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Trace Metal and Phosphorus Loading from Groundwater Seepage into South Fork Coeur d’Alene River After Remediation at the Bunker Hill Superfund Site, Northern Idaho, 2022

Scientific Investigations Report 2023–5125

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

Front cover. Looking southwest across the South Fork Coeur d'Alene River toward the Central Impoundment Area between Kellogg and Smelterville, Idaho, August 29, 2022. Treated effluent from the groundwater collection system diffusely discharges underneath the river bottom in line with the cleanout ports and air relief valves visible in the photograph's center. Photograph by Lauren Zinsser, U.S. Geological Survey.

Back cover (clockwise from top left).
Iron staining associated with groundwater discharge to the South Fork Coeur d'Alene River between Kellogg and Smelterville, Idaho, August 16, 2016. Photograph by Lauren Zinsser, U.S. Geological Survey.

Filamentous algae at Seep 3, South Fork Coeur d'Alene River, August 16, 2016. Photograph by Lauren Zinsser, U.S. Geological Survey.

Filamentous algae at Seep 3, South Fork Coeur d'Alene River, August 29, 2022. Note less filamentous algae present than in August 2016 photograph. Photograph by Erin Murray, U.S. Geological Survey.

Looking north at an overview of the Central Impoundment Area of the Bunker Hill Superfund Site, August 29, 2022. U.S. Geological Survey personnel are shown in the foreground. Photograph by Lauren Zinsser, U.S. Geological Survey.

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	0.004047	square kilometer (km^2)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	0.003785	cubic meter (m^3)
million gallons (Mgal)	3,785	cubic meter (m^3)
cubic foot (ft^3)	0.02832	cubic meter (m^3)
	Flow rate	
foot per second (ft/s)	0.3048	meter per second (m/s)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
	Mass	
pounds per day (lb/d)	0.4536	kilograms per day (kg/d)

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
meter (m)	3.281	foot (ft)
	Area	
square kilometer (km^2)	0.3861	square mile (mi^2)
	Flow rate	
meter per second (m/s)	3.281	foot per second (ft/s)
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
cubic meter per second (m^3/s)	22.83	million gallons per day (Mgal/d)
	Concentration and load	
kilograms per day (kg/d)	2.20462	pounds per day (lb/d)
milligrams per liter (mg/L)	0.001	parts per million (ppm)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
°F = (1.8 × °C) + 32.

Datums

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

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

Elevation, as used in this report, refers to distance above the vertical datum.

Supplemental Information

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

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

Abbreviations

ADVM	acoustic doppler velocity meter
AWQC	ambient water-quality criteria
CIA	Central Impoundment Area
CTP	Central Treatment Plant
GWCS	groundwater collection system
IDEQ	Idaho Department of Environmental Quality
RPD	relative percent difference
USGS	U.S. Geological Survey

Trace Metal and Phosphorus Loading from Groundwater Seepage into South Fork Coeur d’Alene River After Remediation at the Bunker Hill Superfund Site, Northern Idaho, 2022

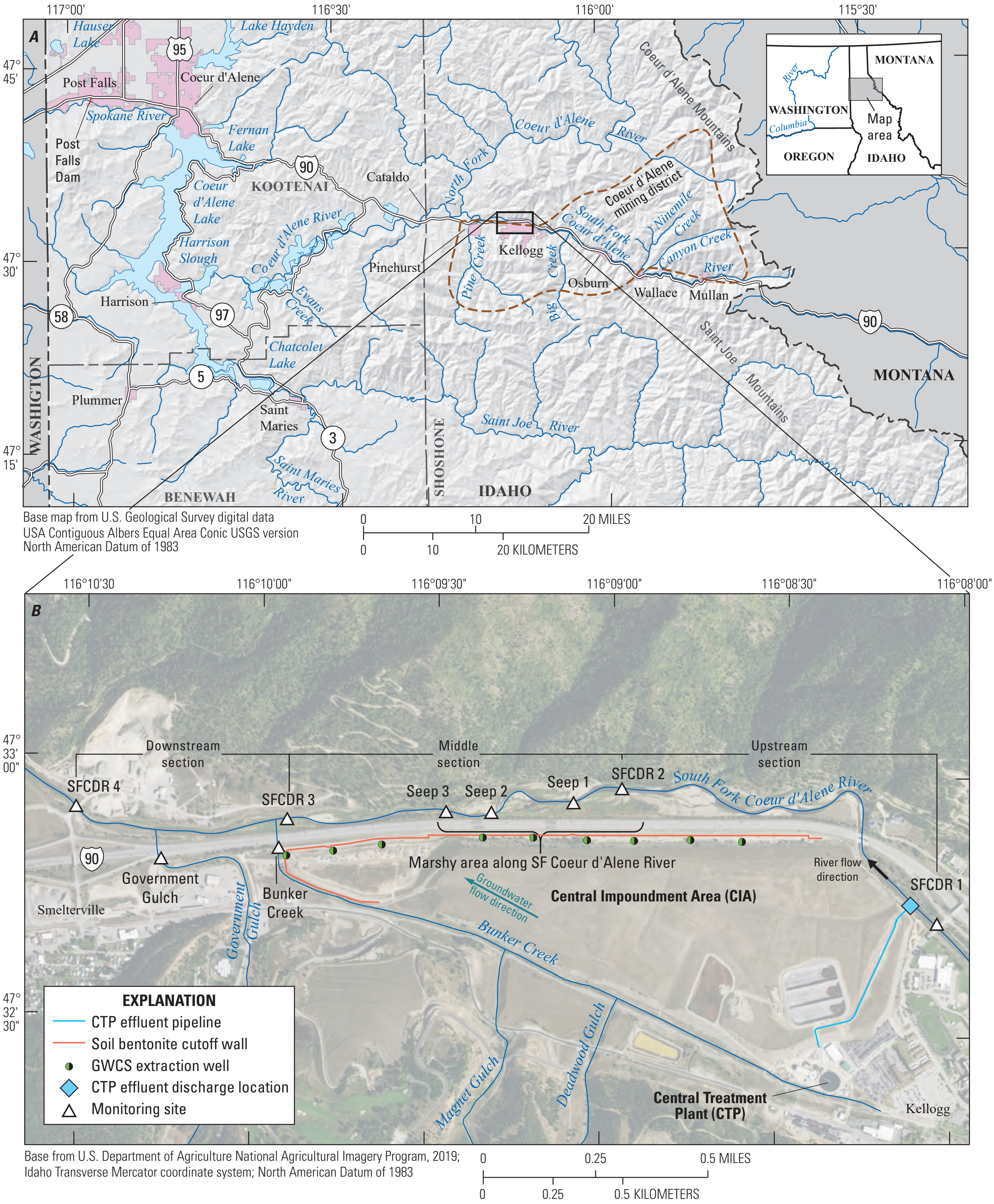
By Erin M. Murray and Lauren M. Zinsser

Abstract

Widely dispersed waste products from historical mining in northern Idaho’s Coeur d’Alene mining district have long been a concern in the Coeur d’Alene River Basin in northern Idaho. The Central Impoundment Area (CIA), an unlined mining waste repository that is part of the Bunker Hill Superfund Site designated in 1983, is adjacent to the South Fork Coeur d’Alene River between Kellogg and Smelterville, Idaho. Previous studies, including a pre-remediation seepage study completed by the U.S. Geological Survey (USGS) in 2017, have identified groundwater seepage from beneath the CIA as a major contributor to trace-metal and nutrient loads (including zinc, cadmium, and phosphorus) in the South Fork Coeur d’Alene River. A major remediation project, led by the U.S. Environmental Protection Agency from late 2017 to 2021, specifically aimed to reduce groundwater loading to the river via a groundwater collection system (GWCS) at the CIA. In 2022, the USGS completed a post-remediation seepage study to quantify zinc, cadmium, and phosphorus loading from groundwater to the South Fork Coeur d’Alene River in the same reach as the 2017 pre-remediation study. Like in the previous USGS study, discharge measurements and water-quality samples were collected during base-flow conditions in the South Fork Coeur d’Alene River between Kellogg and Smelterville as well as in surface-water inputs to the reach. Results of this study show a reduction in groundwater loads of dissolved zinc, dissolved cadmium, and total phosphorus entering the South Fork Coeur d’Alene River compared to 2017. The largest reductions in groundwater loading to the South Fork Coeur d’Alene River occurred in a discrete section (the middle section) of the reach adjacent to the CIA where the GWCS was expected to have the biggest impact. In the South Fork Coeur d’Alene River middle section, loads from groundwater (presented as a mean plus or minus [±] standard deviation) of dissolved zinc decreased from 85 ± 9.3 kilograms per day (kg/d) in 2017 to 11.6 ± 19.2 kg/d in 2022 (86-percent reduction), dissolved cadmium decreased from 0.59 ± 0.10 kg/d in 2017 to 0.11 ± 0.06 kg/d in 2022 (81-percent reduction), and total phosphorus decreased from 6.5 ± 0.45 kg/d in 2017 to 0.79 ± 0.97 kg/d in 2022 (88-percent reduction). In addition to reduced groundwater loading, lower concentrations of dissolved zinc, dissolved cadmium, and total phosphorus were observed at the site farthest downstream from the GWCS. Furthermore, the ambient water-quality-criteria ratios decreased at all river monitoring sites in 2022, although zinc and cadmium concentrations still exceeded the site-specific criteria designated to protect aquatic life. This post-remediation study indicates that the GWCS at the CIA has reduced groundwater loading of trace metals and phosphorus to the South Fork Coeur d’Alene River. This reduction in trace metals and phosphorus in South Fork Coeur d’Alene River also has implications for water quality downstream in the main-stem Coeur d’Alene River and in Coeur d’Alene Lake.

Introduction

The Coeur d’Alene mining district of northern Idaho (fig. 1*A*) was first developed in the 1880s for its lead, zinc, and silver resources. Legacy mine wastes have been a source of contamination to the Coeur d’Alene River Basin and Coeur d’Alene Lake for more than 100 years. The Bunker Hill Mining & Metallurgical Complex Superfund Site (hereafter Bunker Hill Superfund Site) was added to the U.S. Environmental Protection Agency’s National Priorities list in 1983, which identifies hazardous sites that may warrant remedial action. The Bunker Hill Superfund Site encompasses a broad area, which includes mining-contaminated areas in the Coeur d’Alene River corridor, adjacent floodplains, downstream water bodies, tributaries, and fill areas (U.S. Environmental Protection Agency, 2002a). The Bunker Hill Superfund Site includes the Central Impoundment Area (CIA) (fig. 1*B*), which is an unlined repository of mining waste products (U.S. Environmental Protection Agency, 2012) adjacent to the South Fork Coeur d’Alene River between Kellogg and Smelterville.



Base map from U.S. Geological Survey digital data
USA Contiguous Albers Equal Area Conic USGS version
North American Datum of 1983

Base from U.S. Department of Agriculture National Agricultural Imagery Program, 2019;
Idaho Transverse Mercator coordinate system; North American Datum of 1983

Figure 1. General location (A), and monitoring sites and groundwater collection system overview for the seepage study (B), in the Coeur d’Alene River Basin, northern Idaho. Monitoring site names shown in this figure refer to the short names used for brevity in this report; see table 1 for site numbers and formal site names. [GWCS, groundwater collection system].

Table 1. Seepage study monitoring sites, South Fork Coeur d’Alene River, northern Idaho.

[Short site names are used for brevity throughout this report, and data can be found on the National Water Information System web interface (U.S. Geological Survey, 2023) using the site numbers provided in this table. **Abbreviations:** Ave, Avenue; CTP, Central Treatment Plant; SF, south fork; R, river; ID, Idaho; Crk, creek; abv, above; SFCDR, South Fork Coeur d’Alene River; --, no data]

Site number	Site name (formal)	Site name (short)	Latitude	Longitude	River mile
12413250	SF Coeur d’Alene R (at Bunker Ave) at Kellogg ID	SFCDR 1	47.5453	–116.1342	0
--	Central Treatment Plant effluent discharge location	CTP	47.5459	–116.1356	0.1
473256116084001	SF Coeur d’Alene R abv north side seepage site	SFCDR 2	47.5494	–116.1493	0.9
473256116090601	SF Coeur d’Alene R south side seepage site 1	Seep 1	47.5489	–116.1516	1
473255116092001	SF Coeur d’Alene R south side seepage site 2	Seep 2	47.5485	–116.1555	1.2
473254116092701	SF Coeur d’Alene R south side seepage site 3	Seep 3	47.5485	–116.1577	1.3
473253116095501	SF Coeur d’Alene R abv Bunker Crk	SFCDR 3	47.5481	–116.1652	1.7
473252116095301	Bunker Crk at mouth of culvert at Kellogg, ID	Bunker Creek	47.5472	–116.1656	1.71
473251116101701	Government Gulch Crk at SF Coeur d’Alene R, ID	Government Gulch	47.5467	–116.1712	2
12413300	SF Coeur d’Alene R at Smelterville, ID	SFCDR 4	47.5483	–116.1753	2.2

Numerous seepage studies near the CIA have characterized groundwater loading of metals and phosphorus into the Kellogg-to-Smelterville reach of the South Fork Coeur d’Alene River (Barton, 2002; CH2M Hill, 2009; Zinsser, 2019). In this study area, “seepage study” has been used to describe investigations of groundwater discharge to surface water and surface-water recharge of groundwater that occurs in the South Fork Coeur d’Alene River (Barton, 2002; CH2M Hill, 2009; Zinsser, 2019). Groundwater loading refers to the mass per unit time of a constituent entering the South Fork Coeur d’Alene River from groundwater that discharges to the river. Zinc and cadmium are ubiquitous trace metals in mine wastes dispersed throughout the Bunker Hill Superfund Site (U.S. Environmental Protection Agency, 2012). Mine wastes containing phosphorus are present in the CIA as a byproduct of fertilizer and phosphoric acid production that occurred at a facility in Government Gulch, a tributary that flows into the South Fork Coeur d’Alene River (U.S. Environmental Protection Agency, 2012). Balistrieri and others (2003) hypothesized that groundwater interacts with the unlined bottom layer of the tailings piles in the CIA when the groundwater table rises seasonally. This change in water table elevation is thought to mobilize contaminants such as dissolved zinc, dissolved cadmium, and total phosphorus into the groundwater, eventually discharging them into the South Fork Coeur d’Alene River through groundwater.

Remediation has been ongoing in the Bunker Hill Superfund Site since it was designated. Previous remedial actions involving the CIA occurred from years 1995 to 2000 and included installation of a geomembrane cover system to limit precipitation infiltration, installation of surface-water drainage systems, capping of CIA side slopes, and revegetation (U.S. Environmental Protection Agency, 2005). Extensive groundwater remediation efforts took place in the study area from late 2017 to 2021 and are collectively referred to as the groundwater collection system (GWCS; CH2M, 2023; U.S. Environmental Protection Agency, 2017, 2018). A soil-bentonite-cutoff wall was installed along the northern edge of the CIA (fig. 1*B*). The bentonite wall was fully completed in July 2020, and is approximately 25- to 30-feet (ft) deep by approximately 8,500 linear ft (CH2M, 2023). Nine GWCS extraction wells were installed on the south side of the cutoff wall from March to April 2019 to collect groundwater and pump it to the Central Treatment Plant (CTP) for treatment (fig. 1*B*). The CTP began operation in 1974 and previously discharged treated effluent to Bunker Creek. From 2017 to 2021, upgrades were made to improve the performance and capacity of the CTP. Testing and optimization of the CTP began in October 2020, and the CTP was turned over to the Idaho Department of Environmental Quality (IDEQ) for full operation in October 2021. The treated effluent from the groundwater extraction wells is now discharged directly from the CTP into the South Fork Coeur d’Alene River via a pipeline (fig. 1*B*). The GWCS performance was evaluated by CH2M using a groundwater flow model and was estimated to capture over 85 percent of contaminated groundwater below the CIA at the operational extraction well pumping rates (CH2M, 2023). The CTP is also effective at removing metals and phosphorus; typical removal efficiencies of 90 percent are documented for zinc and total phosphorus removal is reported to be greater than 98 percent (U.S. Environmental Protection Agency, 2021).

Purpose and Scope

The U.S. Geological Survey (USGS) conducted a seepage study in 2022 to quantify groundwater loading to the South Fork Coeur d’Alene River after completion of the GWCS within the CIA at the Bunker Hill Superfund Site. The seepage study evaluates the effectiveness of the GWCS at removing groundwater inputs of metals and phosphorous to the South Fork Coeur d’Alene River. This report describes results of the 2022 seepage study, specifically focusing on groundwater loading of dissolved zinc, dissolved cadmium, and total phosphorus to the South Fork Coeur d’Alene River. Results of the 2022 seepage study are compared to results of the 2017 USGS seepage study (Zinsser, 2019) to quantify changes in groundwater loading to the South Fork Coeur d’Alene River for dissolved zinc, dissolved cadmium, total phosphorus, and ambient water-quality-criteria (AWQC) ratios, and to describe general water quality pre- and post-remediation via the GWCS within the CIA.

There are multiple constituents of concern in the Bunker Hill Superfund Site (U.S. Environmental Protection Agency, 1992, 2002a). Within the groundwater, cadmium, lead, and zinc are listed as contaminants of concern (CH2M Hill, 2013). Phosphorus is also sourced to the South Fork Coeur d’Alene River from groundwater (CH2M Hill, 2009; Zinsser, 2019) and is of interest in the Coeur d’Alene River Basin because of nutrient concerns in Coeur d’Alene Lake (Idaho Department of Environmental Quality and Coeur d’Alene Tribe, 2009; National Academies of Sciences, Engineering, and Medicine, 2022). Dissolved zinc occurs at high concentrations and is regarded as one of the most mobile of the heavy metals, making it a valuable indicator for other dissolved metals that occur at low concentrations and are harder to measure (CH2M Hill, 2013). Dissolved lead is not explicitly discussed in this report because it was not found to significantly increase between Kellogg and Smelterville in 2014 prior to installation of the GWCS (Clark and Mebane, 2014), so it is not thought to be a substantial groundwater contaminant in this study reach. Dissolved zinc and dissolved cadmium are toxic to aquatic organisms at certain levels, and AWQC are set to be protective of aquatic life (Idaho Department of Environmental Quality, variously dated). The 2022 seepage study collected necessary information to calculate AWQC ratios for dissolved zinc and dissolved cadmium. An AWQC ratio of 1 or less indicates that the water-quality criteria are met for that constituent.

Previous Work

The 2017 USGS seepage study was completed prior to construction of the GWCS to establish pre-remediation values of groundwater loading to the South Fork Coeur d’Alene River during base flow. The 2017 study results showed consistent increases in streamflow, dissolved zinc loads, dissolved cadmium loads, and total phosphorus loads in a discrete section of the study reach between SFCDR 2 and SFCDR 3 (Zinsser, 2019). The increases in streamflow and constituent loads measured between SFCDR 2 and SFCDR 3 in 2017 exceeded tributary inputs, suggesting that groundwater discharge to this section of river was the main source of increasing zinc, cadmium, and phosphorus. Additional seepage studies were conducted in the South Fork Coeur d’Alene River between Kellogg and Smelterville, Idaho by USGS in 1999 (Barton, 2002); and by CH2M Hill in 2003, 2006, 2007, and 2008 (CH2M Hill, 2009). Prior seepage study monitoring sites and groundwater loading results are summarized in detail in Zinsser (2019).

Diel Cycling

Chemical and physical properties within a river can change throughout the course of a day, a process referred to as diel cycling. For example, water temperature commonly increases with increasing solar radiation throughout daylight hours and decreases at night. Diel cycling of trace metals in the South Fork Coeur d’Alene River was first documented in 2001 and is important to consider in a seepage study with varied sample times at different sites (Nimick and others, 2003). Over the course of 2 days (September 11–13, 2001), concentrations of several trace metals (zinc, cadmium, nickel, and manganese) were observed to be highest in the early morning (0500–0800 hours), consistently dropping to a daily low value shortly after sunset (1700–1800 hours) (Nimick and others, 2003). During the 2-day 2001 study that was designed to capture a full diel cycle, the relative percent difference between daily high and low zinc and cadmium concentrations was substantive—45 percent and 54 percent, respectively (Nimick and others, 2003). The 2017 study measured 20- and 10-percent changes in dissolved zinc and cadmium concentrations, respectively, as a result of diel cycling at South Fork Coeur d’Alene River sites during the sampling timeline (Zinsser, 2019). The 2017 seepage study took place in extremely smoky conditions, and the reduction in direct sunlight may have suppressed diel cycles of temperature and pH as compared to in 2001 (Nimick and others, 2003). However, the 2017 study also was not designed to capture the full range in concentration values, as samples were only collected over a period of 5–6 hours rather than a full 24-hour diel cycle.

Study Area

The South Fork Coeur d’Alene River flows west into the main stem of the Coeur d’Alene River. The river section of interest is between Kellogg, Idaho and Smelterville, Idaho and flows adjacent to the CIA of the Bunker Hill Superfund Site. A study area map (fig. 1*B*) shows the general location, monitoring sites for the seepage study, and key components of the GWCS. The monitoring sites are individually listed in table 1. The same monitoring sites used in the 2017 study were used in the 2022 study so results could be compared. Groundwater flows in a northwest direction underneath the CIA, toward the South Fork Coeur d’Alene River (CH2M, 2018; fig. 1*B*). Additional basin characteristics are discussed in detail in Zinsser (2019).

There are three sections of the study reach between SFCDR 1 and SFCDR 4 discussed within this seepage study (fig. 1*B*). SFCDR 1 to SFCDR 2 is described as the upstream section. The only surface-water input to the upstream section is the CTP effluent discharge. During the 2017 seepage study, CTP effluent was discharged into Bunker Creek, but the discharge location was changed to the South Fork Coeur d’Alene River as part of the GWCS installation in 2020 (CH2M, 2023; fig. 1*B*). Thus, the CTP effluent was not a monitoring site in 2017. The study-reach section between SFCDR 2 and SFCDR 3 is described as the middle section, which has three surface-water inputs—Seep 1, Seep 2, and Seep 3—that enter the South Fork Coeur d’Alene River along the south side of the river (fig. 1*B*). The left riverbank of the middle section is marshy between SFCDR 2 and Seep 3, but the marshy area only contributes measurable surface-water inputs to the South Fork Coeur d’Alene River at Seep 1, Seep 2, and Seep 3. The largest portion of groundwater loading of dissolved zinc, dissolved cadmium, and total phosphorus to the study reach occurred in the middle section in 2017 (Zinsser, 2019). The study-reach section between SFCDR 3 and SFCDR 4 is described in this report as the downstream section. Two tributaries, Bunker Creek and Government Gulch, contribute surface-water flow to the downstream section (fig. 1*B*). There are no surface-water diversions or outflows present in the study reach between SFCDR 1 and SFCDR 4.

Methods

Field Methods

Data collection occurred over two days, August 30–31, 2022, at the monitoring sites presented in table 1. For purposes of comparing results of this and the 2017 seepage study, sampling dates were chosen that reflected similar hydrologic conditions between the two studies (fig. 2).

Three monitoring teams collected water-quality samples and measured streamflow across the study area. A minimum of three samples were collected at each monitoring site. Because the highest groundwater loading was measured between SFCDR 2 and SFCDR 3 in the 2017 seepage study, four samples were collected at SFCDR 2 and SFCDR 3 to better quantify sample variability (Zinsser, 2019). One monitoring site listed in table 1, CTP, refers to the Central Treatment

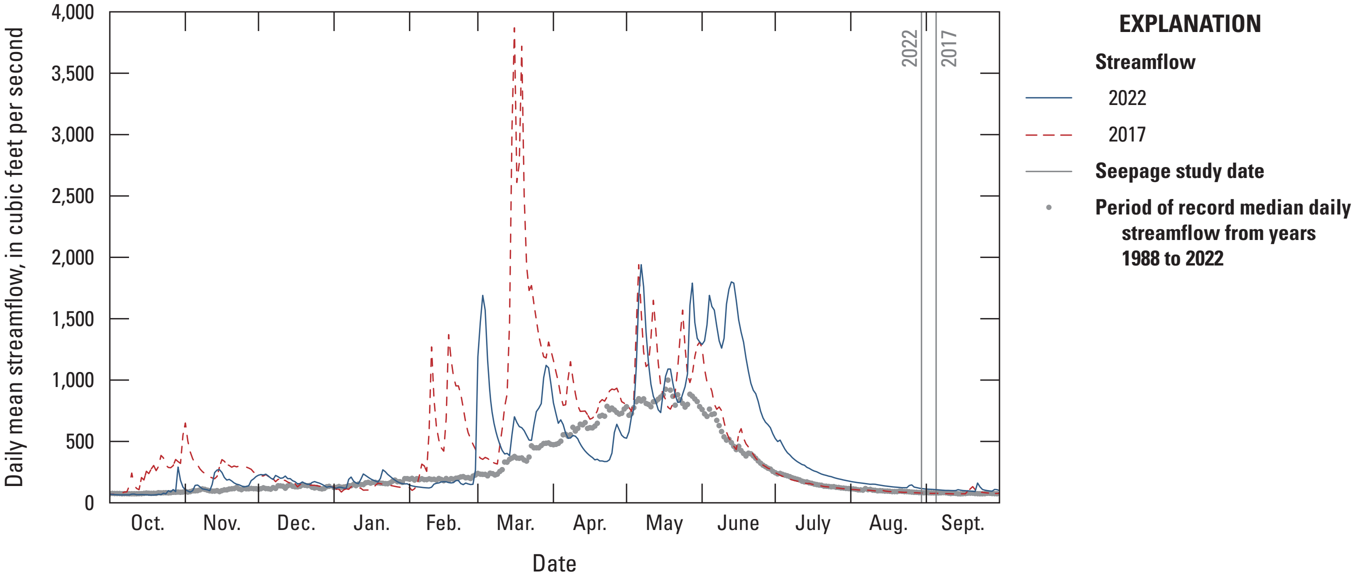


Figure 2. Water-year summary for 2017 and 2022 at U.S. Geological Survey streamgage 12413210, South Fork Coeur d’Alene River at Elizabeth Park near Kellogg, northern Idaho, about 1.4 miles upstream from SFCDR 1. Streamgage data can be found on the National Water Information System web interface (U.S. Geological Survey, 2023). [SFCDR 1, site South Fork Coeur d'Alene River 1].

Plant effluent (fig. 1*B*). The CTP site was not sampled directly by USGS because it discharges diffusely to the stream underneath the river bottom; CTP data were instead obtained from IDEQ effluent records (K. St. John, Idaho Department of Environmental Quality, written commun., 2023).

Fluctuations in trace metal concentrations throughout the day, known as diel cycling, have been extensively characterized within the study reach throughout a full 24-hr diel cycle (Nimick and others, 2003). Ideally, to offset the diel effect, every monitoring site would be sampled at the same time. However, sampling every monitoring site at the exact same time was infeasible. Instead, repeat samples at a monitoring site were staggered to be collected around a similar mean time. The mean time was determined using results of Nimick and others (2003). In their study, which took place during September 11–12, 2001, the average zinc and cadmium concentrations occurred between 1100 and 1300 hours in the South Fork Coeur d'Alene River (Nimick and others, 2003). The staggered sample collection at each site aimed to achieve (1) a mean sample time between 1100–1300 hours, and (2) similar mean sample times between sites, so that no monitoring site had a concentration biased high or low as a result of the timing of repeat samples—for example, if all of one site's samples were collected in the morning while all of another site's samples were collected in the afternoon. Thus, to the extent possible, the sampling design minimized diel cycling impacts on the mean trace metal concentration measured at a monitoring site.

River and tributary samples (SFCDR 1, 2, 3, 4, Bunker Creek and Government Gulch) were collected using a DH-81 sampler with a bottle, using depth-and-width-integrated methods as described in U.S. Geological Survey (variously dated). Integrated samples from the river and tributary sites were composited in a churn splitter prior to sample processing. Because seeps had velocities and sampling depths that were too low for depth-and-width integrated sampling, seep samples were collected as grab samples using an open-mouthed bottle. All samples were processed on site the day of collection according to a locally modified one-person clean-hands-dirty-hands method (U.S. Geological Survey, variously dated; Clark and Perreault, 2017). Samples for dissolved analyses were filtered through a 0.45-micrometer pore-size capsule filter. Samples for nutrient analyses were preserved with sulfuric acid and chilled, and samples for trace-metal analyses were preserved with nitric acid. Processed samples were shipped to the USGS National Water Quality Lab for the following analyses: nutrients (organic nitrogen, ammonia, nitrate plus nitrite, total and dissolved phosphorus, and orthophosphate), major cations (magnesium and calcium), and trace metals (total and dissolved arsenic, cadmium, copper, iron, lead, manganese, and zinc). On-site water-quality measurements of pH, specific conductance, and water temperature were made with an In Situ Aqua Troll 500 multiparameter sonde calibrated in accordance with standard USGS protocols (Wagner and others, 2006).

One split replicate and one equipment blank were collected according to standard USGS procedures (U.S. Geological Survey, variously dated). The split replicate was withdrawn from the churn splitter after the parent sample and was analyzed separately at the laboratory. The split replicate provides an estimate of variability in the sample splitting, filtering, and laboratory analysis processes. The split replicate was collected at SFCDR 1 on August 30 at 0921 hours from the parent sample taken at SFCDR 1 on August 30 at 0920 hours. Because it is effectively the same as the parent sample, the split replicate sample is used in calculations of uncertainties for SFCDR 1, but not in summary statistics. The equipment blank was collected on August 30 at 1258 hours by pouring laboratory-certified inorganic blank water into the sampler and then processing the water through the churn splitter and filtering line. The equipment blank sample provides an assessment of contamination in the sample collection and processing and equipment cleaning procedures (Mueller and others, 2015).

Discharge measurements were taken with a FlowTracker acoustic doppler velocity meter (ADVM) at the four river monitoring sites (SFCDR 1, 2, 3, and 4) and the two tributaries (Bunker Creek and Government Gulch) according to standard USGS procedures (Rantz, 1982; Turnipseed and Sauer, 2010). For each water-quality sample collected, a concurrent discharge measurement was obtained that allowed us to pair discharge measurements with analyte concentrations for calculations of load. Repeated discharge measurements enabled calculations of standard deviation in measured streamflow. The same hydrographer took each discharge measurement at the same monitoring site to minimize operator differences. At the seeps, discharge had to be estimated because the flow at each seep was very low; repeat discharge estimates were not made. At Seeps 1 and 3, velocity was measured using a FlowTracker at a single point. Seep 2 was too shallow for use of a FlowTracker, and the velocity was estimated in feet per second by timing a small twig traveling a known distance between two points. These velocity measurements—either by ADVM or time of travel—were multiplied by a measured cross-sectional area to estimate seep discharge in cubic feet per second. Uncertainty for the streamflow estimates at the seeps was estimated at one-half of the total magnitude of the streamflow estimate, as was done in 2017 (Zinsser, 2019).

Constituent Load and Mass Balance Calculations

Constituent load (load: mass per unit time) of each constituent in a sample was calculated according to equation 1. Calculating the load of a constituent allows for direct comparison of solute mass between monitoring sites and between seepage studies. Load is calculated using the constituent concentration and streamflow to quantify the mass of a constituent moving through stream water during the time of that sample. The load is then extrapolated over a given period (days). The resulting units of constituent load are kilograms per day. Load was calculated for three constituents (dissolved zinc, dissolved cadmium, and total phosphorus). Constituent load is calculated as:

$$\text{Load} = Q \times C \times 2.447 \tag{1}$$

where

Load is mass per unit time, in kilograms per day;
Q is streamflow, in cubic feet per second;
C is concentration, in milligrams per liter; and
2.447 is a unit conversion constant.

The net change (gain or loss) in streamflow as a result of groundwater flow to or from the stream was calculated according to a water balance equation (eq. 2; Simonds and Sinclair, 2002). The net change after accounting for the measured inflows and outflows is inferred to represent groundwater inflow to the stream (gain) or stream outflow to groundwater (loss) and is referred to in this report as the streamflow accrual from groundwater (Riggs, 1972). The same equation was used to calculate gains or losses of dissolved zinc, dissolved cadmium, and total phosphorus, where the calculated load was used in place of streamflow for each term in equation 2. Thus, a net change in load is referred to in this report as the load accrual to streamflow from groundwater and is inferred to represent a constituent gain to the stream from groundwater or constituent loss from the stream to groundwater in units of kilograms per day. The net accrual of streamflow or load from groundwater is calculated as:

$$\text{Net accrual of streamflow (or load)} = Q_d - T - Q_u + D \tag{2}$$

where

Q_d is the streamflow, in cubic feet per second (ft^3/s), or load, in kilograms per day (kg/d), measured at the downstream end of the reach;
T is the sum of tributary inflows, in ft^3/s, or loads, in kg/d;
Q_u is the streamflow, in ft^3/s, or load, in kg/d, measured at the upstream end of the reach; and
D is the sum of the diversion outflows, in ft^3/s, or loads, in kg/d.

In this study, diversion outflows, *D*, are zero, as there are no diversion outflows in the study reach between SFCDR 1 and SFCDR 4. Tributary inflows, *T*, vary depending on the discrete section within the full study reach. In the upstream section between SFCDR 1 and SFCDR 2, *T* refers to the CTP effluent discharge. In the middle section between SFCDR 2 and SFCDR 3, *T* is the sum of Seeps 1, 2, and 3. In the downstream section between SFCDR 3 and SFCDR 4, *T* is the sum of two tributaries (Bunker Creek and Government Gulch). In 2017, the gains and losses were calculated using individual samples that were collected the closest in time to each other. Because of the staggered sampling approach used in this study, net accrual of streamflow or load from groundwater (gains or losses) were calculated using the mean sample result at a site. In the event of censored data, when sample results are less than the method detection limit, a robust median was calculated for a site rather than the mean. The robust median is calculated using the flipped Kaplan-Meier method within the USGS R-package “smwrQW” (Helsel, 2012; R Core Team, 2022). The Kaplan-Meier method is a non-parametric technique that was originally developed for survival analysis of right-censored data (Kaplan and Meier, 1958). The “smwrQW” package flips the data distribution to apply the same method to left-censored data (in this case, less than a method detection level). The accrual in streamflow or load from groundwater in the full study reach (SFCDR 1 to SFCDR 4) is calculated as the sum of accruals in the three sections: upstream (SFCDR 1 to 2), middle (SFCDR 2 to 3), and downstream (SFCDR 3 to 4).

Ambient Water-Quality Criteria

Ambient water-quality criteria (AWQC) values for dissolved zinc and dissolved cadmium, expressed in micrograms per liter, were calculated using the dissolved concentration of zinc or cadmium, and hardness, a measure of the magnesium and calcium ions, in each water sample (Idaho Department of Environmental Quality, variously dated). AWQC values rely on hardness because increasing hardness has the effect of decreasing toxicity of zinc and cadmium (U.S. Environmental Protection Agency, 2002b). Because metal concentrations are so high in this study area, AWQC ratios were calculated by dividing the sample concentration by the AWQC value for that sample. Technically, the chronic AWQC are defined as 4-day average concentrations, and the acute AWQC are defined as 1-hour average concentrations. For zinc, the acute and chronic AWQC are identical, but for cadmium, the chronic are lower than the acute AWQC (Idaho Department of Environmental Quality, variously dated). The 1-hour duration AWQC are more consistent with the type of samples that were collected. However, to be consistent with the remedial action objectives of the U.S. Environmental Protection Agency (2012) Record of Decision, and to best compare our results to other studies, the chronic AWQC is reported in this study. A chronic AWQC ratio of 1 or less for either dissolved zinc or dissolved cadmium indicates that the water-quality criteria were met for either analyte, with 1 being protective of aquatic life (Idaho Department of Environmental Quality, variously dated). The AWQC values and ratios were calculated for each monitoring site using the average measured water hardness and average measured site concentrations.

Central Treatment Plant Data

Idaho Department of Environmental Quality (IDEQ) manages the operation of the CTP. For the 2 days of the seepage study (August 30 and 31, 2022), IDEQ provided effluent flow data (in millions of gallons per day) and daily calculated load (in pounds per day) from a grab sample of effluent. Effluent data, converted to units of cubic feet per second and kilograms per day, are presented in table 2. An average of these data was subtracted as a tributary inflow between SFCDR 1 and SFCDR 2 to calculate net accrual (gain from or loss to groundwater) of streamflow, dissolved zinc load, dissolved cadmium load, and total phosphorus load in the upstream section.

Estimates of Uncertainty and Variability

Careful consideration was given to uncertainty estimates for streamflow measurements and analytical results. Because the groundwater input to the stream is calculated, uncertainty should be accounted for in streamflow and load calculations at each sampling site. The uncertainty associated with each streamflow measurement is calculated by the FlowTracker according to USGS statistical procedures (U.S. Geological Survey, 2017). Uncertainty for analytical results was calculated using the parent and split replicate sample results from SFCDR 1, taken on August 30 at 0920 and 0921 hours, respectively. For a given analyte, the relative percent difference (RPD; eq. 3) was calculated as the absolute value of the difference between the two results, divided by the mean of the two results, multiplied by 100. RPD is thus calculated as:

$$RPD = \left(\frac{|C_{R1} - C_{R2}|}{mean(C_{R1}, C_{R2})} \right) \times 100 \qquad (3)$$

where

RPD is the relative percent difference (unitless);

C_{R1} is the concentration, in milligrams per liter (mg/L), of replicate 1 (the parent sample); and

C_{R2} is the concentration, in mg/L, of replicate 2 (the split replicate sample).

The RPD between split replicate and parent samples quantifies variability in the sample processing and laboratory analysis for a specific analyte. The RPD of a specific analyte was then multiplied by the same analyte results in each individual sample to estimate uncertainty for each analyte result in concentration units (milligrams or micrograms per liter). The RPD, or assumed uncertainty, ranged from 0 to 11.5 percent depending on the analyte. The split replicate and parent samples taken at SFCDR 1 had RPDs of 2.6- and 1.7-percent for dissolved zinc and dissolved cadmium, respectively. Dissolved zinc and dissolved cadmium concentration uncertainties are presented in units of micrograms per liter (table 3). Total phosphorus concentrations were less than the detection limit in the split replicate and parent samples taken at SFCDR 1. Because of this, the RPD between the samples would be calculated as zero. The analyte uncertainty for phosphorus is expected to be greater than zero and may be important to the final estimates. Therefore, the RPD for total phosphorus was approximated by averaging the non-zero RPD of all measured analytes. The resulting RPD for total phosphorus was 3.4 percent, and total phosphorus concentration uncertainties are presented in units of milligrams per liter (table 3). In some cases, a low concentration in a sample multiplied by the error estimate resulted in an extremely low sample uncertainty for dissolved cadmium or total phosphorus. Therefore, a minimum sample uncertainty of 0.01 micrograms per liter for dissolved cadmium and 0.001 milligrams per liter (mg/L) for total phosphorus was reported in samples where the calculated uncertainty was less than this assumed minimum.

Table 2. Effluent data from the Central Treatment Plant, South Fork Coeur d'Alene River, northern Idaho.

[Data from K. St. John, Idaho Department of Environmental Quality, written commun., 2023. **Units:** ft³/s, cubic foot per second; kg/d, kilogram per day]

Date	Streamflow (ft³/s)	Zinc (kg/d)	Cadmium (kg/d)	Total phosphorus (kg/d)
August 30, 2022	6.1	0.062	0.010	0.037
August 31, 2022	6.5	0.144	0.010	0.039

Table 3. Individual measurements of streamflow and concentrations, loads, and uncertainties for dissolved zinc, dissolved cadmium, and total phosphorus by sample, South Fork Coeur d'Alene River, northern Idaho.

[Table 3 is available as .csv and .xlsx files for download at https://doi.org/10.3133/sir20235125]

The uncertainty in load must capture the uncertainty in the terms that were used to calculate load. In this case, constituent concentration and discharge are the terms used to calculate load, and their respective uncertainties are combined to calculate load uncertainty through error propagation. To allow for propagation of errors that are expressed in different units, a fractional uncertainty was calculated for each individual sample load by summing the quadrature of the uncertainties in discharge and concentration as shown in equation 4 (Taylor, 1997). The RPD between parent and split replicate samples is used to represent the concentration uncertainty. Uncertainty in discharge (in units of cubic feet per second) is divided by the measured discharge to calculate a percent uncertainty in discharge. The resulting fractional uncertainty is unitless and can be multiplied by the calculated load to achieve a load uncertainty for each sample in units of kilograms per day. The uncertainty in individual loads, presented in table 3, is calculated as:

$$\delta Load = Load \times \sqrt{\left(\frac{RPD}{100}\right)^2 + \left(\frac{\delta Q}{Q}\right)^2} \qquad (4)$$

where

$\delta Load$ is the uncertainty in calculated load, in kilograms per day (kg/d);

$Load$ is the calculated load (from eq. 1), in kg/d;

RPD is the relative percent difference in analyte concentration (from eq. 3), divided by 100 (unitless);

δQ is the uncertainty in discharge from the FlowTracker acoustic doppler velocity meter, in cubic feet per second (ft^3/s); and

Q is the measured discharge, in ft^3/s.

Mean streamflow, concentration, and load for each monitoring site (table 4) is calculated as the mean of all individual measurements that occurred at that site (table 3), excluding the split replicate sample for SFCDR 1. Because samples were collected at different times of the day and diel cycling of metals has been observed in this river (Nimick and others, 2003; CH2M Hill, 2009; Zinsser, 2019), an estimate of the variability around the mean concentrations and loads represents the most conservative estimate of uncertainty characterized in this study. Therefore, standard deviation is presented in table 4 as an estimate of uncertainty for streamflow, concentration, and load at each site. In the case of streamflow, the standard deviation (table 4) was typically lower than the uncertainty from individual streamflow measurements as reported by the FlowTracker (table 3) and may underestimate the true site mean streamflow uncertainty. However, we expect additional streamflow measurements to decrease the uncertainty in the mean and have thus chosen to report standard deviation as the best uncertainty estimate. A standard deviation is also reported for the CTP streamflow and constituent loads (table 4) from the two reported daily values presented in table 2. The true constituent load and effluent volume discharging to the South Fork Coeur d'Alene River from the CTP may change throughout the day. The standard deviation between two daily samples is the best estimate available for this study but is likely an underestimate.

Because the mean streamflow and mean load at each site were used to calculate the net gain or loss of streamflow and loads from groundwater in a reach section, there is not a standard deviation value associated with accruals as was reported in Zinsser (2019). The accrual uncertainty here is therefore calculated by propagating the site standard deviation associated with each mean site discharge (or load) used to calculate streamflow (or load) accrual within each section of the study reach. Uncertainty in streamflow and load accruals from groundwater were propagated according to the simplified standard error propagation formula in equation 5 (Ku, 1966):

$$s = \sqrt{(\pm a)^2 + (\pm b)^2 \ldots + (\pm n)^2} \qquad (5)$$

where

s is the propagated uncertainty for the streamflow accrual, in cubic feet per second (ft^3/s), or load accrual, in kilograms per day (kg/d); and

$a, b, \ldots, n$ are the standard deviations for the mean site streamflow, in ft^3/s, or load, in kg/d, at each site that was used to calculate accrual (eq. 2).

Table 4. Mean streamflows, concentrations, loads, and standard deviations for dissolved zinc, dissolved cadmium, and total phosphorus by monitoring site, South Fork Coeur d’Alene River, northern Idaho.

[Table 4 is available as .csv and .xlsx files for download at https://doi.org/10.3133/sir20235125. See table 1 for a list of formal (full) site names, site numbers, and site locations. Site mean and standard deviation are derived from data presented in table 3 of this report. **Abbreviations**: SFCDR 1–4, sites South Fork Coeur d’Alene River 1–4; CTP, Central Treatment Plant; --, no data. **Units**: ft^3/s, cubic foot per second; hhmm, hour, minute; mg/L, milligram per liter; kg/d, kilogram per day; µg/L, microgram per liter]

Site name (short)	Mean streamflow (ft^3/s)	Streamflow standard deviation (ft^3/s)	Mean sample time (hhmm)	Mean total phosphorus (mg/L)	Total phosphorus standard deviatio (mg/L)	Mean total phosphorus load (kg/d)	Total phosphorus load standard deviation (kg/d)
SFCDR 1	99.4	2.8	1126	[a,b]0.0013–0.0033	[a,b]0.002	[a,b]0.31–0.80	[a,b]0.56
CTP[c]	6.3	0.3	--	--	--	0.038	0.002
SFCDR 2	111	1.9	1225	[a,d]0.003	[a,b]0.002	[a,d]0.815	[a,b]0.57
Seep 1	[e]0.105	--	1206	[a,d]0.005	[a,b]0.004	[a,d]0.001	[a,b]0.001
Seep 2	[e]0.01	--	1150	25.6	28.5	0.627	0.697
Seep 3	[e]0.004	--	1130	0.51	0.01	0.062	0.001
SFCDR 3	111	0.5	1155	0.008	0.001	2.29	0.36
Bunker Creek	0.1	0.02	1133	1.0	0.1	0.146	0.058
Government Gulch	1.02	0.01	1120	0.053	0.002	0.131	0.005
SFCDR 4	112	1.5	1106	0.0084	0.0004	2.31	0.09

Site name (short)	Mean sample time (hhmm)	Mean dissolved zinc (µg/L)	Dissolved zinc standard deviation (µg/L)	Mean dissolved zinc load (kg/d)	Dissolved zinc load standard deviation (kg/d)	Mean dissolved cadmium (µg/L)	Dissolved cadmium standard deviation (µg/L)	Mean dissolved cadmium load (kg/d)	Dissolved cadmium load standard deviation (kg/d)
SFCDR 1	1126	443	74	108	16	3.1	0.2	0.76	0.04
CTP[c]	--	--	--	0.10	0.06	--	--	0.01	0
SFCDR 2	1225	406	55	110	14	3.0	0.2	0.81	0.05
Seep 1	1206	575	100	0.15	0.03	0.23	0.02	0.0001	0.00001
Seep 2	1150	4,734	443	0.12	0.01	90	30	0.002	0.001
Seep 3	1130	5,237	503	0.051	0.005	1.4	0.3	0.000014	0.000003
SFCDR 3	1155	449	50	122	13	3.4	0.1	0.93	0.04
Bunker Creek	1133	4,639	436	0.7	0.3	26	1	0.004	0.001
Government Gulch	1120	946	75	2.4	0.2	27	2	0.07	0.01
SFCDR 4	1106	509	47	140	15	3.9	0.2	1.1	0.1

[a] Total phosphorus concentration results were less than the method detection limit for some sample replicates (0.003 mg/L).

[b] Means are presented as a range by assigning censored samples a minimum of 0 mg/L and a maximum of 0.003 mg/L. The maximum standard deviation is presented.

[c] Data for CTP effluent was provided by Idaho Department of Environmental Quality and was not directly sampled by U.S. Geological Survey. Numbers should be considered estimates.

[d] Sufficient samples with concentrations greater than the detection limit existed to calculate a robust median rather than a range.

[e] Seep flows and uncertainties were estimated.

Results

Data Quality

No analytes were detected in the field blank sample, which indicates that cleaning procedures and processing methods were not a source of contamination to the samples. Concentrations, loads, and uncertainties, by sample, of dissolved zinc, dissolved cadmium, and total phosphorus are presented in table 3. Concentration data for these and additional sample analytes can be downloaded from the USGS National Water Information System web interface, https://waterdata.usgs.gov/nwis (U.S. Geological Survey, 2023). Uncertainties for each streamflow measurement are also presented in table 3. The standard deviations for all site mean streamflow, concentration, and load results are presented in table 4. In the following sections, site discharge and constituent loads are all reported as a mean ± standard deviation (table 4), and net groundwater accruals are all reported as a mean ± propagated uncertainty (table 5). When streamflow or load accrual from groundwater is positive, it represents a ‘gain’ of streamflow or load to the stream from groundwater. Conversely, when streamflow or load accrual from groundwater is negative, it indicates a ‘loss’ of streamflow or load from the stream to groundwater.

Streamflow

Where repeat streamflow measurements were possible (river sites and tributaries), the uncertainty associated with each measurement (fig. 3*A*; table 3) was larger than the standard deviation between measurements (fig. 3*B*; table 4). In this study, no meaningful streamflow accrual from groundwater (gain) was observed in the middle section of the study reach (0.1 ± 2.0 ft^3/s, mean ± standard deviation; table 5), whereas in 2017 the middle section was a gaining reach (5.8 ± 1.3 ft^3/s of groundwater accrual, mean ± standard deviation; Zinsser, 2019) (fig. 4*A*). Results from this study (presented as mean ± standard deviation) showed the upstream section increasing in streamflow from 99.4 ± 2.8 ft^3/s at SFCDR 1 to 111 ± 1.9 ft^3/s at SFCDR 2 (table 4; fig. 3*B*). From that increase, 6.3 ± 0.3 ft^3/s was reported as CTP effluent (table 4) and 4.8 ± 3.4 ft^3/s was calculated as a net groundwater accrual (table 5; fig. 4*A*). The middle section and downstream section had groundwater accruals within the propagated uncertainty, 0.1 ± 2.0 ft^3/s and 0.5 ± 1.6 ft^3/s, respectively (table 5; fig. 4*A*). Notably, a major zone of groundwater inflow in the middle section in 2017 was neither a gaining nor losing reach in 2022. Because the groundwater accrual of streamflow depends on multiple discharge measurements, it is difficult to measure gains and losses of groundwater from a stream unless they are large enough to exceed measurement uncertainty. Despite no substantial streamflow gains from groundwater to the middle reach in 2022, it is likely there is still diffuse groundwater reaching the South Fork Coeur d’Alene River that is too small to measure with confidence. Therefore, increases or decreases in loads of dissolved zinc, dissolved cadmium, and total phosphorus are still attributed to groundwater accruals in the following results sections, although the total amount of groundwater entering or leaving the river is expected to be small.

Table 5. Mean streamflow and load accruals from groundwater and uncertainties in the full study reach and upstream, middle, and downstream sections, South Fork Coeur d’Alene River, northern Idaho.

[See table 1 for a list of formal (full) site names, site numbers, and site locations. Accruals are calculated by using site means presented in table 4 of this report as terms in equation 2 of this report. Uncertainties are calculated by using site standard deviation presented in table 4 of this report as terms in equation 4 of this report. **Abbreviations**: SFCDR 1–4, sites South Fork Coeur d’Alene River 1–4; **Units:** ft^3/s, cubic foot per second; kg/d, kilogram per day.]

Reach section	Reach description	Mean net streamflow accrual (ft^3/s)	Mean net streamflow accrual uncertainty (ft^3/s)	Mean net dissolved zinc load accrual (kg/d)	Mean net dissolved zinc load accrual uncertainty (kg/d)	Mean net dissolved cadmium load accrual (kg/d)	Mean net dissolved cadmium load accrual uncertainty (kg/d)	Mean net total phosphorus load accrual (kg/d)	Mean net total phosphorus load accrual uncertainty (kg/d)
Upstream section	SFCDR 1 to SFCDR 2	4.8	3.4	2.2	21.1	0.05	0.06	–0.023 to 0.47	0.80
Middle section	SFCDR 2 to SFCDR 3	0.1	2.0	11.6	19.2	0.11	0.06	0.79	0.97
Downstream section	SFCDR 3 to SFCDR 4	0.5	1.6	15.3	19.6	0.08	0.08	–0.26	0.37
Full study reach	SFCDR 1 to SFCDR 4	5.4	4.2	29.0	29.0	0.24	0.10	[a]0.5	1.12

[a] Phosphorus accrual is calculated using minimum phosphorus load accrual from groundwater (the most plausible value) from the upstream reach.

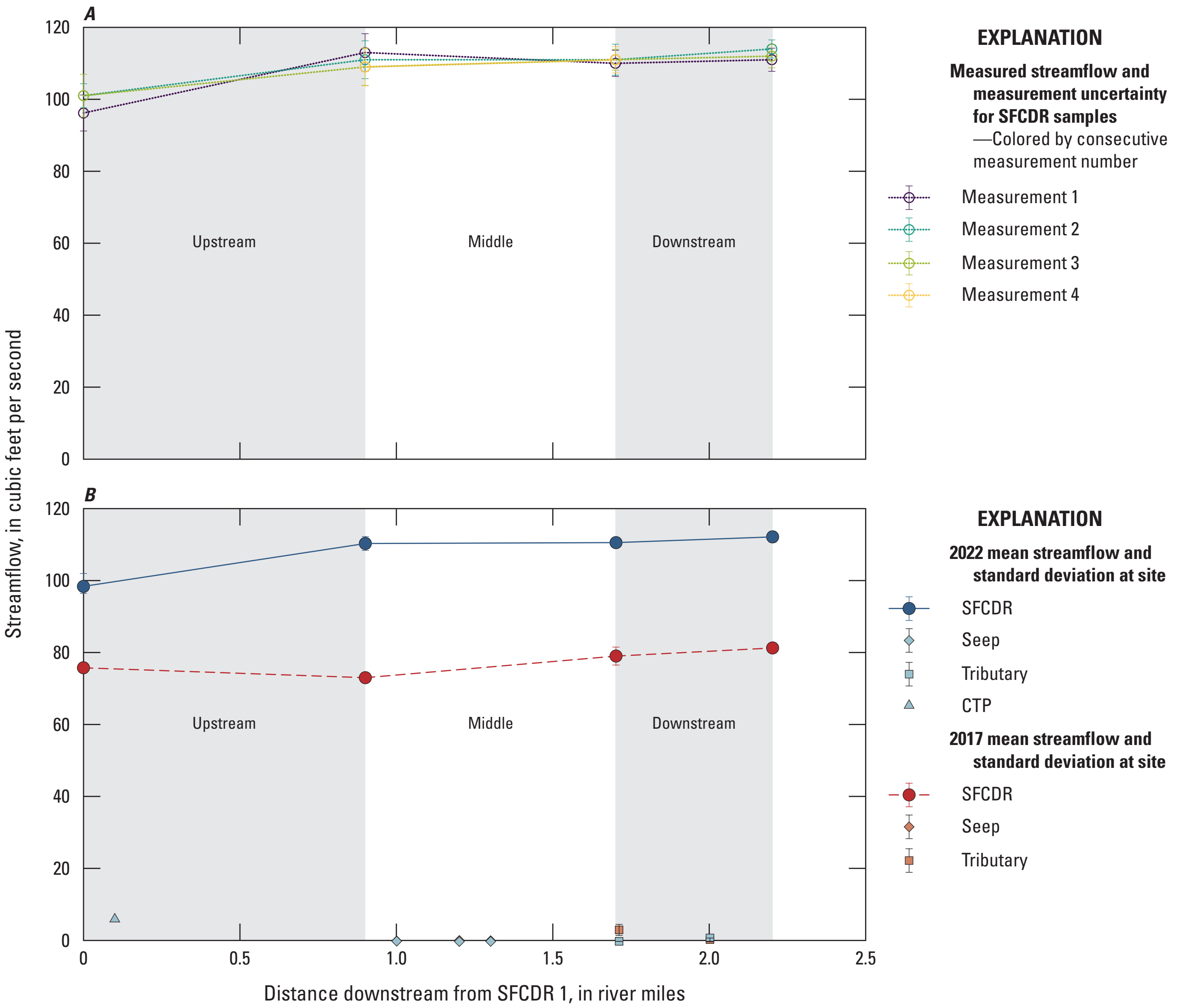


Figure 3. Individual streamflow measurements and measurement uncertainties in 2022 (U.S. Geological Survey, 2023) at SFCDR site locations (*A*) and mean streamflow and standard deviation in 2017 (Zinsser, 2019) and 2022 (table 4) seepage studies (*B*), in the upstream, middle, and downstream sections, South Fork Coeur d'Alene River, northern Idaho. Error bars are not visible for some points with low standard deviations. [CTP, Central Treatment Plant; SFCDR, South Fork Coeur d'Alene River].

Zinc and Cadmium

The dissolved zinc loads (presented as mean ± standard deviation) in the full study reach between SFCDR 1 and SFCDR 4 increased from 108 ± 16 kg/d at SFCDR 1 to 140 ± 15 kg/d at SFCDR 4 during this study (table 4; fig. 5). Discrete surface-water inputs (summed from CTP, Seeps 1–3, Bunker Creek, and Government Gulch in table 4) accounted for 3.5 kg/d of the full study reach dissolved zinc gain, and groundwater loading accounted for most of the zinc gained (29.0 ± 29.0 kg/d) (table 5). The CTP effluent contributed minimal dissolved zinc to the South Fork Coeur d'Alene River: an average of 0.10 ± 0.06 kg/d was calculated from IDEQ-reported effluent (table 4; fig. 5). The upstream, middle, and downstream sections had a net mean gain from groundwater loading that fell within the propagated accrual uncertainty of 2.2 ± 21.1 kg/d, 11.6 ± 19.2 kg/d, and 15.3 ± 19.6 kg/d dissolved zinc, respectively (table 5; fig. 4*B*). In 2017, the net mean gain of dissolved zinc from groundwater loading to the upstream, middle, and downstream sections was, respectively, –4.7 kg/d (insufficient measurements at SFCDR 1 in 2017 to calculate standard deviation), 85 ± 9.3 kg/d (mean ± standard deviation), and 3.9 ± 18 kg/d (mean ± standard deviation) (fig. 4*B*; Zinsser, 2019). The middle section had a pronounced decrease in dissolved zinc load accruals from groundwater from 2017 to

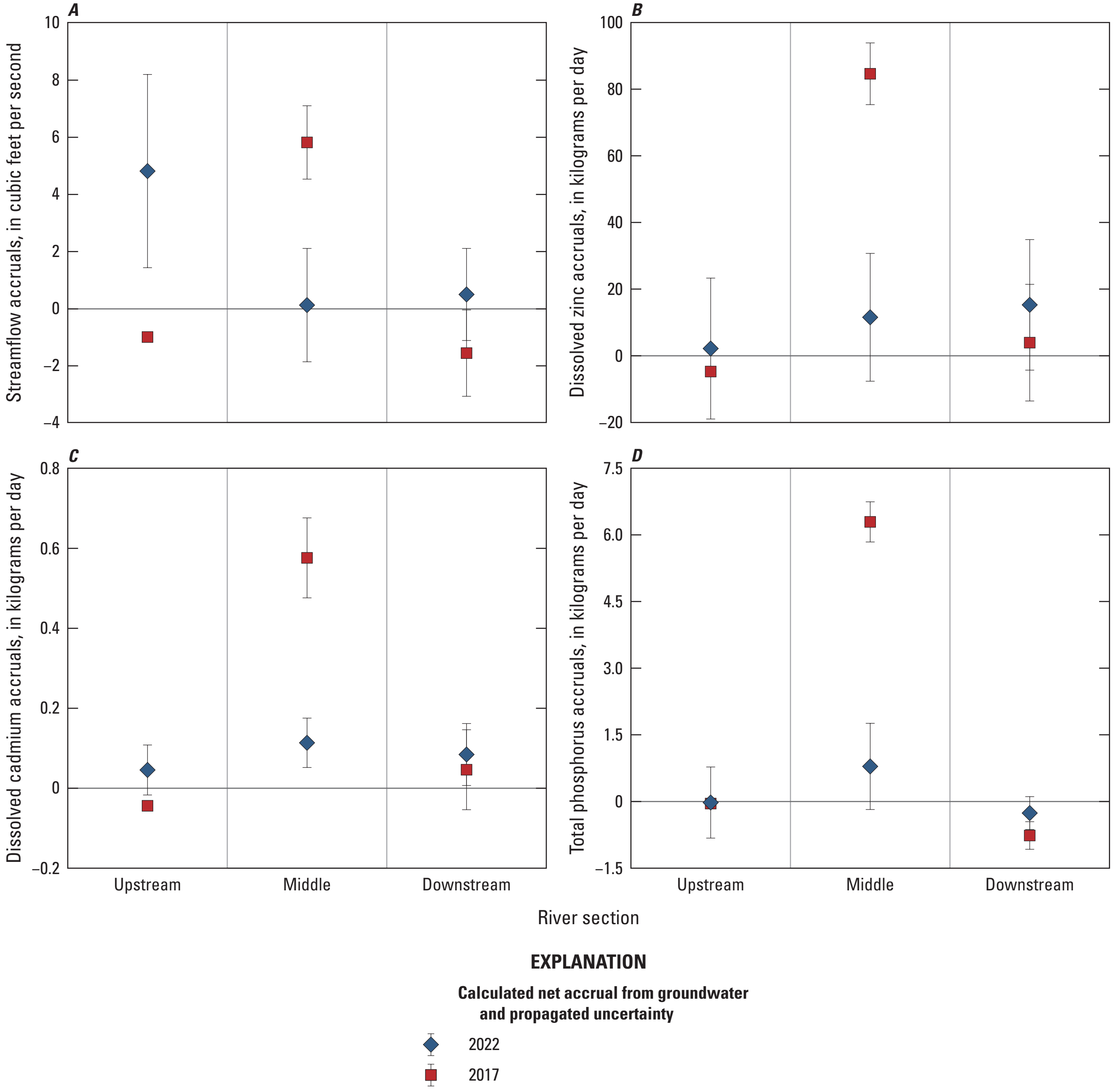


Figure 4. Streamflow accruals (*A*), dissolved zinc accruals (*B*), dissolved cadmium accruals (*C*), and total phosphorus accruals (*D*) in 2017 (Zinsser, 2019) and 2022 (table 5) seepage studies in the upstream, middle, and downstream sections, South Fork Coeur d'Alene River, northern Idaho.

2022: 85 ± 9.3 kg/d (mean ± standard deviation) in 2017 and 11.6 ± 19.2 kg/d (mean ± propagated uncertainty) in 2022 (86 percent reduction) (fig. 4*B*). A measured increase occurred in the dissolved zinc load accrued from groundwater in the farthest downstream section, SFCDR 3 to SFCDR 4, from 2017 to 2022, from 3.9 ± 18 kg/d (mean ± standard deviation) measured during the 2017 study to 15.3 ± 19.6 kg/d (mean ± propagated uncertainty) measured in the 2022 study (fig. 4*B*). However, the increase in zinc loading to the downstream reach in 2022 is within propagated uncertainty and therefore cannot be definitively described as gaining. In the study reach (SFCDR 1 to SFCDR 4), mean net groundwater loading of dissolved zinc in 2022 was 29 ± 29 kg/d (mean ± propagated uncertainty), also within propagated uncertainty, and the decreases in the middle section from 2017 to 2022 exceed our uncertainty estimates (fig. 4*B*). The mean dissolved zinc

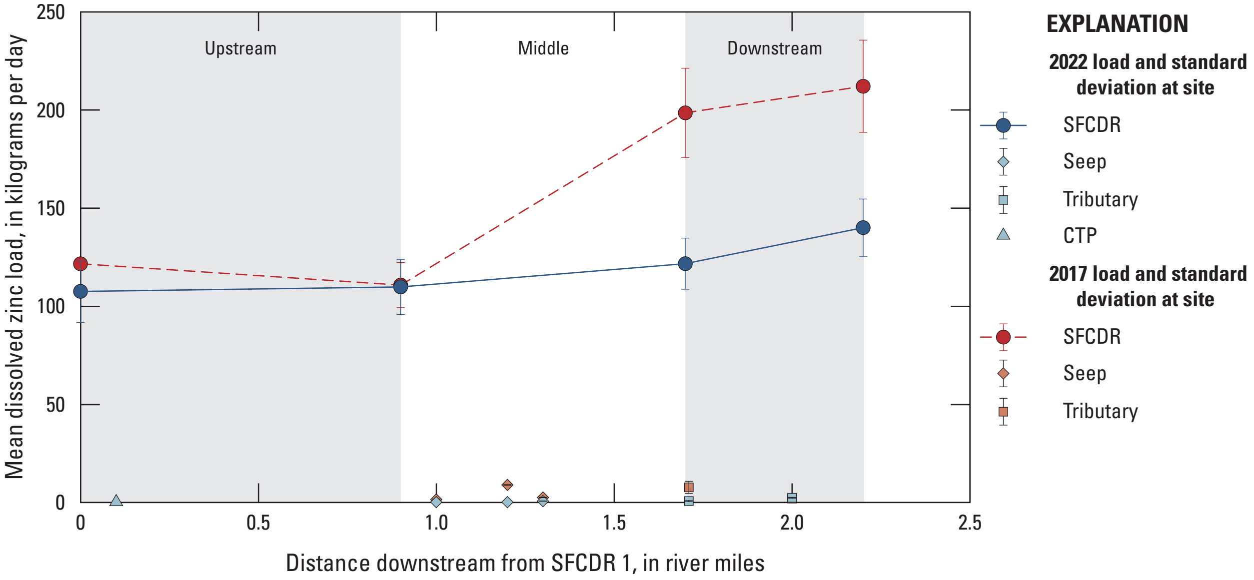


Figure 5. Mean dissolved zinc loads in all monitoring sites measured in 2017 (Zinsser, 2019) and 2022 (table 4) in the upstream, middle, and downstream sections, South Fork Coeur d'Alene River, northern Idaho. Error bars represent standard deviations and symbols represent means. Error bars are not visible for some points with low standard deviations. [CTP, Central Treatment Plant; SFCDR, South Fork Coeur d'Alene River].

load at the farthest downstream river site (SFCDR 4) was also substantially higher in 2017 (212 ± 24 kg/d, mean ± standard deviation) than in 2022 (140 ± 15 kg/d, mean ± standard deviation) (table 4; fig. 5).

Dissolved cadmium loads (presented as mean ± standard deviation) in the full study reach increased from 0.76 ± 0.04 kg/d at SFCDR 1 to 1.1 ± 0.1 kg/d at SFCDR 4 (table 4; fig. 6). Discrete surface-water inputs (summed from CTP, Seeps 1–3, Bunker Creek, and Government Gulch in table 4) accounted for 0.08 kg/d of the full study reach dissolved cadmium gain, and groundwater loading accounted for most of the cadmium gained (0.24 ± 0.10 kg/d; table 5). The CTP effluent contributed minimal dissolved cadmium to the South Fork Coeur d'Alene River: an average of 0.01 ±

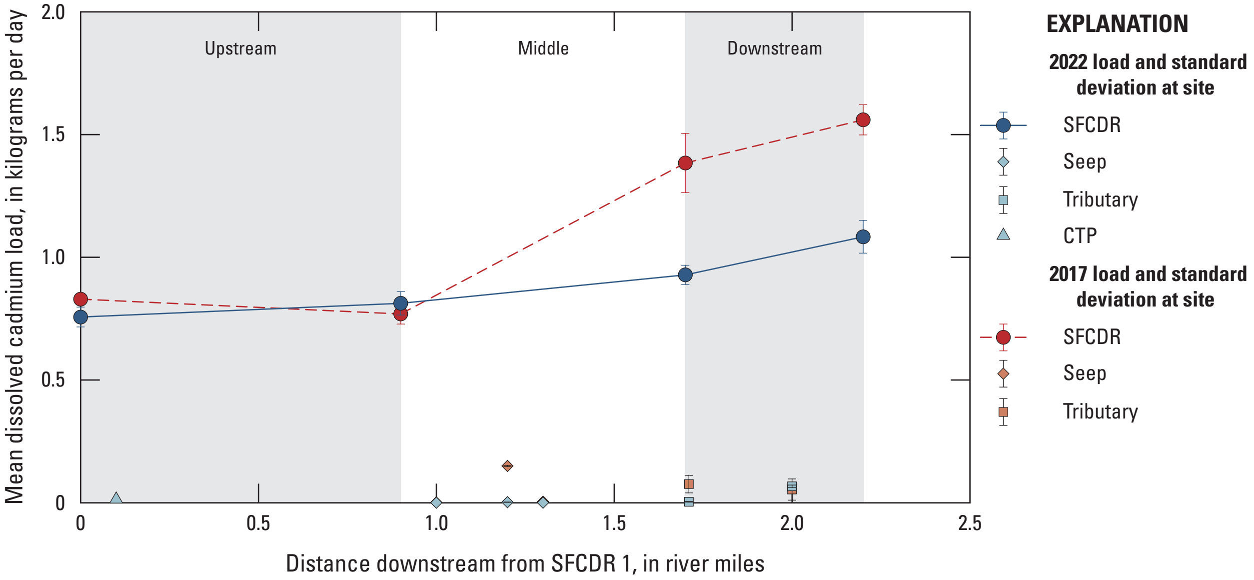


Figure 6. Mean dissolved cadmium loads in all monitoring sites measured in 2017 (Zinsser, 2019) and 2022 (table 4) in the upstream, middle, and downstream sections, South Fork Coeur d'Alene River, northern Idaho. Error bars represent standard deviations and symbols represent means. Error bars are not visible for some points with low standard deviations. [CTP, Central Treatment Plant; SFCDR, South Fork Coeur d'Alene River].

0 kg/d was calculated from IDEQ-reported effluent (table 4; fig. 6). In 2022, the upstream, middle, and downstream sections had net mean groundwater inputs of 0.05 ± 0.06 kg/d, 0.11 ± 0.06 kg/d, and 0.08 ± 0.08 kg/d dissolved cadmium, respectively (table 5; fig 4*C*). A net dissolved cadmium gain from groundwater exceeding uncertainty propagation was measured in the middle section only (table 5; fig. 4*C*). In 2017, the net mean load accrual of dissolved cadmium in the upstream, middle, and downstream sections, respectively, was –0.04 kg/d (insufficient data were collected to calculate a standard deviation at SFCDR 1), 0.58 ± 0.10 kg/d (mean ± standard deviation), and 0.05 ± 0.10 kg/d (mean ± standard deviation) (fig. 4*C*; Zinsser, 2019). The middle section had a pronounced decrease in dissolved cadmium load accruals from groundwater from 2017 to 2022: 0.58 ± 0.10 kg/d (mean ± standard deviation) in 2017 and 0.11 ± 0.06 kg/d (mean ± propagated uncertainty) in 2022 (81 percent reduction) (fig. 4*C*). In the full study reach (SFCDR 1 to SFCDR 4), mean net groundwater loading of dissolved cadmium in 2022 was 0.24 ± 0.10 (mean ± propagated uncertainty; table 5). The mean dissolved cadmium load at the farthest downstream river site (SFCDR 4) also decreased from 2017 (1.6 ± 0.06 kg/d, mean ± standard deviation) to 2022 (1.1 ± 0.1 kg/d, mean ± standard deviation) (fig. 6).

The mean sample time at monitoring sites ranged between 1106 to 1225 hours (figs. 7 and 8), which falls within the expected timeframe of trace metals being at the daily concentration “average” between 1100 and 1300 hours found by Nimick and others (2003). With regard to diel concentration fluctuations, dissolved zinc (fig. 7) and dissolved cadmium (fig. 8) concentrations decreased throughout the day in river and tributary sites, with later samples generally being lower in concentration and earlier samples being higher in concentration, consistent with other published observations (CH2M Hill, 2009; Nimick and others, 2003; Zinsser, 2019). By using standard deviation as the measure of uncertainty for concentration and load at each site, the observed diel fluctuations at each site are included in the propagated accrual uncertainties. The impact of diel cycling on mean site sample concentrations of dissolved zinc and dissolved cadmium is therefore expected to be minimized as much as possible, and calculated groundwater loads are expected to be robust.

Ambient Water-Quality Criteria

The zinc AWQC ratios decreased in the upstream section from 3.0 at SFCDR 1 to 1.9 at SFCDR 2, increased in the middle section to 2.3 at SFCDR 3, and stayed relatively constant in the downstream section (2.4 at SFCDR 4) (table 6). The cadmium AWQC ratios also decreased in the upstream section from 4.2 at SFCDR 1 to 2.7 at SFCDR 2, increased in the middle section to 3.3 at SFCDR 3, and stayed relatively constant in the downstream section (3.5 at SFCDR 4) (table 6). An increase in hardness was also observed in the upstream section between SFCDR 1 (65 mg/L as $CaCO_3$) and SFCDR 2 (111 mg/L as $CaCO_3$) (fig. 9). In 2017, both zinc and cadmium AWQC ratios were similar between SFCDR 1 and SFCDR 2, increased in the middle section with increased loading from groundwater, and then slightly decreased in the downstream section. Zinc AWQC ratios in 2017 at the four river sites moving downstream were 4.3, 4.1, 6.2, and 5.2, respectively, at SFCDR 1, 2, 3, and 4 (Zinsser, 2019; table 7). Cadmium AWQC ratios in 2017 at the four river sites moving downstream were 5.8, 5.5, 8.4, and 7.2, respectively, at SFCDR 1, 2, 3, and 4 (Zinsser, 2019; table 7). Although AWQC ratios decreased at the sampled river sites in 2022 relative to 2017 and decreased more at sites affected by loading from groundwater, all ratios were still greater than 1, which indicates that the ambient water-quality criteria for neither zinc nor cadmium were met during this study.

The AWQC ratios for zinc and cadmium in Government Gulch—a tributary presumably outside the area impacted by the GWCS at the CIA—were similar in 2017 and 2022 (table 7). Bunker Creek had a higher AWQC ratio in 2022 than in 2017 for dissolved zinc (2.1 increased to 11) and dissolved cadmium (3.4 increased to 10) (table 7). The increased AWQC ratios are consistent with other results from this study that show higher trace metal concentrations and lower streamflow in Bunker Creek as a result of moving the CTP effluent discharge from Bunker Creek to the South Fork Coeur d’Alene River.

Phosphorus

Some samples at SFCDR 1, SFCDR 2, and Seep 1 had total phosphorus concentrations less than the detection limit of 0.003 mg/L; specifically, two of the three samples collected at SFCDR 1, two of the four samples collected at SFCDR 2, and one of the three samples collected at Seep 1 (table 3). Because two samples had concentrations greater than the detection limit at SFCDR 2 and Seep 1, a robust median could be calculated for the total phosphorus concentration for censored data (presented in table 4). At SFCDR 1, the sample size was too small to calculate a robust median, so a range in mean total phosphorus load is instead presented in table 4. The minimum possible total phosphorus load at SFCDR 1 was calculated by assuming all samples less than the detection limit (<0.003 mg/L) were equal to zero. The maximum possible total phosphorus load at SFCDR 1 was calculated by assuming all samples were equal to the method detection limit of 0.003 mg/L. Although the data are presented as a range, the true concentration and load at SFCDR 1 are expected to be closer to the maximum value because one sample had a total phosphorus concentration greater than the detection limit (0.0039 mg/L; table 3).

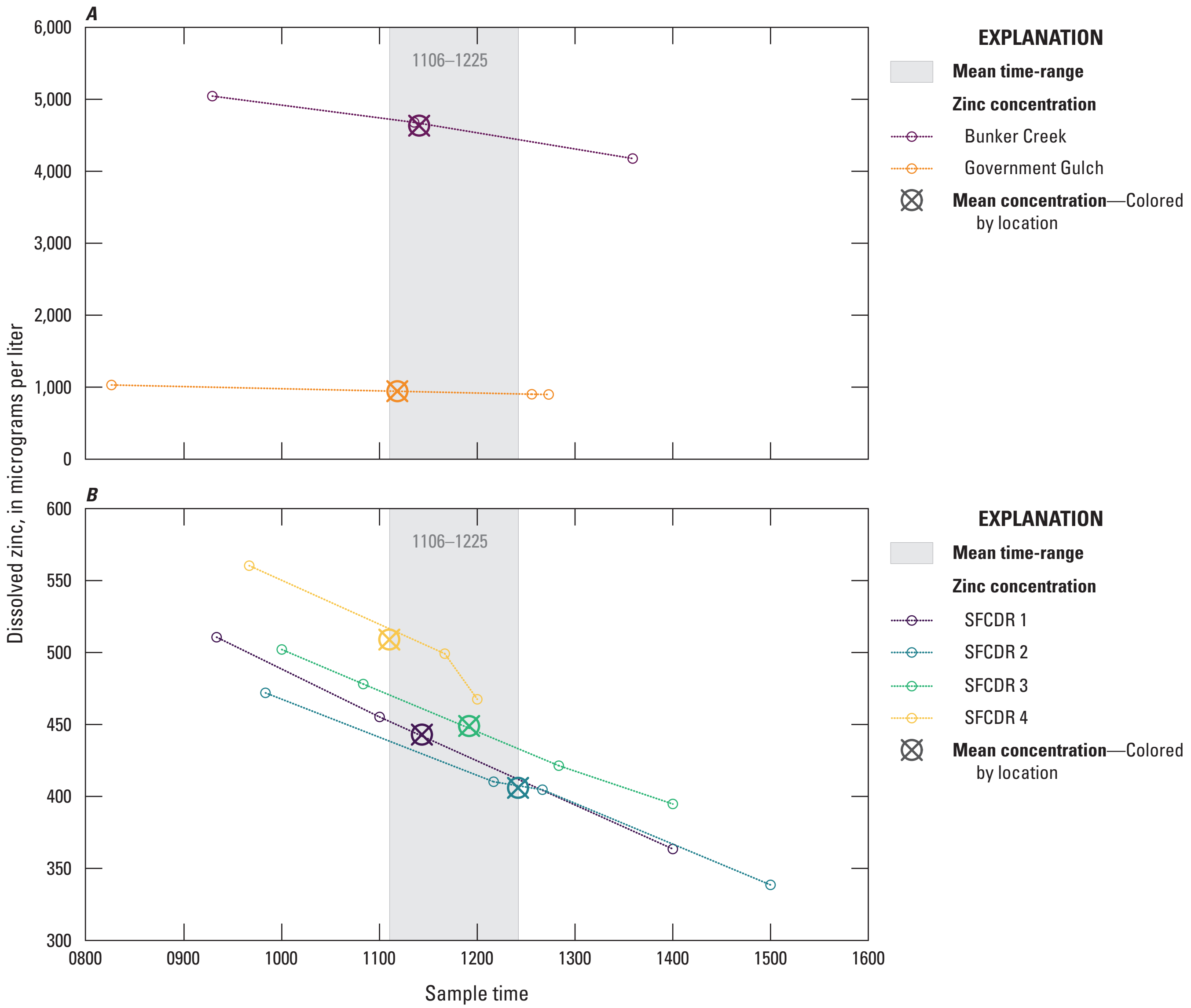


Figure 7. Dissolved zinc concentrations over time in the tributaries *(A)* and South Fork Coeur d'Alene River sites *(B)*, northern Idaho, August 30–31, 2022 (U.S. Geological Survey, 2023). Circles represent sample concentrations. The mean sample time range for all monitoring site samples (1106–1225 hours) is shaded in gray. The mean sample concentration by sample time is plotted as a bullseye and colored by site location for the South Fork Coeur d'Alene River monitoring sites SFCDR 1–4. [SFCDR 1–4, sites South Fork Coeur d'Alene River 1–4].

The full study reach increased in total phosphorus load, presented as mean ± standard deviation, from 0.31–0.80 ± 0.56 kg/d at SFCDR 1 to 2.31 ± 0.09 kg/d at SFCDR 4 (table 4; fig. 10). Because non-detect samples were most likely closer to the method detection limit than to zero, the high-end load at SFCDR 1 (0.80 ± 0.56 kg/d, table 4) was used to calculate the most plausible mean phosphorus gain for the full study reach of 1.51 kg/d (table 5). Of the full study reach mean phosphorus gain of 1.51 kg/d, a sum of 1.01 kg/d was measured in discrete surface-water inputs (summed from CTP effluent, Seeps 1–3, Bunker Creek, and Government Gulch in table 4), accounting for 67 percent of the full study reach phosphorus gain. Total phosphorus concentration was highly variable between the seeps—ranging from less than or near the method detection limit at Seep 1, to a maximum sample concentration of about 58 mg/L at Seep 2 (table 3). The calculated mean phosphorus load at each seep was 0.001 ± 0.001 kg/d at Seep 1, 0.627 ± 0.697 kg/d at Seep 2, and 0.062 ± 0.001 kg/d at Seep 3 (table 4; fig. 10). The CTP effluent and tributaries each contributed minimal total phosphorus to the South Fork Coeur d'Alene River: 0.038 ± 0.002 kg/d from CTP effluent, 0.146 ± 0.058 kg/d from Bunker Creek, and 0.131 ± 0.005 kg/d from Government Gulch (table 4; fig. 10). Phosphorus concentrations are not

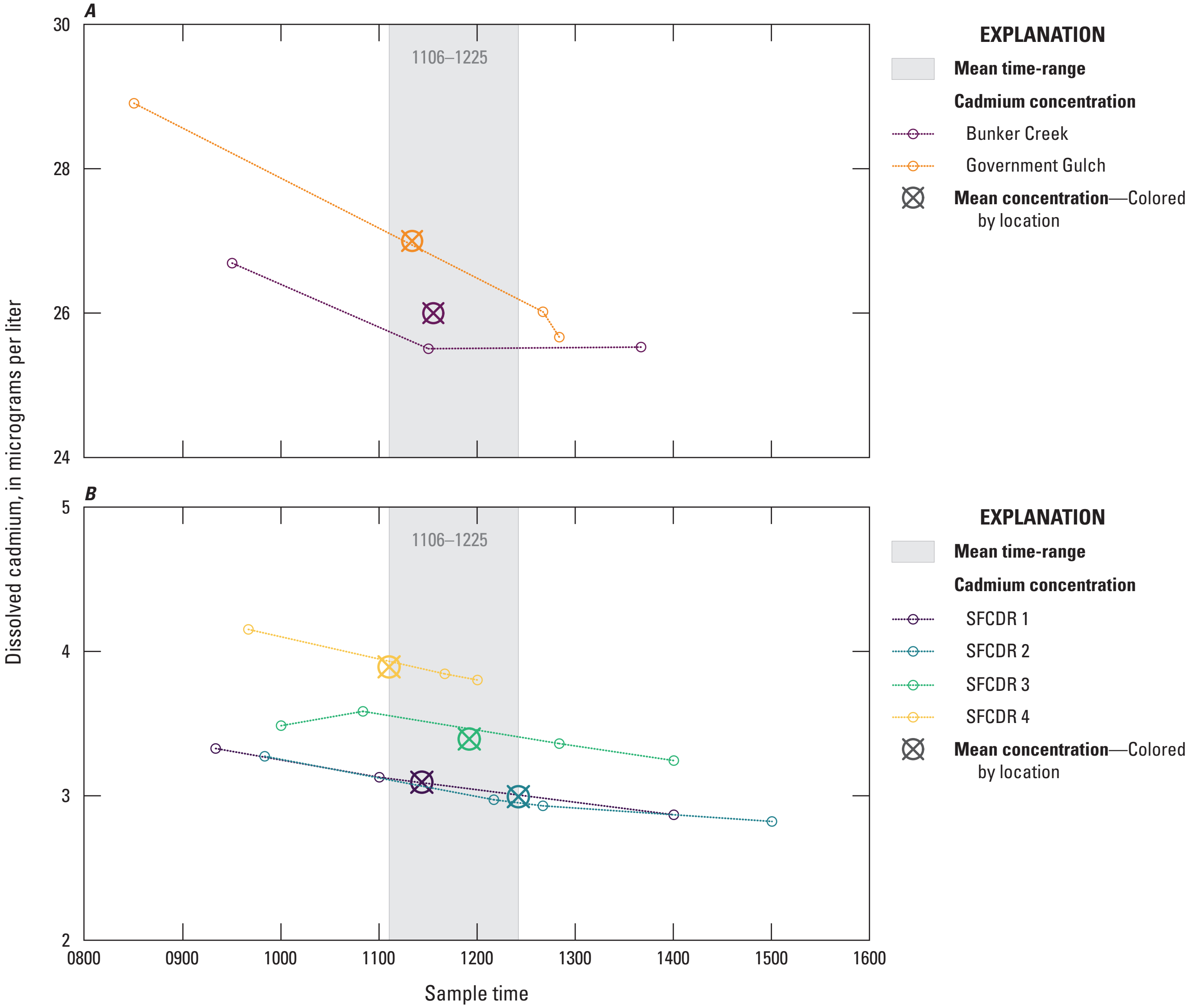


Figure 8. Dissolved cadmium concentrations over time in the tributaries *(A)* and South Fork Coeur d'Alene River sites *(B)*, northern Idaho, August 30–31, 2022 (U.S. Geological Survey, 2023). Circles represent sample concentrations. The mean sample time range for all monitoring site samples (1106–1225 hours) is shaded in gray. The mean sample concentration by sample time is plotted as a bullseye and colored by site location for the South Fork Coeur d'Alene River monitoring sites SFCDR 1–4. [SFCDR 1–4, sites South Fork Coeur d'Alene River 1–4].

conservative, that is, the concentration can change throughout a reach as a result of biological processes. Although reported gains or losses in phosphorus are attributed to groundwater in the Results section, biological release or uptake can also be a source or sink of total phosphorus. This is discussed in section, "Discussion." In the upstream section, the mean net total phosphorus accrual from groundwater, presented as mean ± propagated uncertainty, is measured to be between –0.023 to 0.47 ± 0.80 kg/d (table 5), with –0.023 kg/d (plotted in fig. 4*D*) being the most plausible if non-detect samples were equal to the detection limit at SFCDR 1. The middle section gained 0.79 ± 0.97 kg/d (mean ± propagated uncertainty) of total phosphorus from groundwater and the downstream section lost 0.26 ± 0.37 kg/d (mean ± propagated uncertainty) of total phosphorus to groundwater (table 5; fig. 4*D*). The total phosphorus gains and losses from groundwater in each river section were within the propagated uncertainties as was the case for dissolved zinc, so no section can definitively be said to be gaining total phosphorus from groundwater during this study. In the full study reach, from 0.50 to 1.0 ± 1.12 kg/d (mean ± propagated uncertainty) of total phosphorus was estimated to be the groundwater-specific loading, and actual loading from groundwater is most likely to be closest to 0.50 ± 1.12 kg/d (mean ± propagated uncertainty) if the

Table 6. Summary of site-specific zinc and cadmium ambient water-quality criteria and ratios, South Fork Coeur d’Alene River, northern Idaho.

[See table 1 for a list of formal (full) site names, site numbers, and site locations. AWQC ratios for seeps are shown for comparative purposes only. **Zinc and cadmium AWQC ratios:** The ratio of the mean dissolved zinc or cadmium concentration, divided by their respective AWQC concentration. Data for hardness, dissolved zinc, and dissolved cadmium are available on the National Water Information System web interface (U.S. Geological Survey, 2023). **Abbreviations:** SFCDR 1–4, sites South Fork Coeur d'Alene River 1–4; AWQC, chronic ambient water-quality criteria. **Units:** mg/L as $CaCO_3$, milligram per liter as calcium carbonate; µg/L, microgram per liter]

Site name (short)	Mean hardness (mg/L as $CaCO_3$)	Mean dissolved zinc (µg/L)	Zinc AWQC (µg/L)	Zinc AWQC ratio (unitless)	Mean dissolved cadmium (µg/L)	Cadmium AWQC (µg/L)	Cadmium AWQC ratio (unitless)
SFCDR 1	65	443	146	3.0	3.11	0.75	4.2
SFCDR 2	111	406	208	1.9	3.01	1.11	2.7
Seep 1	121	575	221	2.6	0.23	1.18	0.2
Seep 2	126	4,734	228	21	90	1.23	73
Seep 3	174	5,237	282	19	1.39	1.55	0.9
SFCDR 3	102	449	198	2.3	3.43	1.05	3.3
Bunker Creek	342	4,639	440	11	26	2.55	10
Government Gulch	21	946	69	14	27	0.32	83
SFCDR 4	112	509	210	2.4	3.94	1.12	3.5

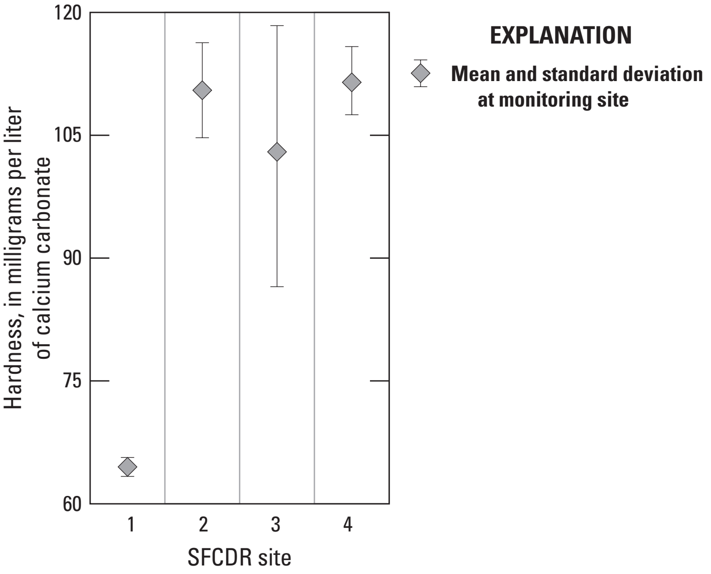


Figure 9. Hardness, in milligrams per liter of calcium carbonate, at monitoring sites SFCDR 1–4, South Fork Coeur d’Alene River, northern Idaho, August 30–31, 2022 (U.S. Geological Survey, 2023). [SFCDR 1–4, sites South Fork Coeur d’Alene River 1–4].

non-detect sample concentrations at SFCDR 1 were closer to the detection limit than to zero (table 5). In 2017, the net mean groundwater gain of total phosphorus in the upstream, middle, and downstream sections, respectively, was 0.05 kg/d (insufficient data were collected to calculate a standard deviation at SFCDR 1 in 2017), 6.3 ± 0.45 kg/d, and –0.76 ± 0.31 kg/d (mean ± standard deviation) (Zinsser, 2019; fig. 4*D*). Accruals of total phosphorus from groundwater were notably lower in 2022 in the middle section relative to 2017 (fig. 4*D*). The mean total phosphorus load (presented as mean ± standard deviation) at the farthest downstream river site (SFCDR 4) was also lower in 2022 (2.31 ± 0.09 kg/d) than in 2017 (7.6 ± 0.49 kg/d) (table 4; fig. 10).

Table 7. Summary of the exceedance ratios of the site-specific zinc and cadmium ambient water-quality criteria, South Fork Coeur d'Alene River, northern Idaho, 2008–22.

[See table 1 for formal (full) site names. **Zinc and cadmium AWQC ratio:** The ratio of the mean dissolved zinc or cadmium concentration, divided by their respective AWQC concentration. **2008**: Data from CH2M Hill, 2009. **2009–13**: Data from Clark and Mebane, 2014. **2017**: Data from Zinsser, 2019. **2022**: Data from this study, table 6. **Abbreviations:** SFCDR 1–4, sites South Fork Coeur d'Alene River 1–4; AWQC, chronic ambient water-quality criteria; --, no data.]

Site name (short)	2008	2009–13	2017	2022
Zinc AWQC exceedance ratio (unitless)				
SFCDR 1	3.6	4.4	4.3	3.0
SFCDR 2	--	--	4.1	1.9
SFCDR 3	6.0	--	6.2	2.3
SFCDR 4	--	5.3	5.2	2.4
Bunker Creek	0.9	--	2.1	11
Government Gulch	21	--	14	14
Cadmium AWQC exceedance ratio (unitless)				
SFCDR 1	5.1	5.6	5.8	4.2
SFCDR 2	--	--	5.5	2.7
SFCDR 3	7.3	--	8.4	3.3
SFCDR 4	--	7.5	7.2	3.5
Bunker Creek	2.3	--	3.4	10
Government Gulch	134	--	81	83

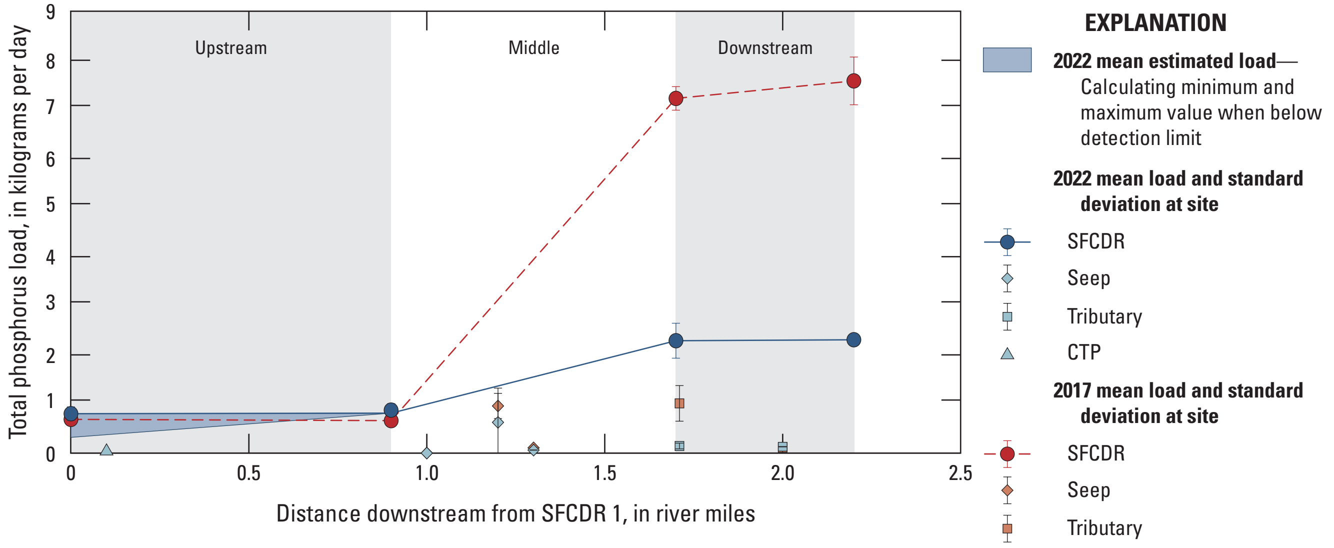


Figure 10. Total phosphorus loads in all monitoring sites measured in 2017 (Zinsser, 2019) and 2022 (table 4), in the upstream, middle, and downstream sections, South Fork Coeur d'Alene River, northern Idaho. Error bars represent standard deviations and symbols represent means. Error bars are not visible for some points with low standard deviations. [CTP, Central Treatment Plant; SFCDR, South Fork Coeur d'Alene River].

Discussion

The 2022 seepage study shows that the groundwater collection system (GWCS) has substantially decreased groundwater loading to the South Fork Coeur d’Alene River adjacent to the Central Impoundment Area (CIA) by reducing the amount of contaminated groundwater discharging to the river in the middle section of the study reach. In 2017, the middle section between SFCDR 2 and SFCDR 3, which has a marshy area along the left riverbank that contributes groundwater to this section (fig. 1*B*), had large gains of streamflow, trace metals (dissolved zinc and cadmium), and nutrients (total phosphorus) from groundwater discharge (Zinsser, 2019). Because large groundwater accruals were observed in the middle section in 2017 (Zinsser, 2019), we expected to measure the biggest impact from the GWCS in the middle section. In this study, substantial reductions in accruals from groundwater of streamflow, dissolved zinc, dissolved cadmium, and total phosphorus were measured relative to 2017 in this section (fig. 4). Additionally, anecdotal field observations indicated a reduction in groundwater discharge to the middle section in 2022, including a drier marshy area, less filamentous algae instream, and less iron and manganese flocculant.

Increases in streamflow in the upstream section between SFCDR 1 and SFCDR 2 are mostly attributed to the CTP effluent that now discharges downstream from SFCDR 1; 60 percent of the streamflow gain was accounted for by CTP discharge during August 30–31, 2022 (6.3 ± 0.3 ft^3/s). Groundwater input to the upstream section exceeded the propagated uncertainty (4.8 ± 3.4 ft^3/s; table 5), implying that untreated groundwater flowing east of the groundwater collection system may possibly still discharge to the South Fork Coeur d’Alene River in this section (fig. 1*B*). However, the CTP may be discharging more effluent throughout the day than is represented in a daily mean as reported by IDEQ, so there is likely more uncertainty around groundwater gains in the upstream section than is calculated in this study. The middle and downstream sections were considered neither gaining nor losing because the streamflow accruals from groundwater were very small (0.1 ft^3/s and 0.5 ft^3/s, respectively) and within the propagated uncertainty (table 5). The downstream section has been identified as a losing reach in previous studies (Barton, 2002; CH2M Hill, 2009), but calculated streamflow and constituent accruals were highly variable in 2017 within this section (Zinsser, 2019), and it could not be identified as either gaining or losing in 2022.

In 2017, the middle section was a gaining reach. The lack of measurable flow increases in the middle section in 2022 provides independent evidence that the soil-bentonite-cutoff wall is preventing groundwater discharge to the middle section while the GWCS is effectively pumping a portion of the captured groundwater to be treated at the CTP (CH2M, 2023). The marshy area between SFCDR 2 and Seep 3 was notably drier in 2022 than in 2017 according to photographs and field notes, despite streamflow during the 2022 seepage study dates being greater than in 2017 (112 ft^3/s and 79 ft^3/s respectively). Seeps 2 and 3 also had measurably lower discharge in 2022 than in 2017. The 2022 reductions in seep discharges, drier marshy area, and no increases in streamflow between SFCDR 2 and 3 all support that the GWCS has decreased the amount of groundwater discharging to the South Fork Coeur d’Alene River, Seep 2, and Seep 3 within the middle section of the South Fork Coeur d’Alene River study reach.

In addition to reductions in groundwater flow to the South Fork Coeur d’Alene River, dissolved zinc and dissolved cadmium loads were lower in 2022 than in 2017 at the farthest downstream river site (SFCDR 4; figs. 5 and 6), and smaller load accruals from groundwater were calculated in the middle reach for both of these trace metals in 2022 relative to 2017 (figs. 4*B* and 4*C*). Dissolved zinc load accruals from groundwater especially decreased in the middle section, from 85.0 ± 9.3 kg/d in 2017 to 11.6 ± 19.2 kg/d in 2022, an 86-percent reduction (table 8; fig. 4*B*). All dissolved zinc accruals in 2022 were within propagated uncertainty, as were cadmium accruals in the upstream and downstream reaches. A small amount of cadmium accrual from groundwater was measured in the middle section (fig. 4*C*). Despite this, the cadmium accrual decreased 81 percent from 2017 (0.59 ± 0.10 kg/d) to 2022 (0.11 ± 0.06 kg/d) (Zinsser, 2019; table 8; fig. 4*C*). Anecdotally, less flocculant was observed in the middle section of the river adjacent to the seeps in 2022 than in 2017. Flocculation is a process by which particles come out of suspension, and a notable amount of orange and shiny flocculant was observed in 2017 (Zinsser, 2019). In 2017, orange flocculant was attributed to iron, and shiny flocculant was attributed to manganese, both of which are trace metals documented within the CIA waste repository tailings piles and are hypothesized to discharge from contaminated groundwater into the South Fork Coeur d’Alene River (Zinsser, 2019). A visual reduction in flocculant in the middle section between SFCDR 2 and SFCDR 3, which had high trace metal loading of dissolved zinc and cadmium in 2017, could indicate that the GWCS has lowered the amount of contaminated groundwater that discharges to this section. Although we did not measure a substantial increase in streamflow in the downstream section between SFCDR 3 and SFCDR 4 (streamflow increased 0.5 ± 6.2 ft^3/s; mean ± propagated uncertainty), we did see increases in dissolved zinc and dissolved cadmium accruals in 2022 relative to 2017 within the downstream section. Measured increases in dissolved zinc and cadmium loads in the downstream section may indicate that a small amount of contaminated groundwater flowing west of the GWCS is discharging to the South Fork Coeur d’Alene River, or it may indicate that metals are being released from contaminated sediments in the banks and channel under changing oxidation-reduction conditions (Balistrieri and Stillings, 2002). In either case, the streamflow, dissolved cadmium, and dissolved zinc net groundwater accruals were within the propagated uncertainty, and therefore the downstream section cannot be definitively described as gaining in this study.

Table 8. Summary of seepage study dissolved zinc, dissolved cadmium, and total phosphorus load accruals from groundwater, South Fork Coeur d'Alene River middle section, northern Idaho, 1999–2022.

[**1999:** Data from Barton, 2002. **2003–08**: Data from CH2M Hill, 2009. **2017**: Data from Zinsser, 2019. **2022**: Data from this study, presented in table 5. **Abbreviation:** --, no data. **Units**: kg/d, kilogram per day]

Calendar year	Dissolved zinc load (kg/d)	Dissolved cadmium load (kg/d)	Total phosphorus load (kg/d)
1999	254	0.79	--
2003	71.2	0.64	--
2006	63.5	0.41	--
2007	64.4	0.36	--
2008	143	1.1	8.4
2017	85.0	0.59	6.5
2022	11.6	0.11	[a]0.79

[a] The net total phosphorus load from groundwater is calculated using the robust median sample result, from table 4.

Reductions in groundwater loading of trace metals to the South Fork Coeur d'Alene River also had a meaningful impact on AWQC ratios and therefore instream water quality. At the river sites (SFCDR 1, 2, 3, and 4), the AWQC ratios for zinc and cadmium all decreased from 2017 to 2022 (table 7). Base-flow conditions generally produce the highest AWQC ratios because there is less streamflow to "dilute" the trace metal concentrations (Clark and Mebane, 2014). The reduction in AWQC ratios in 2022 is attributed to three likely factors. First, ratios have been observed in previous studies to be declining because of regionally decreasing metal concentrations as a result of ongoing remediation activities throughout the Bunker Hill Superfund Site (Clark and Mebane, 2014; Zinsser, 2019). Second, this study supports that the GWCS at the CIA reduced groundwater loading of dissolved zinc and dissolved cadmium into the South Fork Coeur d'Alene River, and thus locally reduced base-flow concentrations of both trace metals in the river. Third, increased hardness decreases the toxicity of the metals, and hardness was observed to increase in the upstream reach of the South Fork Coeur d'Alene River (fig. 9), within which CTP effluent discharges. These factors likely all contributed to reduced AWQC ratios, which indicate the South Fork Coeur d'Alene River's suitability for aquatic life increased from 2017 to 2022. However, although the AWQC ratios were reduced, they are still exceeding the criteria of one for zinc and cadmium.

Changes in streamflow and metal loading in the Bunker Creek and Government Gulch tributaries were consistent with expectations. The CTP, prior to 2020, discharged treated effluent to Bunker Creek (CH2M, 2023), and the lowered streamflow observed in Bunker Creek in 2022 relative to 2017 was expected because the effluent location moved into the South Fork Coeur d'Alene River downstream from SFCDR 1. The concentrations of all measured analytes were also higher in Bunker Creek in 2022 relative to 2017, presumably because the CTP effluent is no longer diluting metals in Bunker Creek, a finding that was expected. Despite the higher concentrations of all measured analytes in Bunker Creek, lower streamflow led to lower calculated constituent loads from Bunker Creek to the South Fork Coeur d'Alene River in 2022 compared to 2017.

Dissolved metal loads in Government Gulch were slightly higher in 2022 than in 2017 due to higher measured streamflow in 2022, despite lowered concentrations of dissolved zinc, dissolved cadmium, and total phosphorus in 2022. Streamflow at Government Gulch was highly variable in 2017 as a result of construction activities (Zinsser, 2019), and load calculations may not have been representative of baseline conditions because discharge was fluctuating over the course of the 2-day study. The increase in loads in Government Gulch from 2017 to 2022 is likely a function of the increase in streamflow that we measured in 2022 (from 0.55 ft^3/s in 2017 to 1.02 ft^3/s in 2022), although the increase in both flow and loads in Government Gulch possibly indicates that more contaminated groundwater is discharging to Government Gulch in 2022 relative to 2017.

Similar to streamflow and metals, the total phosphorus load was lower in 2022 than in 2017 at the farthest downstream river site (SFCDR 4; fig. 10), and smaller load accruals from groundwater were calculated in the middle reach in 2022 relative to 2017. From 2017 to 2022, mean net accrual of total phosphorus from groundwater in the middle reach decreased by 88 percent (fig. 4*D*). Anecdotally, far less filamentous algae growth was observed in the downstream river sites during our study in 2022 than during the 2017 seepage study dates. Because algae growth is dependent on nutrients, the reduction in algae may be in response to the reduction in total phosphorus concentration measured in the South Fork Coeur d'Alene River in 2022. The reduction in total phosphorus accrual from groundwater in the middle section and full study reach in 2022 relative to 2017 and anecdotal observations support our general conclusion that the GWCS at the CIA has decreased groundwater loading of total phosphorus to the South Fork Coeur d'Alene River (table 8), consistent with modeling results (CH2M, 2023) and CTP efficacy data (U.S. Environmental Protection Agency, 2021). However, although total phosphorus concentrations decreased overall, there are some interesting patterns in spatial occurrence and changes in the phosphorus species between 2017 and 2022.

In calculating total phosphorus gained in the South Fork Coeur d'Alene River from groundwater, we are assuming that phosphorus is conservatively moving downstream; in other words, no other process is changing concentrations of phosphorus between upstream and downstream river sites aside from inflow of phosphorus from tributaries. However, because the middle section has wetlands lining the left riverbank, biological activity is likely to impact phosphorus concentrations between SFCDR 2 and 3 in addition to groundwater loads. Wetlands can either contribute phosphorus to the system as a decay product or remove phosphorus from the system through phosphorus uptake (Withers and Jarvie, 2008). In the marshy area, Seep 2 contributed a relatively high load of total phosphorus (0.627 ± 0.697 kg/d) despite its small estimated discharge (0.01 ft^3/s), although the mean Seep 2 phosphorus load was within the standard deviation of repeat samples (table 4). The high phosphorus load from Seep 2 is consistent with findings in 2017. Seep 2 may be impacted by organic debris in samples because it is particularly shallow with low velocity making it difficult to collect a clean sample, but high phosphorus from Seep 2 also possibly represents increased biological activity in the marshy area. Interestingly, although total phosphorus loads decreased overall at SFCDR 3 and SFCDR 4 from 2017 to 2022 (fig. 10), the ratio of orthophosphate to total phosphorus increased at these two river sites from 2017 to 2022 (fig. 11). Orthophosphate is generally more biologically accessible than total phosphate; thus, the shift in the orthophosphate to total phosphorus ratio may indicate that an increasing proportion of phosphorus in the South Fork Coeur d'Alene River has a biological origin (for example, from the marshy area or from instream algae) rather than coming from groundwater. The actual ratio of total phosphorus to orthophosphate in SFCDR 1 and SFCDR 2 is unknown because total phosphorus samples with concentrations less than the method reporting limit (<0.003 mg/L) are lower than the method reporting limit for orthophosphate (<0.004 mg/L). All ratios plotted in fig. 11 assume that the non-detect samples were equal to the method reporting limit and ratios could not exceed a value of one.

Other seepage studies, from as early as 1999, have quantified groundwater-specific constituent loading to the middle section between SFCDR 2 and 3. Not only did dissolved zinc, dissolved cadmium, and total phosphorus loads from groundwater decrease in the middle section since 2017 (86 percent, 81 percent, and 88 percent respectively), the lowest accruals from groundwater of these three constituents were measured in this middle river section to

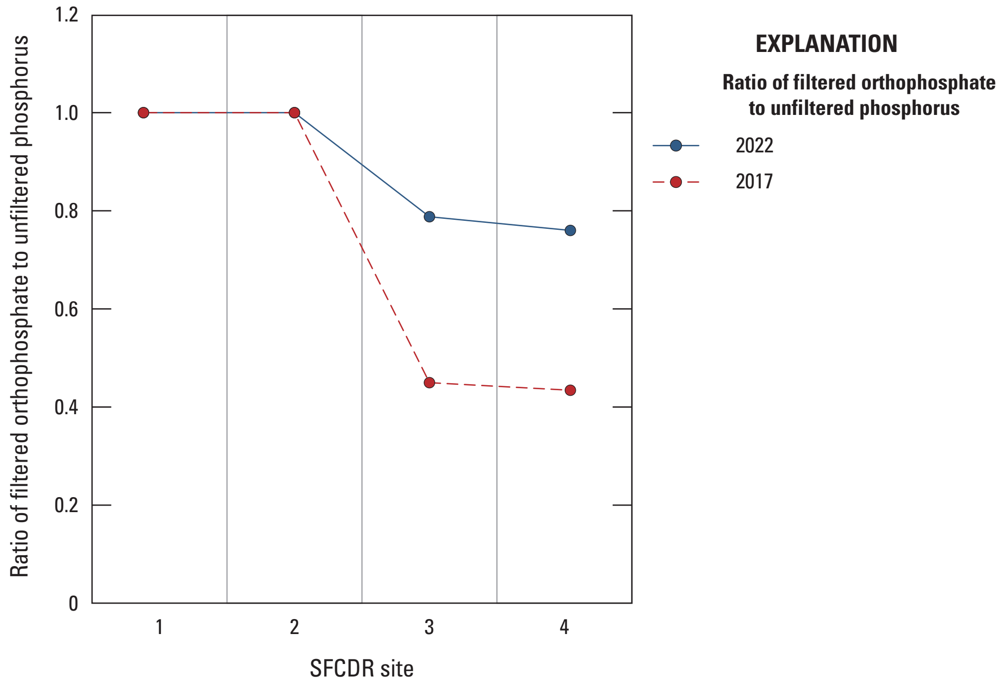


Figure 11. Ratio of filtered orthophosphate to unfiltered (total) phosphorus at monitoring sites SFCDR 1– 4, South Fork Coeur d'Alene River, northern Idaho, August 30–31, 2022 (U.S. Geological Survey, 2023). [SFCDR 1–4, sites South Fork Coeur d'Alene River 1–4].

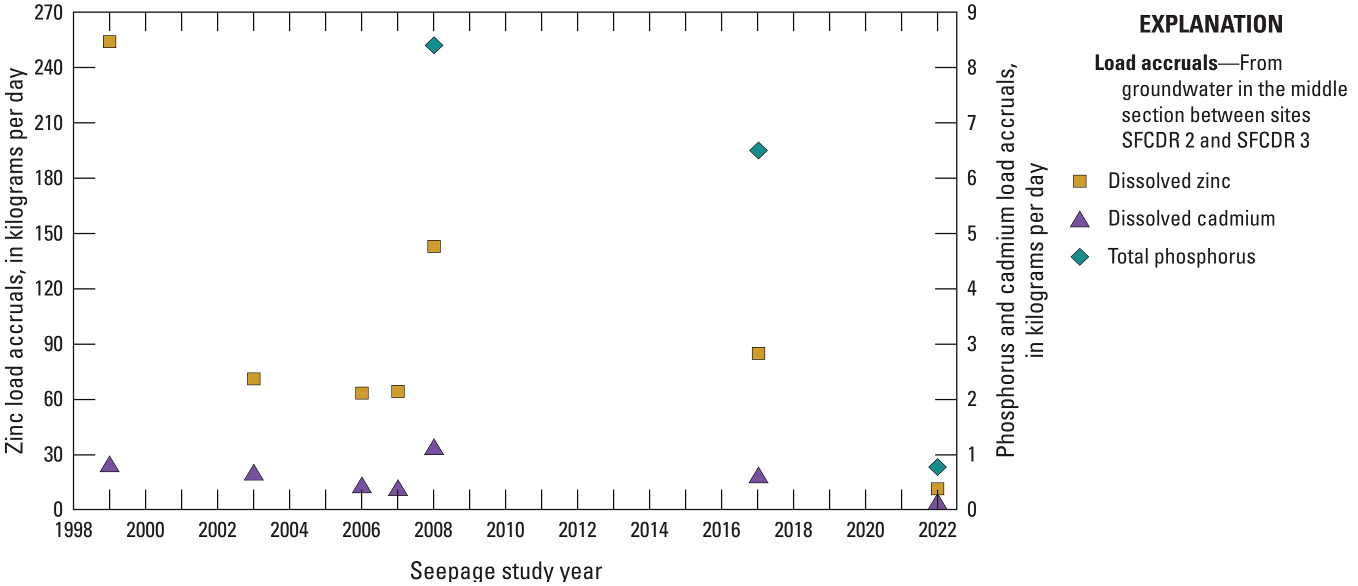


Figure 12. Historical dissolved zinc, dissolved cadmium, and total phosphorus accruals from groundwater in the middle section from monitoring sites SFCDR 2 to SFCDR 3, South Fork Coeur d'Alene River, northern Idaho, 1999–2022. [SFCDR 2 and SFCDR 3, sites South Fork Coeur d'Alene River 2 and 3. 1999: Data from Barton, 2002. 2003–08: Data from CH2M Hill, 2009. 2017: Data from Zinsser, 2019. 2022: Data from this study, presented in table 8].

date (table 8; figs. 4 and 12). Because there was a net increase of dissolved zinc, dissolved cadmium, and total phosphorus load accruals from groundwater in the downstream section, some contaminated groundwater plausibly is still flowing west of the GWCS. However, there were no measurable gains in streamflow from groundwater in the downstream section, and all load accruals in the downstream section were within propagated accrual uncertainty. To assess whether groundwater loading is persisting in the downstream section, one might focus a seepage study within that section or evaluate gains in a groundwater flow model. The uncertainty around propagated accruals could be minimized by simultaneously collecting samples at all sites, thereby minimizing the diel-cycling impact on sample results. Although it was infeasible to accomplish concurrent sampling in the full study reach during this study, concurrent sampling may be more attainable in a study focused on only the downstream section with fewer monitoring sites.

The reach of river between Kellogg and Smelterville has been estimated to represent about 20–30 percent of the annual trace metal loads and 11 percent of the nutrient loads delivered to Coeur d'Alene Lake (Clark and Mebane, 2014). Thus, the reduction in load accruals from groundwater and total loads at the farthest downstream site (SFCDR 4) quantified in this study also have implications for reduced loading of trace metals and nutrients to the main-stem Coeur d'Alene River and Coeur d'Alene Lake.

Summary

The U.S. Geological Survey (USGS) conducted a seepage study in 2022 to quantify groundwater loading to the South Fork Coeur d'Alene River, in northern Idaho, following installation of the groundwater collection system (GWCS) at the Central Impoundment Area (CIA) within the Bunker Hill Superfund Site. The calculated groundwater inputs of dissolved zinc, dissolved cadmium, and total phosphorus to the South Fork Coeur d'Alene River were substantially less in 2022 than in 2017 (pre-remediation), a change we attribute to performance of the GWCS at the Bunker Hill Superfund site. Despite the Central Treatment Plant (CTP) effluent location moving from Bunker Creek to the South Fork Coeur d'Alene River, the CTP effluent did not contribute substantial loading of dissolved zinc, dissolved cadmium, or total phosphorus to the South Fork Coeur d'Alene River. The ambient water-quality criteria ratio for zinc and cadmium also decreased at each sampled river site, indicating that the observed improvement to the South Fork Coeur d'Alene River water quality is meaningful to aquatic life although concentrations still exceed criteria. At the farthest downstream location of the study reach (SFCDR 4), measured concentrations of dissolved zinc, dissolved cadmium, and total phosphorus in 2022 were substantially less than in 2017. Reduced concentrations and loads of trace metals and nutrients in the South Fork Coeur d'Alene River as a direct result of the GWCS implemented at the CIA during 2017–2021 also have implications for improved water quality downstream in the Coeur d'Alene River and in Coeur d'Alene Lake.

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