovery, in percent (values in parentheses indicate 95 percent confidence intervals)—Continued														
2011	105 (97.9, 111)	95.7 (92.4, 99)	96.2 (89.4, 103)	93.9 (91.6, 96.2)	111 (89.3, 132)	107 (98.2, 117)	106 (98.8, 113)	99.8 (98.4, 101)	101 (97.0, 104)	98.9 (97.8, 100)	108 (94.3, 122)	96.1 (92.2, 100)	105 (102, 109)	94.7 (90.2, 99.3)
2012	102 (93.2, 112)	101 (95.1, 108)	98.4 (93.1, 104)	100 (92.5, 107)	105 (102, 108)	106 (96.2, 117)	102 (96.8, 106)	103 (98.4, 107)	105 (101, 110)	101 (95.4, 106)	103 (96.5, 109)	100 (94.9, 106)	98.1 (90.4, 106)	101 (94.3, 108)
2013	96.3 (92.4, 100)	96.6 (92.9, 100)	92.4 (87, 97.9)	96.3 (92.6, 100)	103 (95.5, 111)	105 (98.2, 112)	97.5 (92.3, 103)	99.9 (97.1, 103)	98.1 (92.3, 104)	98.5 (94.8, 102)	98.6 (90.9, 106)	95.2 (91.7, 98.7)	98 (93.1, 103)	99.3 (96, 103)
2014	99.4 (95.1, 104)	101 (99.0, 104)	98.1 (91.0, 105)	100 (98.8, 102)	103 (95.8, 111)	103 (99.7, 106)	102 (100, 104)	103 (100, 107)	99.2 (91.6, 107)	100 (97.7, 103)	110 (103, 117)	101 (97.1, 104)	94.7 (87.6, 102)	102 (99.0, 105)
2015	98.7 (95.2, 102)	102 (94, 110)	101 (93.9, 108)	105 (90.1, 120)	103 (95.3, 111)	103 (101, 106)	99.7 (96.7, 103)	100 (89.6, 111)	104 (99.2, 108)	110 (97.5, 122)	104 (99.5, 109)	118 (103, 132)	97.3 (89.2, 105)	99.8 (91.7, 108)

Table 1–3. Summary information relating to quality-control samples (laboratory-spiked stream-water samples) collected at sampling sites in the upper Clark Fork Basin, Montana, water years 1993–2015.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. F, filtered; UFR, unfiltered-recoverable]

Water year	Cadmium, F	Cadmium, UFR	Copper, F	Copper, UFR	Iron, F	Iron, UFR	Lead, F	Lead, UFR	Manganese, F	Manganese, UFR	Zinc, F	Zinc, UFR	Arsenic, F	Arsenic, UFR
Mean spike recovery, in percent (values in parentheses indicate 95 percent confidence intervals)														
1993	97.1 (92.3, 102)	98.1 (95.2, 101)	97.4 (95.8, 99.0)	97.2 (92.3, 102)	94.6 (86.7, 103)	102.2 (94.4, 110)	104.7 (98.5, 111)	96 (93.0, 99.0)	95.7 (92.1, 99.3)	100.2 (96.4, 104)	105.7 (93.4, 118)	95.7 (92.2, 99.2)	95.2 (92.0, 98.3)	99.9 (96.5, 103)
1994	101.3 (97.5, 105)	97.9 (94.4, 101)	96.6 (93.3, 99.8)	98.4 (91.1, 106)	98.2 (94.8, 102)	99.3 (90.6, 108)	103 (101, 105)	99.3 (95.6, 103)	98.1 (95.4, 101)	100.4 (95.4, 105)	97.5 (92.4, 102)	106 (95.4, 117)	97.3 (90.4, 104)	106.9 (101, 113)
1995	101.3 (96.7, 106)	102.9 (98.0, 108)	99.8 (96.2, 103)	98 (92.7, 103)	99.5 (96.1, 103)	101.4 (96.2, 107)	102.9 (98.6, 107)	100 (96.7, 103)	97.4 (92.9, 102)	103.8 (99.0, 109)	104.7 (101, 108)	101.1 (99.1, 103)	103.8 (94.6, 113)	102.2 (97.1, 107)
1996	100.2 (91.5, 109)	88.4 (57.8, 119)	101.1 (91.9, 110)	100.3 (92.3, 108)	93.8 (73.3, 114)	101.5 (88.5, 114)	105.1 (90.4, 120)	105.6 (98.4, 113)	90.3 (79.1, 102)	99.5 (92.9, 106)	103.2 (90.2, 116)	99.3 (74.8, 124)	105.9 (94.4, 117)	102.8 (96.0, 110)
1997	98.1 (83.5, 113)	84.3 (75.0, 93.6)	97.3 (88.3, 106)	100.5 (71.9, 129)	99.3 (81.0, 118)	97.5 (78.2, 117)	100.8 (91.6, 110)	102.1 (99.1, 105)	93 (84.0, 102)	99.8 (94.5, 105)	97 (89.9, 104)	92.7 (74.4, 111)	93.3 (73.5, 113)	107.1 (99.9, 114)
1998	104.4 (97.3, 112)	99.5 (92.7, 106)	97.2 (90.6, 104)	99.1 (88.4, 110)	97.5 (82.8, 112)	101.8 (90.2, 113)	102.2 (94.3, 110)	105 (92.9, 117)	99.5 (85.8, 113)	101.5 (98.0, 105)	99.5 (89.1, 110)	98.8 (85.6, 112)	90.1 (85.5, 94.7)	104 (95.8, 112)
1999	102.6 (92.4, 113)	103 (100, 106)	102.7 (89.1, 116)	100.5 (97.5, 104)	97.2 (93.5, 101)	99.9 (90.6, 109)	100.2 (94.0, 106)	101.1 (93.7, 108)	99.8 (92.8, 107)	98.8 (89.3, 108)	98.6 (95.7, 102)	96.2 (91.1, 101)	105.2 (97.5, 113)	103.6 (96.4, 111)
2000	104.2 (100, 108)	98.1 (88.9, 107)	101.6 (97.3, 106)	94.6 (87.7, 102)	96.5 (88.0, 105)	98 (88.3, 108)	101.4 (97.3, 106)	105.3 (103, 108)	97.3 (83.3, 111)	101.7 (91.4, 112)	101.5 (90.9, 112)	97.8 (91.1, 104)	102.5 (97.5, 108)	98.9 (87.8, 110)
2001	103.2 (100, 106)	105.8 (95.9, 116)	106.8 (104, 110)	91.8 (87.7, 95.9)	95.8 (91.4, 100)	101.6 (92.1, 111)	99.7 (95.2, 104)	97.3 (95.3, 99.3)	100 (84.4, 116)	100.9 (90.3, 112)	100.8 (85.7, 116)	96.9 (75.9, 118)	102.8 (95.1, 110)	100.1 (96.7, 104)
2002	106 (97.5, 114)	102 (98.6, 101)	97.3 (91.2, 103)	96.9 (92.9, 101)	92.6 (83.3, 102)	107.1 (103, 111)	101.4 (91.9, 111)	98.9 (92.2, 106)	98.3 (92.5, 104)	94.3 (88.4, 100)	101.3 (92.6, 110)	95.8 (89.9, 102)	105.8 (97.1, 114)	99.9 (86.0, 114)
2003	100.5 (91.4, 110)	99 (94.4, 104)	95.8 (88.9, 103)	91.6 (89.7, 93.5)	106.4 (100, 113)	96.7 (91.6, 102)	96 (90.2, 102)	96.8 (93.7, 99.9)	93.9 (78.8, 109)	99.3 (86.2, 112)	98.4 (93.6, 103)	93 (87.5, 98.5)	94.6 (80.2, 109)	108.6 (100, 117)
2004	101 (94.2, 108)	101 (100, 103)	95.4 (93.8, 97)	93.8 (89.5, 98.1)	104 (99.5, 108)	111 (91.2, 130)	98.7 (93, 104)	100 (98.6, 102)	103 (89.8, 117)	96 (91.8, 100)	100 (95.3, 105)	94.4 (91, 97.8)	97.3 (86.9, 108)	112 (106, 118)
2005	97.8 (62.7, 133)	98.2 (88.5, 108)	93.6 (57.9, 129)	93 (84.8, 101)	102 (95.9, 108)	99.3 (95.6, 103)	102 (96.1, 109)	103 (99.7, 106)	88.3 (78.3, 98.3)	97.5 (87.3, 108)	94.3 (60.8, 128)	91.6 (80.8, 102)	103 (98.3, 107)	104 (101, 108)
2006	104 (99.0, 108)	99.6 (94.7, 104)	101 (96.7, 104)	94.8 (91.0, 98.6)	105 (102, 109)	102 (93.6, 110)	102 (94.2, 111)	100 (92.9, 106)	94.9 (88.2, 102)	106 (97.9, 113)	108 (93.3, 123)	91.2 (87.8, 94.6)	96.5 (89.0, 104)	99.1 (94.9, 103)
2007	108 (102, 114)	98 (92.2, 104)	100 (89.8, 110)	96.3 (91.8, 101)	107 (103, 111)	103 (94.7, 112)	109 (103, 115)	104 (102, 107)	106 (100, 113)	101 (96.1, 106)	104 (95.7, 113)	98 (89.2, 107)	106 (100, 113)	102 (98.2, 106)
2008	101 (91, 112)	97 (93.6, 100)	98.9 (92, 106)	92.8 (86.4, 99.1)	105 (94.1, 117)	99.4 (92, 107)	100 (91.3, 109)	103 (99.5, 106)	98.9 (90.3, 108)	98.4 (92.5, 104)	106 (88.1, 124)	95.7 (93.1, 98.2)	100 (90.2, 110)	101 (98.5, 104)
2009	106 (101, 112)	94.7 (89.5, 99.8)	96.2 (91.2, 101)	91.4 (87.8, 95.0)	107 (89.7, 124)	102 (86.9, 118)	100 (97.0, 103)	100 (98.8, 101)	97 (88.0, 106)	92.8 (81.7, 104)	114 (104, 124)	89.8 (80.4, 99.2)	106 (97.7, 114)	100 (89.6, 111)
2010	110 (87.6, 132)	98.2 (87.1, 109)	93.8 (83.6, 104)	96.5 (84.4, 108)	105 (91.7, 119)	111 (103, 118)	101 (87.7, 115)	104 (91.5, 116)	104 (93.3, 114)	98.7 (86.4, 111)	109 (101, 118)	94 (81.3, 107)	106 (96.0, 116)	102 (90.1, 113)

Table 1–3. Summary information relating to quality-control samples (laboratory-spiked stream-water samples) collected at sampling sites in the upper Clark Fork Basin, Montana, water years 1993–2015.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. F, filtered; UFR, unfiltered-recoverable]

Water year	Cadmium, F	Cadmium, UFR	Copper, F	Copper, UFR	Iron, F	Iron, UFR	Lead, F	Lead, UFR	Manganese, F	Manganese, UFR	Zinc, F	Zinc, UFR	Arsenic, F	Arsenic, UFR
Mean spike recovery, in percent (values in parentheses indicate 95 percent confidence intervals)—Continued														
2011	104 (99.2, 109)	93.9 (91.5, 96.3)	96.6 (79.9, 113)	88.3 (85.4, 91.2)	108 (92.0, 124)	101 (85.2, 117)	104 (98.8, 110)	96.5 (94.5, 98.4)	98.2 (92.2, 104)	91.3 (88.3, 94.2)	102 (90.2, 114)	86.7 (80.7, 92.7)	106 (101, 111)	94.7 (90.5, 99.0)
2012	107 (104, 110)	98.8 (91.9, 106)	94 (90.9, 97)	93.9 (87.2, 101)	108 (102, 114)	100 (98.6, 102)	102 (97.9, 107)	101 (96.3, 105)	101 (97.7, 104)	95.5 (88, 103)	102 (95.2, 109)	89.8 (82.4, 97.2)	104 (101, 106)	97.5 (91.8, 103)
2013	94.8 (90.4, 99.3)	91.3 (87, 95.7)	90.9 (86, 95.8)	90 (87.5, 92.4)	102 (94.8, 110)	101 (92.6, 110)	101 (92.8, 108)	96.7 (92.3, 101)	97.2 (95.4, 99)	93 (84.9, 101)	99.5 (92, 107)	84.1 (79.5, 88.7)	99.5 (91.2, 108)	94.9 (91, 98.8)
2014	103 (95.6, 110)	95.5 (92.0, 99.0)	96.6 (90.1, 103)	93.8 (89.8, 97.8)	97.6 (92.7, 103)	101 (92.7, 109)	100 (96.7, 103)	99.7 (94.9, 104)	97.1 (90.4, 104)	94.8 (89.3, 100)	101 (94.2, 108)	88.9 (82.7, 94.6)	92.4 (82.7, 102)	97.7 (93.5, 102)
2015	104 (97.6, 111)	106 (96.6, 115)	97.4 (92.3, 102)	97.8 (92.9, 103)	93.5 (83.2, 104)	104 (101, 106)	103 (101, 105)	106 (96.0, 115)	102 (98.3, 105)	101 (92.0, 110)	93.8 (86.2, 101)	98.1 (88.9, 107)	96.8 (86.5, 107)	104 (87.3, 121)

Table 1–4. Aquatic-life standards (based on median hardness for water years 2011–15) for selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. $CaCO_3$, calcium carbonate]

Sampling site number (fig. 1, table 1)	Abbreviated sampling site name (table 1)	Aquatic-life standards (Montana Department of Environmental Quality, 2012), in micrograms per liter								
		Median hardness for water years 2011–15, in milligrams per liter as $CaCO_3$	Cadmium		Copper		Lead		Zinc	
			Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Chronic
8	Silver Bow Creek at Warm Springs	170	3.66	0.401	23.1	14.7	160	6.25	188	188
11	Clark Fork near Galen	164	3.53	0.390	22.3	14.2	153	5.97	182	182
14	Clark Fork at Deer Lodge	200	4.32	0.452	26.9	16.9	197	7.69	216	216
15	Clark Fork near Garrison	202	4.36	0.456	27.2	17.0	199.8	7.79	217	217
16	Clark Fork at Goldcreek	165	3.54	0.391	22.4	14.3	154	6.00	183	183
18	Clark Fork near Drummond	190	4.09	0.435	25.6	16.1	184	7.18	206	206
20	Clark Fork at Turah Bridge	132	2.82	0.331	18.1	11.8	116	4.51	151	151
22	Clark Fork above Missoula	109	2.33	0.288	15.2	10.0	91	3.55	129	129

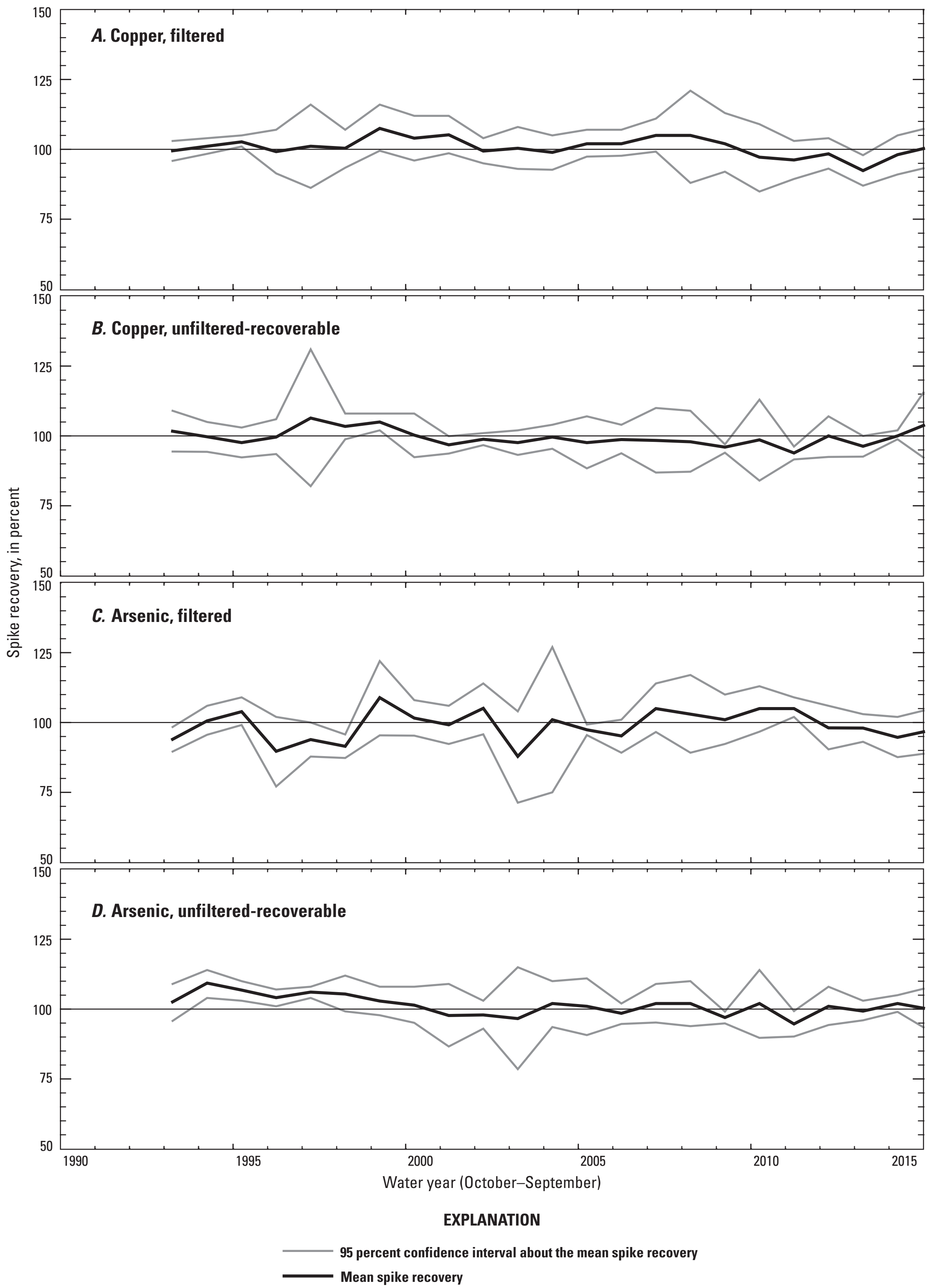


Figure 1–1. Spike recoveries for laboratory-spiked deionized-water blank samples, water years 1993–2015. *A*, copper, filtered; *B*, copper, unfiltered-recoverable; *C*, arsenic, filtered; *D*, arsenic, unfiltered-recoverable.

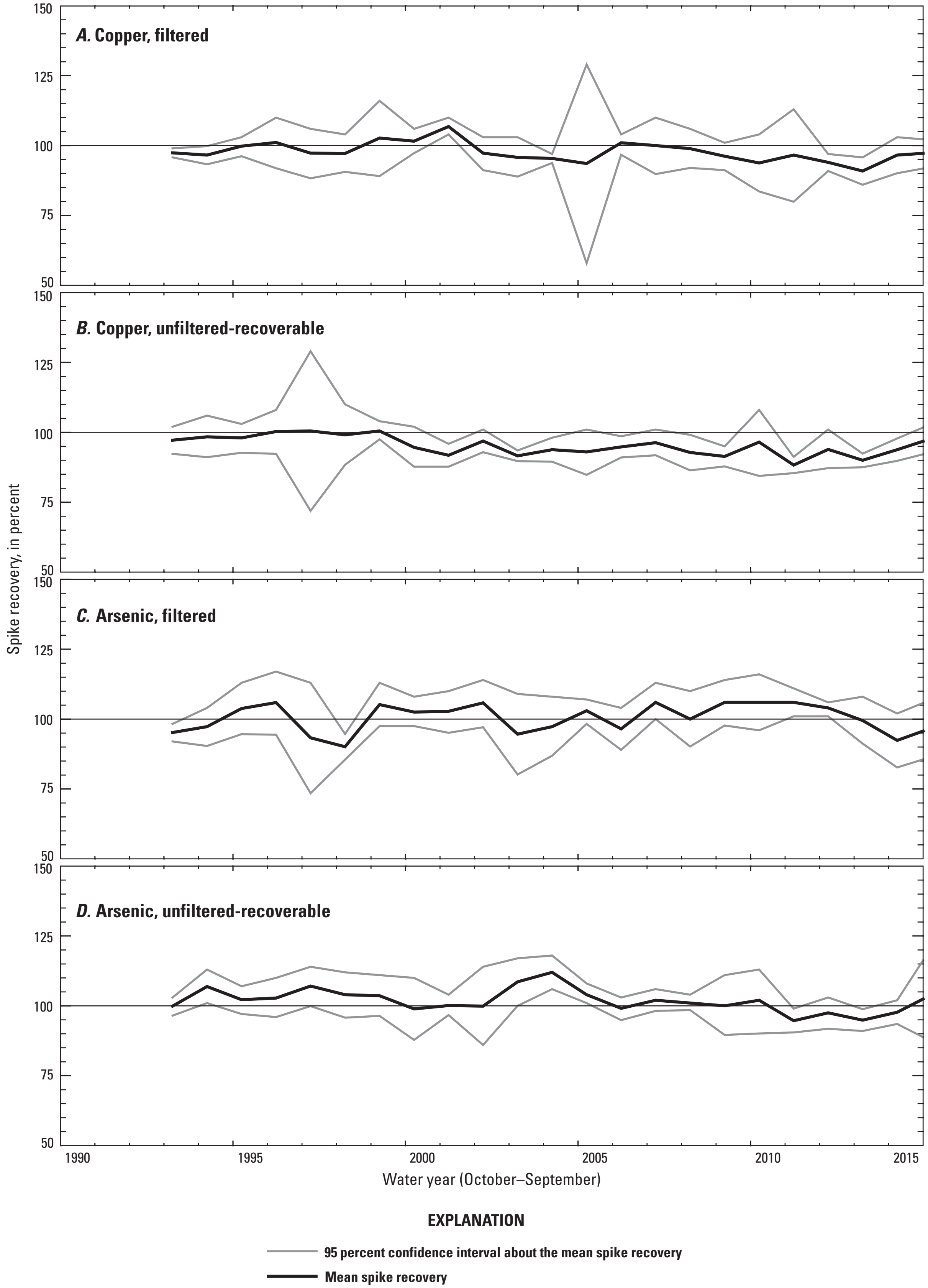


Figure 1–2. Spike recoveries for laboratory-spiked stream-water samples, water years 1993–2015. *A*, copper, filtered; *B*, copper, unfiltered-recoverable; *C*, arsenic, filtered; *D*, arsenic, unfiltered-recoverable.

Appendix 2—Summary of the Time-Series Model as Applied in this Study

This appendix presents somewhat detailed information on theoretical and computational aspects of the time-series model (TSM). Also, specific aspects of the application of the TSM in this study are described.

Theoretical and Computational Information

The theory and parameter estimation for the TSM are described in detail in Vecchia (2005). In the TSM, log-transformed concentration data are partitioned into several components according to equation 1:

$$\log(C) = M_C + ANN_C + SEAS_C + TREND + HFV_C \qquad (1)$$

where

log denotes the base-10 logarithm;
C is the concentration, in milligrams per liter;
M_C is the long-term mean of the log-transformed concentration, as the base-10 logarithm of milligrams per liter;
ANN_C is the annual concentration anomaly (dimensionless);
$SEAS_C$ is the seasonal concentration anomaly (dimensionless);
$TREND$ is the concentration trend (dimensionless); and
HFV_C is the high-frequency variability of the concentration (dimensionless).

In equation 1, ANN_C, $SEAS_C$, and HFV_C terms represent natural variability in concentration for different timescales. The term ANN_C is an estimate of the interannual variability in concentration that can be attributed to long-term variability in streamflow. The term ANN_C is quantified by relating annual means (for the 365-day period immediately before a given sample) of log concentration and log streamflow to long-term means (for the entire period of record). Extended droughts and wet periods can change the chemical and suspended-material composition of streamflow by changing the degree of contact between surface runoff and soil particles, availability of particulate material in stream channels and near-stream areas, and the relative composition of runoff among groundwater, overland flow, and subsurface flow (Vecchia, 2005).

The term $SEAS_C$ is an estimate of the seasonal variability in concentration that can be attributed to seasonal variability in streamflow or to factors other than variability in streamflow. The term $SEAS_C$ is quantified by relating seasonal means (for the 30-day period immediately before a given sample was collected) of log concentration and log streamflow to annual means (for the 365-day period immediately before a given sample was collected). For example, the seasonal snow-accumulation and snowmelt cycle causes seasonal fluctuations in streamflow and water quality. Seasonal differences in the relative amount of streamflow that comes from natural sources compared to anthropogenic contributions (such as wastewater inputs) also might cause seasonal fluctuations in concentration that are more complicated than a simple relation between concentration and streamflow could produce.

The term HFV_C is an estimate of the variability in concentration for timescales that are smaller than the seasonal timescale (timescales of several days to several weeks). Thus, high-frequency variability is the variability that remains after the removal of seasonal and annual anomalies and trends. The term HFV_C is quantified by relating log concentration and log streamflow for the day of sampling to log concentration and log streamflow for each of the two 10-day periods immediately before a given sample. Short-term changes in meteorological conditions might cause high-frequency variability in concentration and streamflow. The high-frequency variability depends on a periodic autoregressive moving average model that accounts for the presence of serial correlation among concentrations (for example, the tendency for high or low values to persist for several days to several weeks before returning to normal levels; Vecchia, 2005).

The term *TREND* is an estimate of the long-term systematic changes in concentration during the study period that are unrelated to long-term variability in streamflow. For this report, a significant trend might indicate changes in the extent to which mining wastes affect chemical composition of surface water or changes in other activities that can change the amount of suspended sediment or trace elements that reach the stream. The term *TREND* consists of piecewise monotonic trends during specified trend-analysis periods. The overall significance of *TREND* (determined by using the generalized likelihood ratio principle; appendix 1 of Vecchia, 2005) specifies whether there were any significant changes during any of the specified trend-analysis periods. If *TREND* was determined to be nonsignificant for a given sampling-site and constituent combination, the trends for all of the specified trend-analysis periods were considered nonsignificant, and *p*-values were not reported. If *TREND* was determined to be significant for a given sampling-site and constituent combination, the slope coefficient (γ; appendix 1 of Vecchia, 2005) for the trend for each specified trend-analysis period was used to determine the significance and magnitude of the trend for the specified trend-analysis period. The null hypothesis in the test for trend significance in a given trend-analysis period is that there is no trend (that is, $\gamma = 0$). If the two-tailed *p*-value for γ was less than the selected alpha level (0.01 in this report), the null hypothesis was rejected, and the trend was determined to be significant. Determination of a nonsignificant trend (that is, a *p*-value greater than 0.01) does not imply that the null hypothesis is accepted (that is, that there is no trend). It indicates that in the statistical framework of the analysis, a significant trend was not detected. The magnitude of the trend for a specified trend-analysis period is expressed as the percent difference between the geometric mean concentration at the end of the period and the geometric mean concentration at the start of the period and is determined by the equation

$$\%\Delta FAC = 100\left(10^{\gamma} - 1\right), \quad (2)$$

where

$\%\Delta FAC$ is the percentage change in the geometric mean of the flow-adjusted concentration, and

γ is the slope coefficient of the trend for the specified trend-analysis period in log-transformed units.

Log-transformed concentrations that have ANN_C and $SEAS_C$ removed are referred to in this report as "flow-adjusted concentrations." By using equation 1, the flow-adjusted concentration is defined as

$$FAC = \log(C) - ANN_C - SEAS_C = M_C + TREND + HFV_C \quad (3)$$

where *FAC* is the flow-adjusted value, as the base-10 logarithm of the original units of measurement. The *FAC*s defined by equation 3 are analogous to *FACs* defined in other publications as the residuals from a regression model that relates concentration to concurrent daily streamflow (Helsel and Hirsch, 2002); however, the TSM approach generally is more effective than a regression-based approach for removing streamflow-related variability (Vecchia, 2005). Time-series plots showing *FAC*s along with the fitted trend ($M_C + TREND$) illustrate long-term changes in geometric mean concentration that might indicate changes in effects of mining wastes on water-quality in the selected watersheds.

The key to making TSM a powerful trend-analysis tool is that the entire time series of daily streamflow data are used in the model, not just streamflow for the days when concentration samples are available. The model uses a three-per-month, or approximately 10-day, sampling frequency. Each month is divided into three intervals—days 1–10, days 11–20, and day 21 through the end of the month. If a water-quality sample is available for a particular interval, it is paired with daily streamflow for the same day of the water-quality sample. If no water-quality sample is available, the concentration value for the interval is missing, and streamflow for the middle of the interval (day 5, 15, or 25) is used. If more than one concentration sample is available for the interval, the value nearest to the midpoint of the interval is used. The log-transformed streamflow time series (consisting of three values per month) is divided into an annual anomaly, seasonal anomaly, and high-frequency variability according to the following equation:

$$\log(Q) = M_Q + ANN_Q + SEAS_Q + HFV_Q \quad (4)$$

where

Q is daily mean streamflow, in cubic feet per second;

M_Q is the mean of the log-transformed streamflow for the entire trend-analysis period, as the base-10 logarithm of cubic feet per second;

ANN_Q is the annual streamflow anomaly, computed as the 1-year lagged moving average of $\log(Q) - M_Q$ (dimensionless);

$SEAS_Q$ is the seasonal streamflow anomaly, computed as the 3-month lagged moving average of $\log(Q) - M_Q - ANN_Q$ (dimensionless); and

HFV_Q is the high-frequency streamflow variability, computed as $\log(Q) - M_Q - ANN_Q - SEAS_Q$ (dimensionless).

The water-quality time-series model (equation 1) is directly tied to the streamflow time-series model because the streamflow anomalies (ANN_Q and $SEAS_Q$ from equation 4) are used as predictor variables for concentration (equation 1). For example, ANN_C is assumed to equal a constant coefficient (estimated from the TSM) times ANN_Q. The different scales of streamflow variability often affect concentration in different ways. The relation between HFV_C and HFV_Q can be particularly complicated, changing depending on the time of year and the degree of serial correlation in the concentration data and cross-correlation between concentration and streamflow.

Specific Aspects of the Application of the Time-Series Model in this Study

The TSM residuals for each sampling-site and constituent combination were examined graphically to verify the model assumptions that the residuals had constant variance, were serially uncorrelated, and were approximately normally distributed. Because of the application of the TSM to the large number of sampling-site and constituent combinations and practical considerations to keep the trend periods comparable among sampling sites and constituents, some minor deviations of the residuals from model assumptions were tolerated. Such deviations included small changes in residual variance through time and short-term (about 1–2 years) unresolved trending in the residuals. In cases where unresolved residual trends were considered to be large enough to possibly affect the magnitudes and significance levels of reported fitted trends, more complicated trend models were tested, and in all cases the more complicated models did not substantially affect the overall descriptions of the trends and also did not change the general findings and conclusions of this report. Thus, the reported TSM results were judged to provide acceptable fits representative of linearity through nearly all of the range in FACs for a given sampling-site and constituent combination. Standard errors of estimates (SEEs) for the TSM analyses are presented in table 2–1. In this report, SEEs are expressed in percent and were converted from log units by using procedures described by Tasker (1978). Mean SEEs for all trace elements combined range from 20.8 to 50.7 percent. Mean SEEs for unfiltered-recoverable copper and arsenic concentrations are 48.3 and 27.3 percent, respectively. Mean SEE for suspended-sediment concentration (65.2 percent) is substantially higher than mean SEEs for trace elements. The SEEs indicate reasonably accurate definition of concentration and streamflow relations for the purpose of trend analysis; however, a higher mean SEE for suspended sediment than mean SEEs for trace elements indicates lower confidence in results. For each sampling-site and constituent combination, the fit of the TSM can be assessed by examination of the fitted trends in relation to FACs that are shown in figures 3–1 through 3–7 in appendix 3. The distribution of FACs about the fitted trend lines shows the extent to which the residuals might exhibit nonconstant variance or unresolved trends.

Application of the TSM in this study generally followed the methods applied by Sando and others (2014) who reported water-quality trends for 22 sampling sites in the upper Clark Fork Basin for water years 1996–2010. However, two factors might contribute to differences between Sando and others (2014) and this study: (1) this study included additional data collected after the study period of Sando and others (2014), and (2) this study included preliminary dummy trend periods that were inserted prior to period 1. The additional data after the study period of Sando and others (2014) represent an increase of about 25 percent and provide improvement in definition of concentration and streamflow relations used in determining FACs. Also, during exploratory analysis for this study, close scrutiny of the fitted trends reported by Sando and others (2014) indicated that in some cases the fitted trend values at the start of period 1 (1996) were not precisely centered at the median FAC at the start of period 1. In this study, dummy trend periods were inserted before period 1 to more precisely center the 1996 fitted trend values at the median FAC. The combination of the two factors (inclusion of additional data and insertion of preliminary dummy trends) sometimes resulted in generally minor differences in the fitted trend lines between this report and Sando and others (2014). The trend results of this report supersede the trend results of Sando and others (2014).

Exploratory analyses were conducted to investigate two ancillary factors that might affect trend results, including potential effects of (1) temporal changes in spike recoveries (as discussed in appendix 1) and (2) diel cycling of trace elements. The potential effects of temporal changes in spike recoveries (as discussed in appendix 1) on trend results were evaluated by using two approaches: (1) exploratory trend analysis with inclusion of a step trend in the trend model and (2) exploratory trend analysis on constituent concentrations adjusted based on annual mean spike recoveries. For the exploratory step-trend approach, a step trend for the period water years 1996–99 was included in the TSM model for each sampling-site and constituent combination, in addition to including trends for periods 1–4. Inclusion of a step trend allowed evaluation of whether there was a distinct change in data structure between pre-2000 and post-2000 data that might have affected trend results. Results of the exploratory step-trend analysis indicated that among all sampling-site and constituent combinations, statistically significant step trends were infrequently detected (less than 20 percent of analyses). In all cases of statistically significant step trends, the difference in the percent change from the start of period 1 to the end of period 4 between the exploratory analysis including the step trend and the reported analysis without the step trend was less than 5 percent. Thus, it was concluded that temporal changes in spike recoveries did not have a substantial effect on the overall trend results and the study objectives of evaluating relative spatial and temporal changes in FACs in the upper Clark Fork Basin as a whole. For the exploratory spike-recovery adjustment approach, constituent concentrations for each year were adjusted by multiplying the concentrations times the annual mean spike recovery for laboratory-spiked stream-water samples; then exploratory trend analysis was done. Results of the exploratory spike-recovery adjustment analysis were similar to the results for the exploratory step-trend approach and resulted in the same general conclusion that temporal differences in spike recoveries had minor effects on trend results.

An important consideration in trend analysis for trace elements is potential effects of diel cycling in trace-element concentrations. Complex biogeochemical processes affected by the daily solar photocycle produce regular and dynamic changes in many physical and chemical characteristics of streams (Nimick and others, 2011). In some streams (including some of the sampling sites in this study), the biogeochemical processes can result in diel variability in trace-element concentrations (Nimick and others, 2003).

Diel cycling in trace-element concentrations has the potential to affect trend results if (1) there is strong diel cycling for a given sampling-site and constituent combination and (2) there is a systematic temporal bias in the dataset with respect to the time of day of sampling. During exploratory analysis, potential effects of diel cycling on the trend results were quantitatively evaluated by including decimal day (time of sampling) as an ancillary variable in the trend models. The decimal day variable indicates the strength of diel cycling for a given sampling-site and constituent combination and also allows evaluation of the effect of temporal variability in time of sampling on the trend results. Although some sampling-site and constituent combinations had statistically significant diel cycling, in no case did the inclusion of the decimal day variable in trend models provide substantially different trend results from the reported results. Thus, potential effects on trend results of diel cycling of trace elements were determined to be minor; however, it should be noted that samples were collected during daylight hours and diel variations in the night cannot be evaluated.

Table 2–1. Statistical summaries of standard errors of estimates for the trend models.

[SEE, standard error of estimate]

Constituent or property	Number of sites for which trend results are reported	SEE, in percent		
		Minimum	Mean	Maximum
Specific conductance	7	8.2	11.0	13.1
Copper, filtered	7	24.6	31.6	37.4
Copper, unfiltered-recoverable	7	38.3	48.3	60.7
Zinc, unfiltered-recoverable	7	41.0	50.7	65.7
Arsenic, filtered	7	15.2	20.8	26.7
Arsenic, unfiltered-recoverable	7	21.8	27.3	34.0
Suspended sediment	7	57.4	65.2	80.5

Appendix 3—Trend-Analysis Results

For all constituents investigated, detailed results for trend magnitudes, computed as the total percent changes in FAC geometric means from the beginning to the end of each 5-year period, are presented in tables 3–1 (for most sampling sites) and 3–2 (for Clark Fork above Missoula, Montana [sampling site 22]). Detailed trend results are graphically presented in figures 3–1 through 3–7. The detailed graphical presentations in appendix 3 present fitted trends for all constituents and allow evaluation of the fitted trends for a given sampling site in conjunction with FACs.

Table 3–1. Flow-adjusted trend results for selected water-quality constituents and properties for selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 1996–2015.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. Values in parentheses indicate *p*-values for associated percentage change. Gray shading indicates statistical significance at *p*-value less than 0.01. *p*-value, statistical probability level; SEE, standard error of estimate; <, less than; NR, not reported]

Constituent or property	Number of samples	Total percentage change for water years 1996–2000 (period 1)	Total percentage change for water years 2001–5 (period 2)	Total percentage change for water years 2006–10 (period 3)	Total percentage change for water years 2011–15 (period 4)	*p*-value for overall trend analysis[1]	SEE, in percent	Percentage of values affected by recensoring at study reporting level used in the application of the time-series model[2]
Silver Bow Creek at Warm Springs, Montana (sampling site 8, fig. 1, table 1)								
Specific conductance	186	-1 (0.645)	-3 (0.226)	2 (0.380)	-13 (<0.001)	<0.001	10.5	0.0
Copper, filtered	186	-48 (<0.001)	-12 (0.187)	-8 (0.427)	-24 (0.023)	<0.001	32.9	0.0
Copper, unfiltered-recoverable	186	-38 (<0.001)	-14 (0.105)	-12 (0.246)	-28 (0.005)	<0.001	38.3	0.0
Zinc, unfiltered-recoverable	178	-54 (<0.001)	-47 (<0.001)	16 (0.112)	-37 (<0.001)	<0.001	45.0	4.5
Arsenic, filtered	186	1 (0.902)	5 (0.449)	5 (0.481)	-18 (0.015)	0.002	24.8	0.0
Arsenic, unfiltered-recoverable	186	-1 (0.907)	5 (0.303)	1 (0.894)	-16 (0.004)	0.002	24.5	0.0
Suspended sediment	188	17 (0.450)	-27 (0.072)	-40 (0.010)	15 (0.515)	<0.001	65.9	0.0
Clark Fork near Galen, Montana (sampling site 11, fig. 1, table 1)								
Specific conductance	217	1 (0.134)	-8 (NR[3])	7 (NR[3])	-12 (NR[3])	0.027	12.7	0.0
Copper, filtered	215	-45 (<0.001)	-5 (0.593)	-17 (0.085)	4 (0.759)	<0.001	28.4	0.0
Copper, unfiltered-recoverable	213	-31 (<0.001)	7 (0.527)	-5 (0.702)	-24 (0.035)	<0.001	44.4	0.0
Zinc, unfiltered-recoverable	205	-56 (<0.001)	-31 (0.003)	30 (0.060)	-39 (0.001)	<0.001	41.0	4.8
Arsenic, filtered	215	-8 (0.332)	12 (0.165)	-21 (0.014)	11 (0.303)	<0.001	26.7	0.0
Arsenic, unfiltered-recoverable	215	-3 (0.708)	3 (0.741)	-17 (0.082)	13 (0.294)	0.005	29.4	0.0
Suspended sediment	229	12 (0.494)	-19 (0.211)	8 (0.678)	-25 (0.168)	0.002	60.0	0.0
Clark Fork at Deer Lodge, Montana (sampling site 14, fig. 1, table 1)								
Specific conductance	264	1 (0.747)	-4 (0.089)	-2 (0.419)	1 (0.860)	<0.001	11.2	0.0
Copper, filtered	231	-16 (0.003)	6 (0.400)	-12 (0.087)	8 (0.397)	<0.001	28.9	0.0
Copper, unfiltered-recoverable	229	-22 (0.019)	5 (0.661)	1 (0.963)	-8 (0.595)	<0.001	52.7	0.0
Zinc, unfiltered-recoverable	227	-37 (<0.001)	-2 (0.850)	-7 (0.560)	-13 (0.334)	<0.001	54.0	0.9
Arsenic, filtered	231	-3 (0.501)	17 (<0.001)	-16 (<0.001)	4 (0.540)	0.001	15.6	0.0
Arsenic, unfiltered-recoverable	230	-8 (0.184)	7 (0.308)	-12 (0.114)	2 (0.828)	0.357	27.0	0.0
Suspended sediment	281	-17 (0.121)	-8 (0.555)	8 (0.643)	-17 (0.294)	0.001	80.5	0.0

Table 3–1. Flow-adjusted trend results for selected water-quality constituents and properties for selected sampling sites in the Milltown Reservoir/Clark Fork River Superfund Site in the upper Clark Fork Basin, Montana, water years 1996–2015.—Continued

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. Values in parentheses indicate *p*-values for associated percentage change. Gray shading indicates statistical significance at *p*-value less than 0.01. *p*-value, statistical probability level; SEE, standard error of estimate; <, less than; NR, not reported]

Constituent or property	Number of samples	Total percentage change for water years 1996–2000 (period 1)	Total percentage change for water years 2001–5 (period 2)	Total percentage change for water years 2006–10 (period 3)	Total percentage change for water years 2011–15 (period 4)	*p*-value for overall trend analysis[1]	SEE, in percent	Percentage of values affected by recensoring at study reporting level used in the application of the time-series model[2]
Clark Fork at Goldcreek, Montana (sampling site 16, fig. 1, table 1)								
Specific conductance	186	-2 (0.372)	-3 (0.063)	-2 (0.317)	0 (0.972)	<0.001	9.9	0.0
Copper, filtered	185	-20 (0.003)	13 (0.046)	-12 (0.077)	3 (0.752)	0.002	24.6	0.0
Copper, unfiltered-recoverable	185	-5 (0.688)	-18 (0.036)	-6 (0.564)	7 (0.569)	0.002	44.0	0.0
Zinc, unfiltered-recoverable	183	-25 (0.015)	-37 (<0.001)	24 (0.103)	-14 (0.349)	<0.001	43.8	1.7
Arsenic, filtered	186	-13 (NR[3])	8 (0.048)	-3 (0.548)	-4 (0.365)	0.026	15.2	0.0
Arsenic, unfiltered-recoverable	186	-17 (NR[3])	3 (0.582)	-4 (0.522)	-3 (0.616)	0.086	21.8	0.0
Suspended sediment	187	15 (0.396)	-51 (<0.001)	54 (0.012)	-17 (0.352)	<0.001	58.4	0.0
Clark Fork near Drummond, Montana (sampling site 18, fig. 1, table 1)								
Specific conductance	186	0 (0.535)	-2 (0.018)	-3 (<0.001)	6 (<0.001)	<0.001	11.3	0.0
Copper, filtered	183	0 (0.991)	10 (0.037)	-24 (<0.001)	13 (0.194)	0.013	33.5	0.0
Copper, unfiltered-recoverable	184	-13 (0.219)	-9 (0.369)	-10 (0.408)	-5 (0.730)	0.002	47.6	0.0
Zinc, unfiltered-recoverable	182	-48 (<0.001)	-18 (0.067)	12 (0.437)	-23 (0.147)	<0.001	50.7	2.2
Arsenic, filtered	186	-6 (0.093)	4 (0.107)	-11 (NR[3])	3 (0.378)	0.907	15.9	0.0
Arsenic, unfiltered-recoverable	186	-15 (0.001)	3 (0.398)	-6 (0.171)	0 (0.930)	0.003	23.9	0.0
Suspended sediment	187	-24 (0.134)	-20 (0.174)	29 (0.190)	-23 (0.242)	0.065	65.6	0.0
Clark Fork at Turah Bridge near Bonner, Montana (sampling site 20, fig. 1, table 1)								
Specific conductance	259	-5 (<0.001)	-2 (0.378)	3 (0.184)	-2 (0.502)	<0.001	13.1	0.0
Copper, filtered	228	-23 (<0.001)	9 (0.357)	-6 (0.525)	-20 (0.077)	<0.001	35.0	0.0
Copper, unfiltered-recoverable	227	-13 (0.073)	-8 (0.385)	-1 (0.920)	-4 (0.762)	0.002	50.3	0.0
Zinc, unfiltered-recoverable	219	-36 (<0.001)	-32 (0.005)	52 (0.004)	-31 (0.026)	<0.001	55.1	5.0
Arsenic, filtered	229	-5 (<0.001)	5 (0.002)	3 (0.435)	-16 (0.002)	<0.001	21.6	0.0
Arsenic, unfiltered-recoverable	229	-10 (0.051)	-1 (0.879)	9 (0.258)	-16 (0.052)	0.204	30.3	0.0
Suspended sediment	284	-13 (0.222)	-25 (0.059)	36 (0.067)	-21 (0.246)	0.002	57.4	0.0

[1]Determination of and distinction between *p*-value for individual trend period and *p*-value for overall trend analysis are discussed in the section of this report “Appendix 2—Summary of the Time-Series Model as Applied in this Study.”

[2]Procedures for determining and applying the study reporting level used in the application of the time-series model are discussed in the section of this report “General Description of the Time-Series Model.”

[3]Results not reported because of nonsignificant overall trend analysis (*p*-value greater than 0.01).

Table 3–2. Flow-adjusted trend results for selected water-quality constituents and properties for Clark Fork above Missoula, Montana (sampling site 22), water years 1996–2015.

[Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. Values in parentheses indicate *p*-values for associated percentage change. Gray shading indicates statistical significance at *p*-value less than 0.01. *p*-value, statistical probability level; SEE, standard error of estimate; <, less than; NR, not reported]

Constituent or property	Number of samples	Total percentage change for water years 1996–2000 (period 1)	Total percentage change for water years 2001–5 (period 2)	Total percentage change for October 1, 2005–March 27, 2008 (period 3A)	Total percentage change for March 28, 2008–September 30, 2010 (period 3B)	Total percentage change for water years 2011–15 (period 4)	*p*-value for overall trend analysis[1]	SEE, in percent	Percentage of values affected by recensoring at study reporting level used in the application of the time-series model[2]
Clark Fork above Missoula, Montana (sampling site 22, fig.1, table 1)									
Specific conductance	227	0 (0.840)	-2 (0.250)	1 (0.585)	4 (0.101)	-7 (NR[3])	0.161	8.2	0.0
Copper, filtered	206	-25 (0.006)	25 (0.057)	13 (0.357)	-21 (0.089)	-27 (0.032)	<0.001	37.4	0.0
Copper, unfiltered-recoverable	205	-23 (0.035)	41 (0.017)	120 (<0.001)	-59 (<0.001)	-52 (0.002)	<0.001	60.7	0.0
Zinc, unfiltered-recoverable	186	-49 (<0.001)	43 (0.082)	192 (<0.001)	-65 (<0.001)	-52 (0.003)	<0.001	65.7	8.5
Arsenic, filtered	207	-15 (0.005)	14 (0.033)	10 (0.171)	-3 (0.664)	-24 (<0.001)	<0.001	26.1	0.0
Arsenic, unfiltered-recoverable	207	-21 (0.006)	16 (0.110)	25 (0.036)	-17 (0.099)	-25 (0.012)	<0.001	34.0	0.0
Suspended sediment	250	-4 (0.796)	25 (0.242)	168 (<0.001)	-60 (<0.001)	-40 (0.032)	<0.001	68.7	0.0

[1]Determination of and distinction between *p*-value for individual trend period and *p*-value for overall trend analysis are discussed in the section of this report "Appendix 2—Summary of the Time-Series Model as Applied in this Study."

[2]Procedures for determining and applying the study reporting level used in the application of the time-series model are discussed in the section of this report "General Description of the Time-Series Model."

[3]Results not reported because of nonsignificant overall trend analysis (*p*-value greater than 0.01).

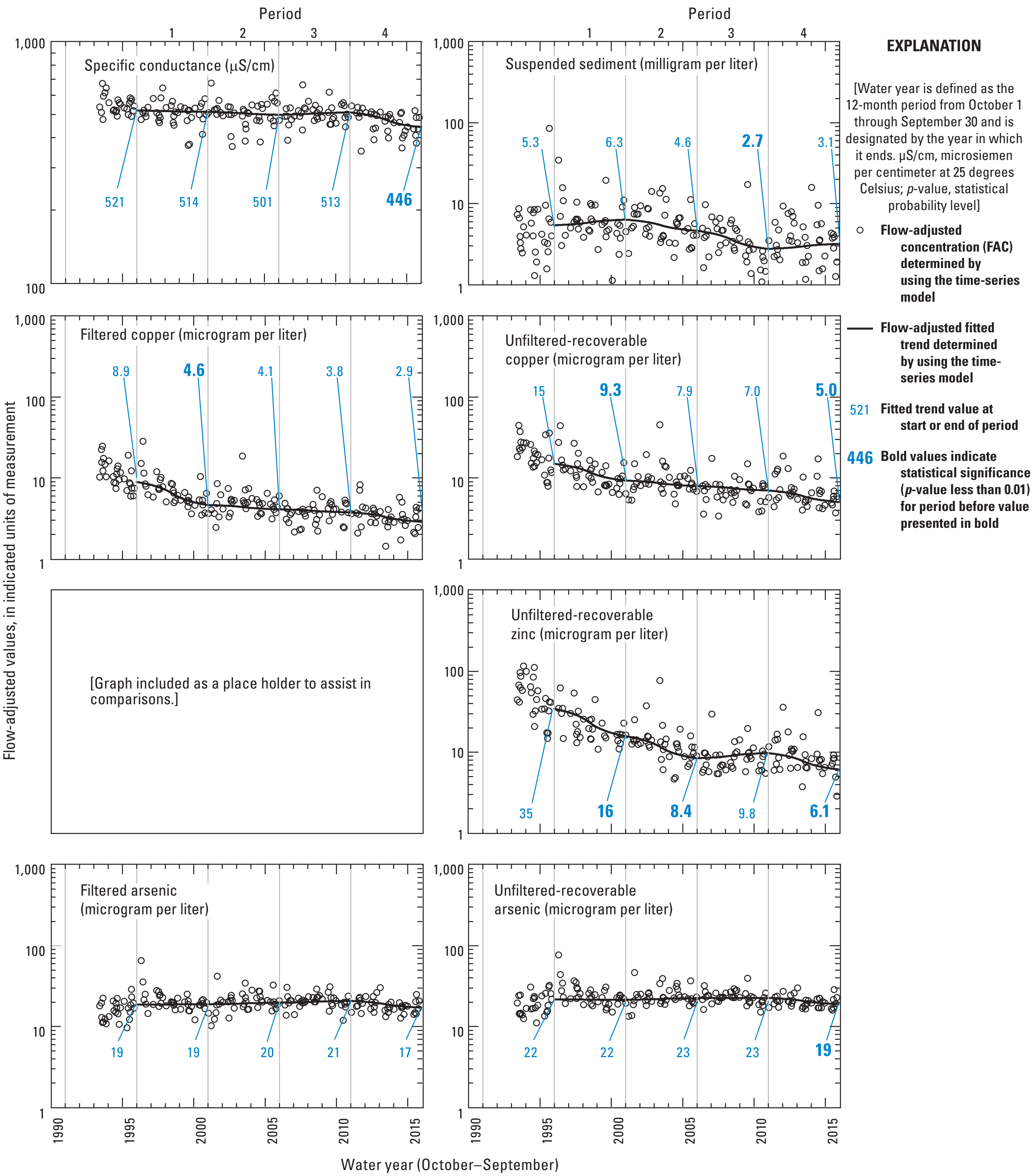


Figure 3–1. Flow-adjusted fitted trends for selected water-quality constituents and properties for Silver Bow Creek at Warm Springs, Montana (sampling site 8), water years 1996–2015.

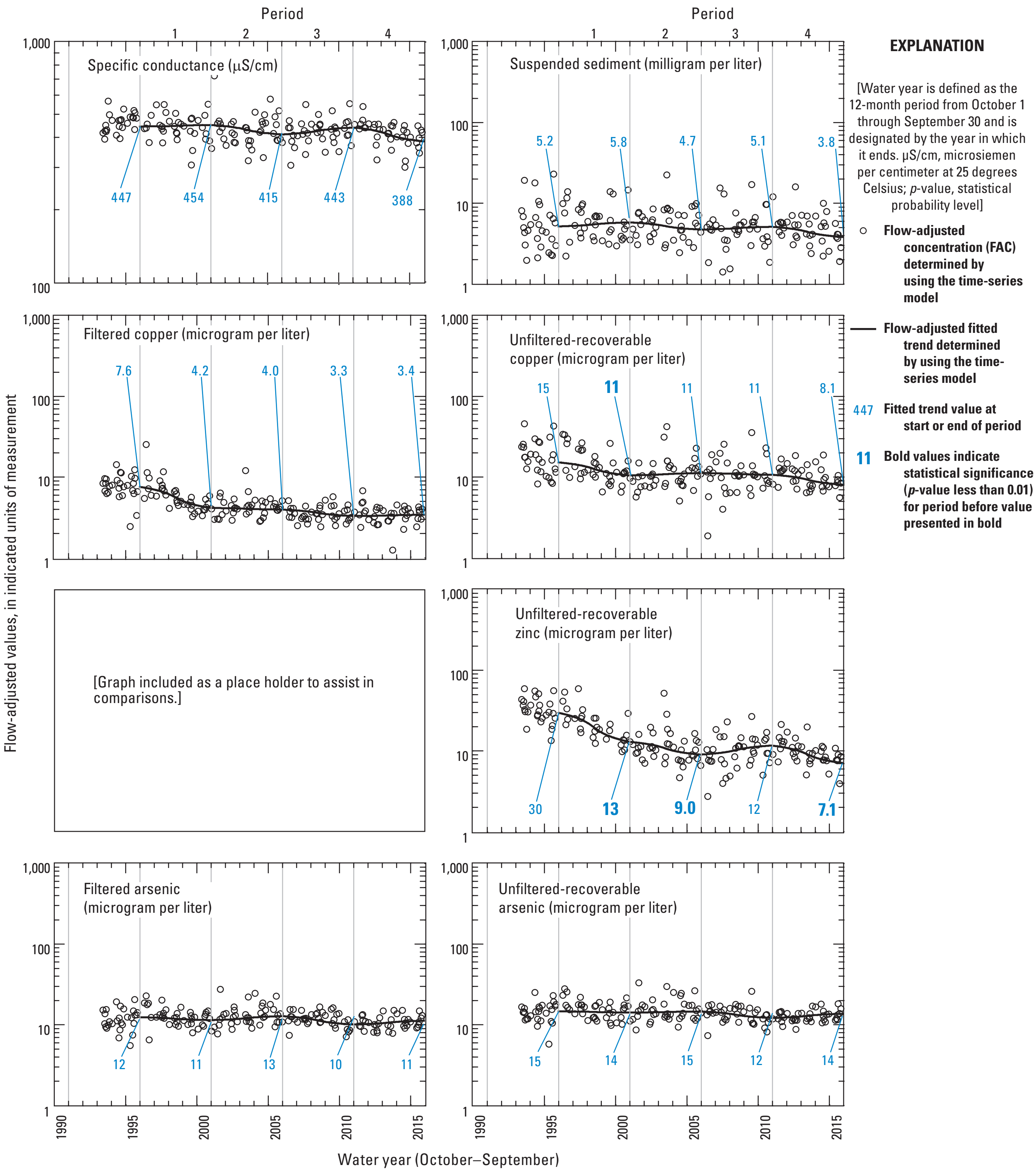


Figure 3–2. Flow-adjusted fitted trends for selected water-quality constituents and properties for Clark Fork near Galen, Montana (sampling site 11), water years 1996–2015.

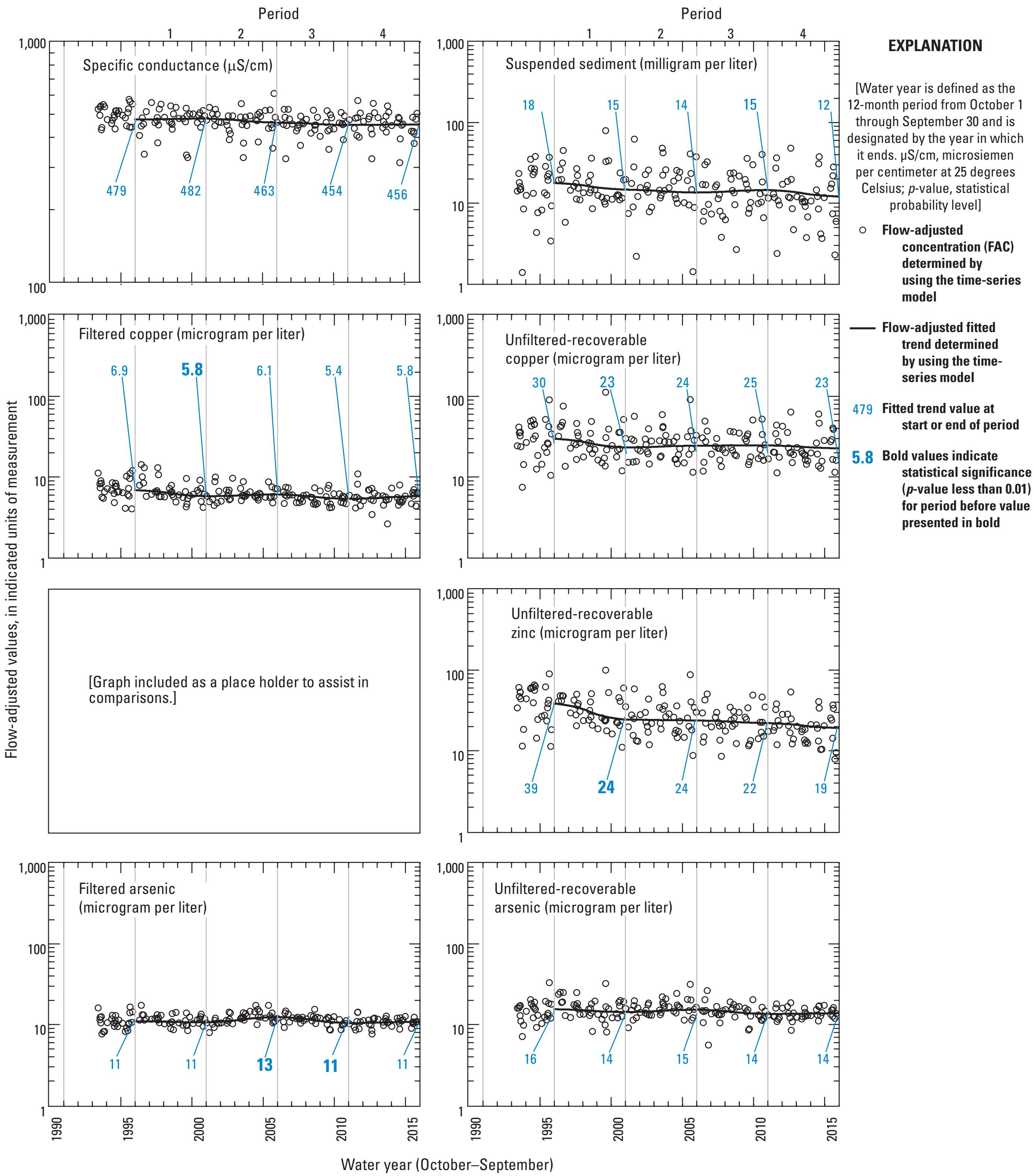


Figure 3–3. Flow-adjusted fitted trends for selected water-quality constituents and properties for Clark Fork at Deer Lodge, Montana (sampling site 14), water years 1996–2015.

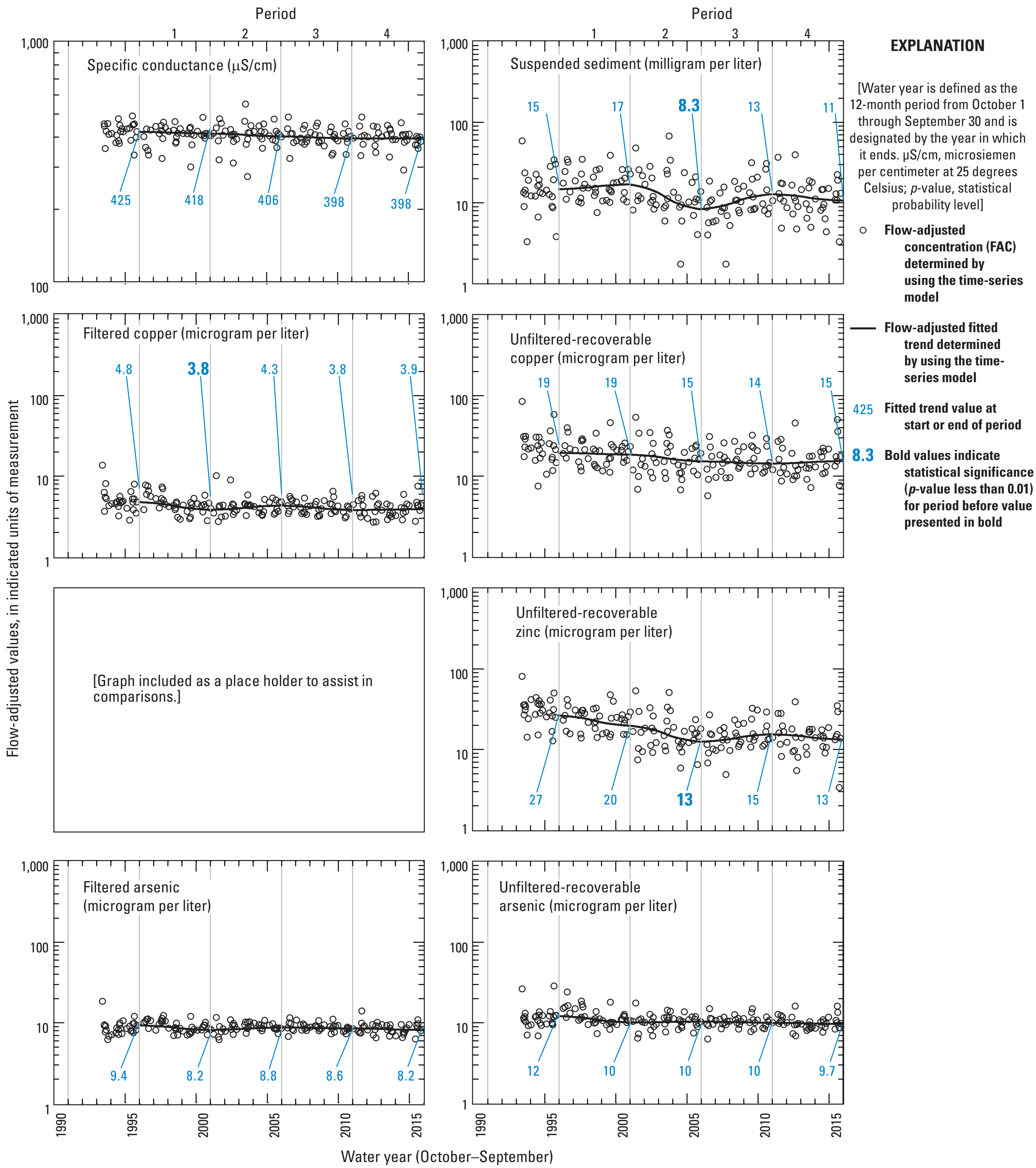


Figure 3–4. Flow-adjusted fitted trends for selected water-quality constituents and properties for Clark Fork at Goldcreek, Montana (sampling site 16), water years 1996–2015.

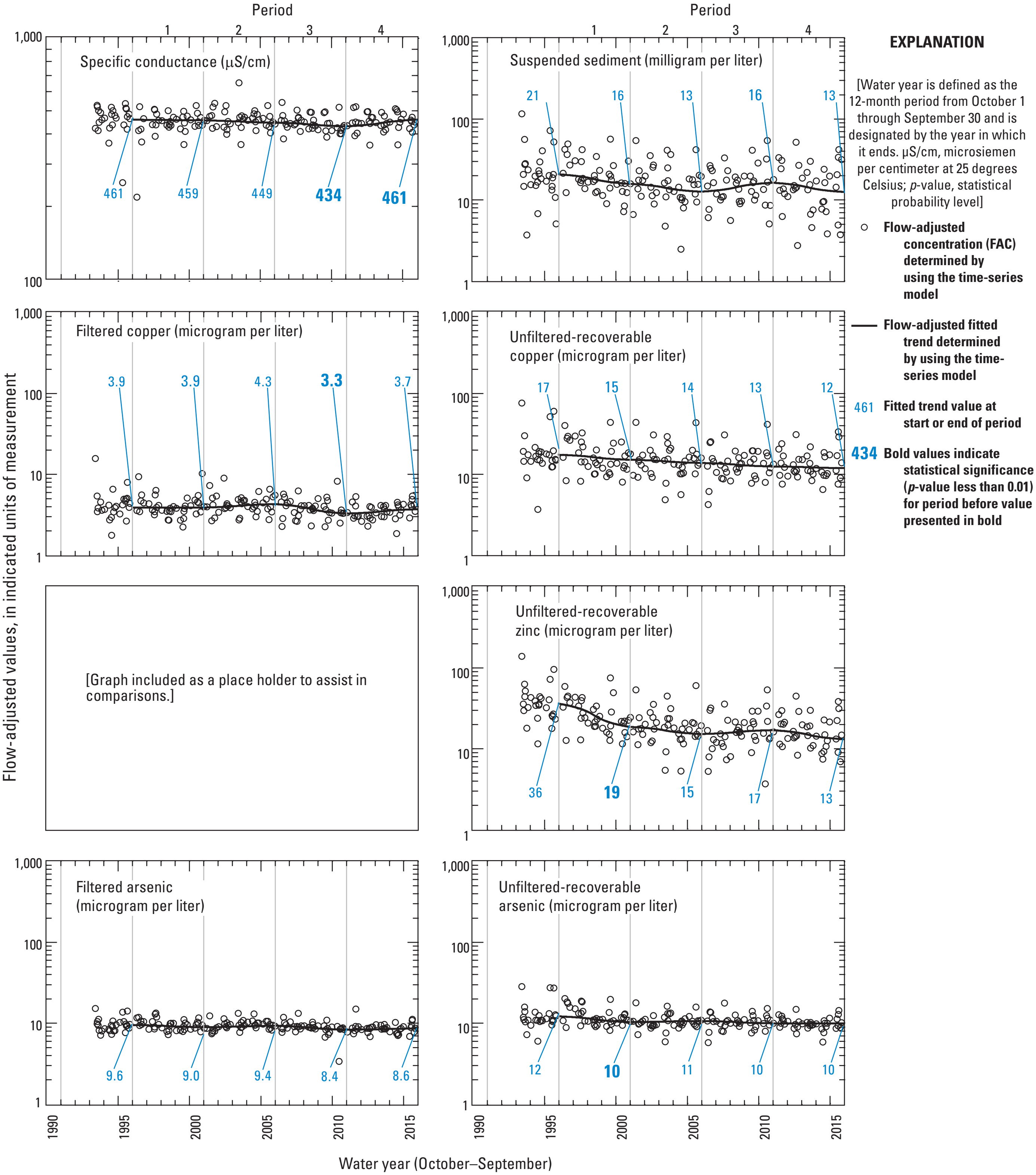


Figure 3–5. Flow-adjusted fitted trends for selected water-quality constituents and properties for Clark Fork near Drummond, Montana (sampling site 18), water years 1996–2015.

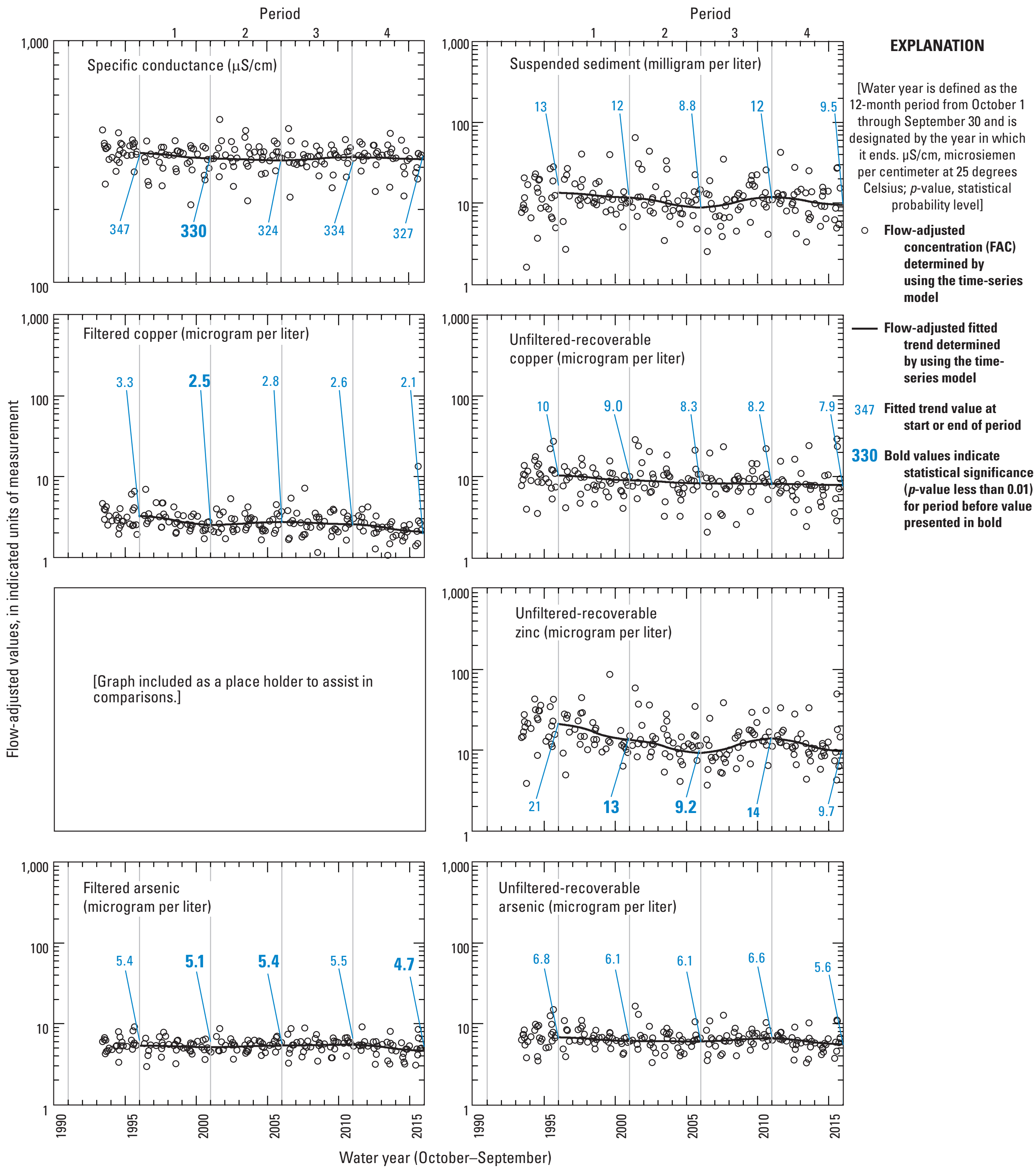


Figure 3–6. Flow-adjusted fitted trends for selected water-quality constituents and properties for Clark Fork at Turah Bridge near Bonner, Montana (sampling site 20), water years 1996–2015.

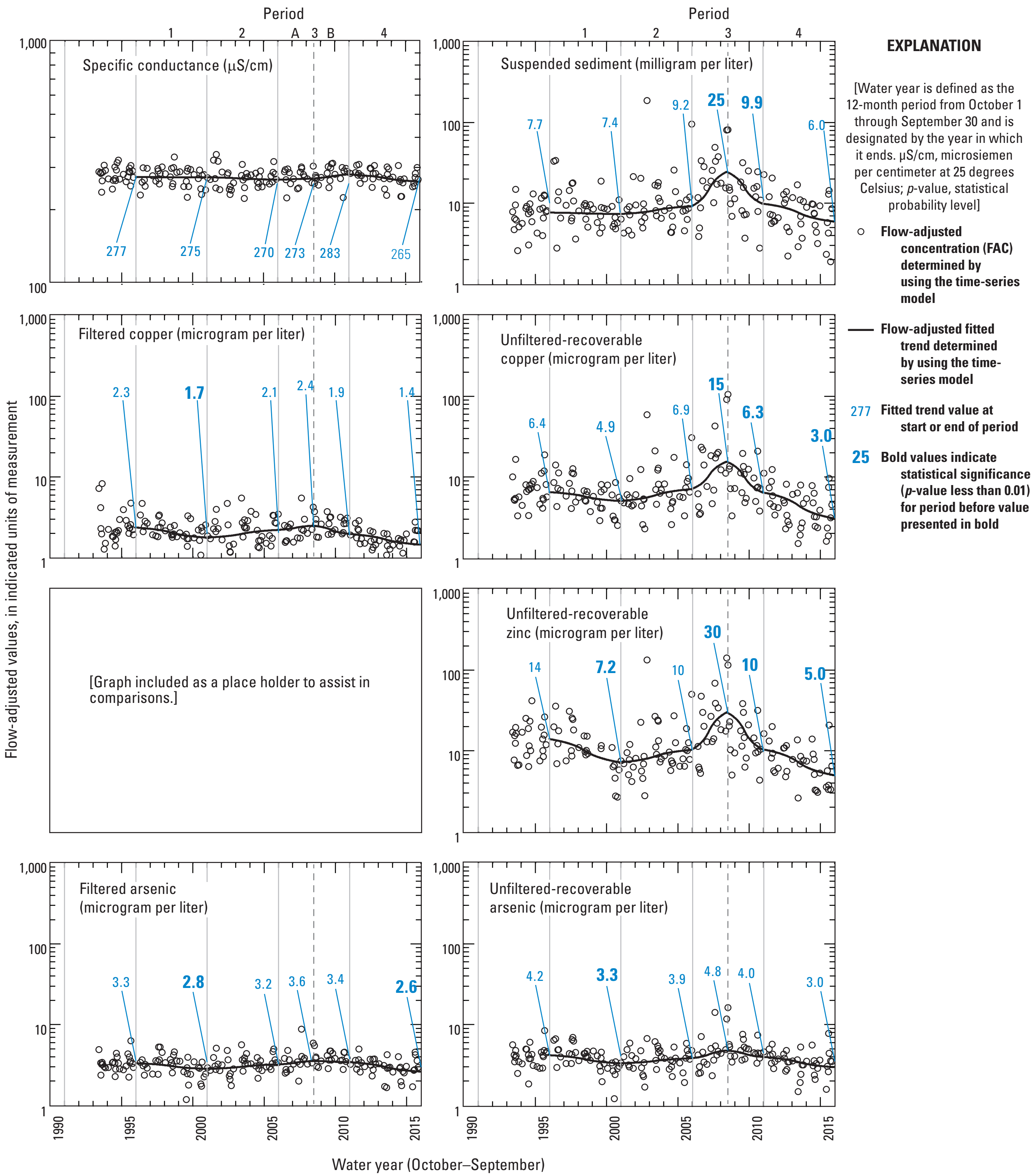


Figure 3–7. Flow-adjusted fitted trends for selected water-quality constituents and properties for Clark Fork above Missoula, Montana (sampling site 22), water years 1996–2015.

Appendix 4—Transport-Analysis Balance Calculations for Data-Summary Reaches

Balance calculations for the transport analysis (that is, differences between reach inflows and reach outflows) are presented in tables 4–1 through 4–6 for reaches 4–9, respectively, in appendix 4. The transport balance calculations indicate within-reach changes in estimated normalized loads and allow assessment of temporal changes in relative contributions from upstream source areas to loads transported past each reach outflow.

Table 4–1. Constituent-transport analysis balance calculations for sampling sites in reach 4, extending from Silver Bow Creek at Warm Springs, Montana (sampling site 8), to Clark Fork near Galen, Montana (sampling site 11), for selected periods, water years 1996–2015.

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

Abbreviated sampling site name (table 1) and number or summation category	Estimated normalized load,[1] in kilograms per day		
	Unfiltered-recoverable copper	Unfiltered-recoverable arsenic	Suspended sediment
Water years 1996–2000 (period 1)			
Inflow			
Silver Bow Creek at Warm Springs (sampling site 8)	1.9	3.4	920
Outflow			
Clark Fork near Galen (sampling site 11)	3.7	4.2	1,600
Total within-reach change in load—outflow (sampling site 11) minus inflow (sampling site 8) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	1.8	0.78	670
Water years 2001–5 (period 2)			
Inflow			
Silver Bow Creek at Warm Springs (sampling site 8)	1.4	3.5	850
Outflow			
Clark Fork near Galen (sampling site 11)	3.1	4.2	1,500
Total within-reach change in load—outflow (sampling site 11) minus inflow (sampling site 8) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	1.8	0.70	670
Water years 2006–10 (period 3)			
Inflow			
Silver Bow Creek at Warm Springs (sampling site 8)	1.2	3.6	570
Outflow			
Clark Fork near Galen (sampling site 11)	3.2	3.9	1,400
Total within-reach change in load—outflow (sampling site 11) minus inflow (sampling site 8) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	2.0	0.31	860
Water years 2011–15 (period 4)			
Inflow			
Silver Bow Creek at Warm Springs (sampling site 8)	0.94	3.3	460
Outflow			
Clark Fork near Galen (sampling site 11)	2.7	3.8	1,300
Total within-reach change in load—outflow (sampling site 11) minus inflow (sampling site 8) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	1.8	0.46	820

[1]The estimated normalized load was computed by multiplying the mean annual fitted trend concentration (determined by using the time-series model) for the indicated period times the geometric mean streamflow for water years 1996–2015 and a units conversion factor according to equation 1 in the section of this report "Estimation of Normalized Constituent Loads." Loads are reported to two significant figures; however, before final rounding, calculations used three significant figures when necessary. As a result, some of the load values have minor rounding artifacts.

Table 4–2. Constituent-transport analysis balance calculations for sampling sites in reach 5, extending from Clark Fork near Galen, Montana (sampling site 11), to Clark Fork at Deer Lodge, Montana (sampling site 14), for selected periods, water years 1996–2015.

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

Abbreviated sampling site name (table 1) and number or summation category	Estimated normalized load,[1] in kilograms per day		
	Unfiltered-recoverable copper	Unfiltered-recoverable arsenic	Suspended sediment
Water years 1996–2000 (period 1)			
Inflow			
Clark Fork near Galen (sampling site 11)	3.7	4.2	1,600
Outflow			
Clark Fork at Deer Lodge (sampling site 14)	13	7.7	8,300
Total within-reach change in load—outflow (sampling site 14) minus inflow (sampling site 11) (positive values indicate net mobilization from within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	9.8	3.5	6,700
Water years 2001–5 (period 2)			
Inflow			
Clark Fork near Galen (sampling site 11)	3.1	4.2	1,500
Outflow			
Clark Fork at Deer Lodge (sampling site 14)	12	7.6	7,200
Total within-reach change in load—outflow (sampling site 14) minus inflow (sampling site 11) (positive values indicate net mobilization from within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	9.0	3.4	5,700
Water years 2006–10 (period 3)			
Inflow			
Clark Fork near Galen (sampling site 11)	3.2	3.9	1,400
Outflow			
Clark Fork at Deer Lodge (sampling site 14)	13	7.4	7,200
Total within-reach change in load—outflow (sampling site 14) minus inflow (sampling site 11) (positive values indicate net mobilization from within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	9.4	3.5	5,800
Water years 2011–15 (period 4)			
Inflow			
Clark Fork near Galen (sampling site 11)	2.7	3.8	1,300
Outflow			
Clark Fork at Deer Lodge (sampling site 14)	12	7.0	6,800
Total within-reach change in load—outflow (sampling site 14) minus inflow (sampling site 11) (positive values indicate net mobilization from within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	9.4	3.3	5,500

[1]The estimated normalized load was computed by multiplying the mean annual fitted trend concentration (determined by using the time-series model) for the indicated period times the geometric mean streamflow for water years 1996–2015 and a units conversion factor according to equation 1 in the section of this report "Estimation of Normalized Constituent Loads." Loads are reported to two significant figures; however, before final rounding, calculations used three significant figures when necessary. As a result, some of the load values have minor rounding artifacts.

Table 4–3. Constituent-transport analysis balance calculations for sampling sites in reach 6, extending from Clark Fork at Deer Lodge, Montana (sampling site 14), to Clark Fork at Goldcreek, Montana (sampling site 16), for selected periods, water years 1996–2015.

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

Abbreviated sampling site name (table 1) and number or summation category	Estimated normalized load,[1] in kilograms per day		
	Unfiltered-recoverable copper	Unfiltered-recoverable arsenic	Suspended sediment
Water years 1996–2000 (period 1)			
Inflow			
Clark Fork at Deer Lodge (sampling site 14)	13	7.7	8,300
Outflow			
Clark Fork at Goldcreek (sampling site 16)	19	11	16,000
Total within-reach change in load—outflow (sampling site 16) minus inflow (sampling site 14) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	5.4	3.5	7,500
Water years 2001–5 (period 2)			
Inflow			
Clark Fork at Deer Lodge (sampling site 14)	12	7.6	7,200
Outflow			
Clark Fork at Goldcreek (sampling site 16)	17	10	12,000
Total within-reach change in load—outflow (sampling site 16) minus inflow (sampling site 14) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	4.6	2.6	5,000
Water years 2006–10 (period 3)			
Inflow			
Clark Fork at Deer Lodge (sampling site 14)	13	7.4	7,200
Outflow			
Clark Fork at Goldcreek (sampling site 16)	15	10	10,000
Total within-reach change in load—outflow (sampling site 16) minus inflow (sampling site 14) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	2.2	2.8	3,200
Water years 2011–15 (period 4)			
Inflow			
Clark Fork at Deer Lodge (sampling site 14)	12	7.0	6,800
Outflow			
Clark Fork at Goldcreek (sampling site 16)	15	9.9	12,000
Total within-reach change in load—outflow (sampling site 16) minus inflow (sampling site 14) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	2.7	2.8	4,900

[1]The estimated normalized load was computed by multiplying the mean annual fitted trend concentration (determined by using the time-series model) for the indicated period times the geometric mean streamflow for water years 1996–2015 and a units conversion factor according to equation 1 in the section of this report "Estimation of Normalized Constituent Loads." Loads are reported to two significant figures; however, before final rounding, calculations used three significant figures when necessary. As a result, some of the load values have minor rounding artifacts.

Table 4–4. Constituent-transport analysis balance calculations for sampling sites in reach 7, extending from Clark Fork at Goldcreek, Montana (sampling site 16), to Clark Fork near Drummond, Montana (sampling site 18), for selected periods, water years 1996–2015.

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

Abbreviated sampling site name (table 1) and number or summation category	Estimated normalized load,[1] in kilograms per day		
	Unfiltered-recoverable copper	Unfiltered-recoverable arsenic	Suspended sediment
Water years 1996–2000 (period 1)			
Inflow			
Clark Fork at Goldcreek (sampling site 16)	19	11	16,000
Outflow			
Clark Fork near Drummond (sampling site 18)	24	16	26,000
Total within-reach change in load—outflow (sampling site 18) minus inflow (sampling site 16) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	4.6	5.2	10,000
Water years 2001–5 (period 2)			
Inflow			
Clark Fork at Goldcreek (sampling site 16)	17	10	12,000
Outflow			
Clark Fork near Drummond (sampling site 18)	21	15	21,000
Total within-reach change in load—outflow (sampling site 18) minus inflow (sampling site 16) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	4.1	5.0	8,300
Water years 2006–10 (period 3)			
Inflow			
Clark Fork at Goldcreek (sampling site 16)	15	10	10,000
Outflow			
Clark Fork near Drummond (sampling site 18)	19	15	21,000
Total within-reach change in load—outflow (sampling site 18) minus inflow (sampling site 16) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	4.3	4.8	10,000
Water years 2011–15 (period 4)			
Inflow			
Clark Fork at Goldcreek (sampling site 16)	15	9.9	12,000
Outflow			
Clark Fork near Drummond (sampling site 18)	18	14	21,000
Total within-reach change in load—outflow (sampling site 18) minus inflow (sampling site 16) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	2.9	4.6	9,100

[1]The estimated normalized load was computed by multiplying the mean annual fitted trend concentration (determined by using the time-series model) for the indicated period times the geometric mean streamflow for water years 1996–2015 and a units conversion factor according to equation 1 in the section of this report "Estimation of Normalized Constituent Loads." Loads are reported to two significant figures; however, before final rounding, calculations used three significant figures when necessary. As a result, some of the load values have minor rounding artifacts.

Table 4–5. Constituent-transport analysis balance calculations for sampling sites in reach 8, extending from Clark Fork near Drummond, Montana (sampling site 18), to Clark Fork at Turah Bridge near Bonner, Montana (sampling site 20), for selected periods, water years 1996–2015.

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

Abbreviated sampling site name (table 1) and number or summation category	Estimated normalized load,[1] in kilograms per day		
	Unfiltered-recoverable copper	Unfiltered-recoverable arsenic	Suspended sediment
Water years 1996–2000 (period 1)			
Inflow			
Clark Fork near Drummond (sampling site 18)	24	16	26,000
Outflow			
Clark Fork at Turah Bridge (sampling site 20)	25	17	33,000
Total within-reach change in load—outflow (sampling site 20) minus inflow (sampling site 18) (negative values indicate net accumulation in reach channel; positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	1.6	0.49	6,300
Water years 2001–5 (period 2)			
Inflow			
Clark Fork near Drummond (sampling site 18)	21	15	21,000
Outflow			
Clark Fork at Turah Bridge (sampling site 20)	22	16	26,000
Total within-reach change in load—outflow (sampling site 20) minus inflow (sampling site 18) (negative values indicate net accumulation in reach channel; positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	1.5	0.58	5,900
Water years 2006–10 (period 3)			
Inflow			
Clark Fork near Drummond (sampling site 18)	19	15	21,000
Outflow			
Clark Fork at Turah Bridge (sampling site 20)	21	16	27,000
Total within-reach change in load—outflow (sampling site 20) minus inflow (sampling site 18) (negative values indicate net accumulation in reach channel; positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	2.3	1.5	5,800
Water years 2011–15 (period 4)			
Inflow			
Clark Fork near Drummond (sampling site 18)	18	14	21,000
Outflow			
Clark Fork at Turah Bridge (sampling site 20)	21	16	28,000
Total within-reach change in load—outflow (sampling site 20) minus inflow (sampling site 18) (negative values indicate net accumulation in reach channel; positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	3.2	1.3	6,900

[1]The estimated normalized load was computed by multiplying the mean annual fitted trend concentration (determined by using the time-series model) for the indicated period times the geometric mean streamflow for water years 1996–2015 and a units conversion factor according to equation 1 in the section of this report "Estimation of Normalized Constituent Loads." Loads are reported to two significant figures; however, before final rounding, calculations used three significant figures when necessary. As a result, some of the load values have minor rounding artifacts.

Table 4–6. Constituent-transport analysis balance calculations for sampling sites in reach 9, extending from Clark Fork at Turah Bridge near Bonner, Montana (sampling site 20), to Clark Fork above Missoula, Montana (sampling site 22), for selected periods, water years 1996–2015.

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

Abbreviated sampling site name (table 1) and number or summation category	Estimated normalized load,[1] in kilograms per day		
	Unfiltered-recoverable copper	Unfiltered-recoverable arsenic	Suspended sediment
Water years 1996–2000 (period 1)			
Inflow			
Clark Fork at Turah Bridge (sampling site 20)	25	17	33,000
Outflow			
Clark Fork above Missoula (sampling site 22)	29	19	39,000
Total within-reach change in load—outflow (sampling site 22) minus inflow (sampling site 20) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	3.7	2.5	6,000
Water years 2001–5 (period 2)			
Inflow			
Clark Fork at Turah Bridge (sampling site 20)	22	16	26,000
Outflow			
Clark Fork above Missoula (sampling site 22)	30	18	42,000
Total within-reach change in load—outflow (sampling site 22) minus inflow (sampling site 20) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	7.7	2.6	16,000
Water years 2006–10 (period 3)			
Inflow			
Clark Fork at Turah Bridge (sampling site 20)	21	16	27,000
Outflow			
Clark Fork above Missoula (sampling site 22)	54	22	83,000
Total within-reach change in load—outflow (sampling site 22) minus inflow (sampling site 20) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	32	5.9	56,000
Water years 2011–15 (period 4)			
Inflow			
Clark Fork at Turah Bridge (sampling site 20)	21	16	28,000
Outflow			
Clark Fork above Missoula (sampling site 22)	23	18	40,000
Total within-reach change in load—outflow (sampling site 22) minus inflow (sampling site 20) (positive values indicate net mobilization from all within-reach sources including groundwater inflow, tributaries, the main-stem channel, and flood plain)	2.2	2.1	12,000

[1]The estimated normalized load was computed by multiplying the mean annual fitted trend concentration (determined by using the time-series model) for the indicated period times the geometric mean streamflow for water years 1996–2015 and a units conversion factor according to equation 1 in the section of this report "Estimation of Normalized Constituent Loads." Loads are reported to two significant figures; however, before final rounding, calculations used three significant figures when necessary. As a result, some of the load values have minor rounding artifacts.

Publishing support provided by:
Rolla and Lafayette Publishing Service Centers

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Sando and Vecchia—**Water-Quality Trends and Constituent-Transport Analysis for Selected Sampling Sites**—Scientific Investigations Report 2016–5100

ISSN 2328-0328 (online)
http://dx.doi.org/10.3133/sir20165100