

Prepared in cooperation with the Cheyenne River Sioux Tribe

Concentrations of Selected Metals in Quaternary-Age Fluvial Deposits along the Lower Cheyenne and Middle Belle Fourche Rivers, Western South Dakota, 2009–10



Data Series 695

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

Front cover. Background: Flood-plain deposits from the bank of the Belle Fourche River at site BF4.
Center right: Sampling activities at the Trask Road reference site along the Cheyenne River.
Center left: Subsurface coring on the Belle Fourche River at site BF3.

Back cover. View north of the Cheyenne River from the Hump Flat reference site.

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U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Volume		
cubic meters (m ³)	1.3069	cubic yards (yd ³)
liter (L)	0.2642	gallon (gal)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
metric ton	1.102	ton

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.

Concentrations of chemical constituents in sediment are given either in milligrams per kilogram (mg/kg) or micrograms per kilogram (µg/kg).

Acronyms and Abbreviations

As	arsenic
C	carbon
CBFRS	Cheyenne and Belle Fourche River sediment
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
$[\text{CH}_3\text{Hg}]^+$	methyl mercury
$[\text{CN}]^-$	cyanide anion
Cr	chromium
Fe	iron
FeAsS	arsenopyrite
GPS	global positioning system
H	hydrogen
Hg	mercury
lidar	Light Detection And Ranging
N	nitrogen
Pb	lead
RPD	relative percent difference
S	sulfur
Se	selenium
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
WRDA	Water Resources Development Act
Zn	zinc

Concentrations of Selected Metals in Quaternary-Age Fluvial Deposits along the Lower Cheyenne and Middle Belle Fourche Rivers, Western South Dakota, 2009–10

By John F. Stamm and Galen K. Hoogestraat

Abstract

The headwaters of the Cheyenne and Belle Fourche Rivers drain the Black Hills of South Dakota and Wyoming, an area that has been affected by mining and ore-milling operations since the discovery of gold in 1875. A tributary to the Belle Fourche River is Whitewood Creek, which drains the area of the Homestake Mine, a gold mine that operated from 1876 to 2001. Tailings discharged into Whitewood Creek contained arsenopyrite, an arsenic-rich variety of pyrite associated with gold ore, and mercury used as an amalgam during the gold-extraction process. Approximately 18 percent of the tailings that were discharged remain in fluvial deposits on the flood plain along Whitewood Creek, and approximately 25 percent remain in fluvial deposits on the flood plain along the Belle Fourche River, downstream from Whitewood Creek. In 1983, a 29-kilometer (18-mile) reach of Whitewood Creek and the adjacent flood plain was included in the U.S. Environmental Protection Agency's National Priority List of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, commonly referred to as a "Superfund site." Listing of this reach of Whitewood Creek was primarily in response to arsenic toxicity of fluvial deposits on the flood plain.

Lands along the lower Cheyenne River were transferred to adjoining States and Tribes in response to the Water Resources Development Act (WRDA) of 1999. An amendment in 2000 to WRDA required a study of sediment contamination of the Cheyenne River. In response to the WRDA amendment, the U.S. Geological Survey completed field sampling of reference sites (not affected by mine-tailing disposal) along the lower Belle Fourche and lower Cheyenne Rivers. Reference sites were located on stream terraces that were elevated well above historical stream stages to ensure no contamination from historical mining activity. Sampling of potentially contaminated sites was performed on transects of the active flood plain and adjacent terraces that could potentially be inundated during high-flow events. Sampling began in 2009 and was completed in 2010. A total of 74 geochemical samples were collected from fluvial deposits at reference sites,

and 473 samples were collected from potentially contaminated sites. Sediment samples collected were analyzed for 23 metals, including arsenic and mercury. Sequential replicate, split duplicate, and field quality-control samples were analyzed for quality assurance of data-collection methods. The metal concentrations in sediment samples and location information are presented in this report in electronic format (Microsoft Excel), along with non-parametric summary statistics of those data. Cross-sectional topography is graphed with arsenic and mercury concentrations on transects at the potentially contaminated sites. The mean arsenic concentration in reference sediment samples was 8 milligrams per kilogram (mg/kg), compared to 250, 650, and 76 mg/kg for potentially contaminated sediment samples at the surface of the middle Belle Fourche River site, the subsurface of the middle Belle Fourche River site, and the surface of the lower Cheyenne River site, respectively. The mean mercury concentration in reference sediment samples was 16 micrograms per kilogram ($\mu\text{g/kg}$), compared to 130, 370, and 71 $\mu\text{g/kg}$ for potentially contaminated sediment samples at the surface of the middle Belle Fourche River site, the subsurface of the middle Belle Fourche River site, and the surface of the lower Cheyenne River site, respectively.

Introduction

The headwaters of the Cheyenne River include the Black Hills of South Dakota and Wyoming (fig. 1). The Belle Fourche River is a major tributary of the Cheyenne River and drains the northern Black Hills. The headwaters of the Belle Fourche River have been affected by mining and ore-milling operations since the discovery of gold near Deadwood, South Dakota, in 1875 (Goddard, 1989). A headwater tributary of the Belle Fourche River is Whitewood Creek (fig. 1), which drains the area of the Homestake Mine, a gold mine that operated from 1876 to 2001 (Mitchell, 2009). Milling operations at the Homestake Mine produced a concentrate of ores that contain arsenic (As), chromium (Cr), lead (Pb) and zinc (Zn), among others (Caddey and others, 1991). Gold ore is associated with

the mineral arsenopyrite (FeAsS), which is rich in iron (Fe), arsenic, and sulfur (S). Caddey and others (1991) estimated that Homestake ore had as much as 60,500 milligrams per kilogram (mg/kg) of arsenic, primarily in the form of arsenopyrite, although the ore probably contained an average concentration of about 25,000 mg/kg arsenic. The gold extraction process utilized mercury (Hg) and an anion of carbon (C) and nitrogen (N) known as cyanide ($[\text{CN}]^-$), which were discharged as milling waste with mine tailings into Whitewood Creek, until December of 1970, when this practice was discontinued (Goddard, 1989).

Sediment Discharges from Milling Operations

The U.S. Environmental Protection Agency (1973) estimated that approximately 2,700 metric tons of suspended solids were discharged from milling operations into Whitewood Creek on a daily basis in June 1971, and this may have been a typical discharge during the period of modern mining operations, since about 1920. The U.S. Environmental Protection Agency (1971) estimated that 5 to 18 kilograms (kg) of mercury per day were discharged into Whitewood Creek in 1970. Marron (1992) estimated that a total of approximately 110,000,000 metric tons of mining and milling wastes from gold-mining activities were discharged into Whitewood Creek from 1876 through 1977. Of that total, nearly 18 percent of the discharged mine tailings remain stored in fluvial sediment on the flood plain along Whitewood Creek, and 25 percent remain stored farther downstream in fluvial deposits on the flood plain of the Belle Fourche River downstream from its confluence with Whitewood Creek (Marron, 1992).

The amount of mine tailings farther downstream in fluvial deposits on the flood plain of the lower Cheyenne River and Lake Oahe (fig. 1) is uncertain. Transport of mine tailings farther downstream by the Missouri River was contained after completion of Oahe Dam around 1960. Discharges of mine tailings into Whitewood Creek ceased in 1977, at which point tailings were discharged into a storage facility (Mitchell, 2009).

Toxic effects of arsenic in fluvial deposits on the flood plain along Whitewood Creek became a concern in 1974–75 with the death of 50 Holstein dairy cattle as a result of arsenotoxicity (Goddard, 1989). Bergeland and others (1976) concluded that those cattle consumed corn silage that was contaminated with mining wastes. In 1983, a 29-kilometer (km; 18-mile) reach of Whitewood Creek and the adjacent flood plain was included in the U.S. Environmental Protection Agency (USEPA) National Priority List under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA). Remedial activities at this site included the removal of approximately 3,400 cubic meters of contaminated soil from 16 residential areas, disposal of contaminated soil in an undeveloped part of the site, and continued surface-water monitoring. Remedial activities were completed in 1993. The site was removed from the USEPA

National Priority List in 1996 (U.S. Environmental Protection Agency, 2011a).

Results of studies by the U.S. Geological Survey (USGS) of the geochemistry of sediment deposited in the flood plain of Whitewood Creek, the Belle Fourche River, and the Cheyenne River are summarized by Goddard (1989). Studies described in that report included estimates of the concentrations of major, minor, and trace elements from 13 fluvial-sediment samples along the Belle Fourche River upstream from Whitewood Creek that would serve as reference or background samples, and 95 fluvial-sediment samples from Whitewood Creek that were visually identified as being contaminated by mine tailings. Arsenic was determined to be the principal potentially toxic contaminant of those sediment samples. The average arsenic concentration of streambank sediment of the Belle Fourche River upstream from Whitewood Creek was 9 mg/kg (range of 4 to 20 mg/kg). Sediment on Whitewood Creek that was visually identified as contaminated by mine tailings had an average arsenic concentration of 1,900 mg/kg (range of 350 to 8,200 mg/kg).

Goddard (1989) collected additional sediment samples to refine estimates of the spatial variability of arsenic concentrations. The 168 channel-sediment samples that were not affected by mine-tailing discharges had an arithmetic mean arsenic concentration of 21 mg/kg and a geometric mean arsenic concentration of 11 mg/kg. Goddard (1989) described a threshold value for contamination as two standard deviations greater than the geometric mean of the arsenic concentration of uncontaminated sediment. Using this approach, a threshold concentration of contamination of 46 mg/kg arsenic was computed by Goddard (1989) for fluvial sediment of the Belle Fourche and Cheyenne Rivers. Samples also were collected from potentially contaminated sediment on the flood plain along Whitewood Creek, the Belle Fourche River, and the Cheyenne River. A total of 236 samples of potentially contaminated fluvial sediment along Whitewood Creek had an arithmetic mean arsenic concentration of 1,600 mg/kg. Mean arsenic concentrations of potentially contaminated fluvial sediment from the Belle Fourche River decreased from about 1,300 mg/kg near the confluence with Whitewood Creek to about 400 mg/kg near the confluence with the Cheyenne River. Arsenic concentrations as high as 530 mg/kg were measured in samples collected downstream from the confluence of the Cheyenne River with the Belle Fourche River, and averaged about 78 mg/kg.

The Water Resources Development Act

In 1944, tribal lands in South Dakota along the Missouri and Cheyenne Rivers were acquired by the U.S. Government under the Pick-Sloan Missouri River Basin Program. In 1959, much of that land was flooded upstream from Oahe Dam, built to impound Lake Oahe (fig. 1). The reservoir and surrounding lands have been subsequently managed by the U.S. Army Corps of Engineers (USACE). In 1999, Public Law 106–53,

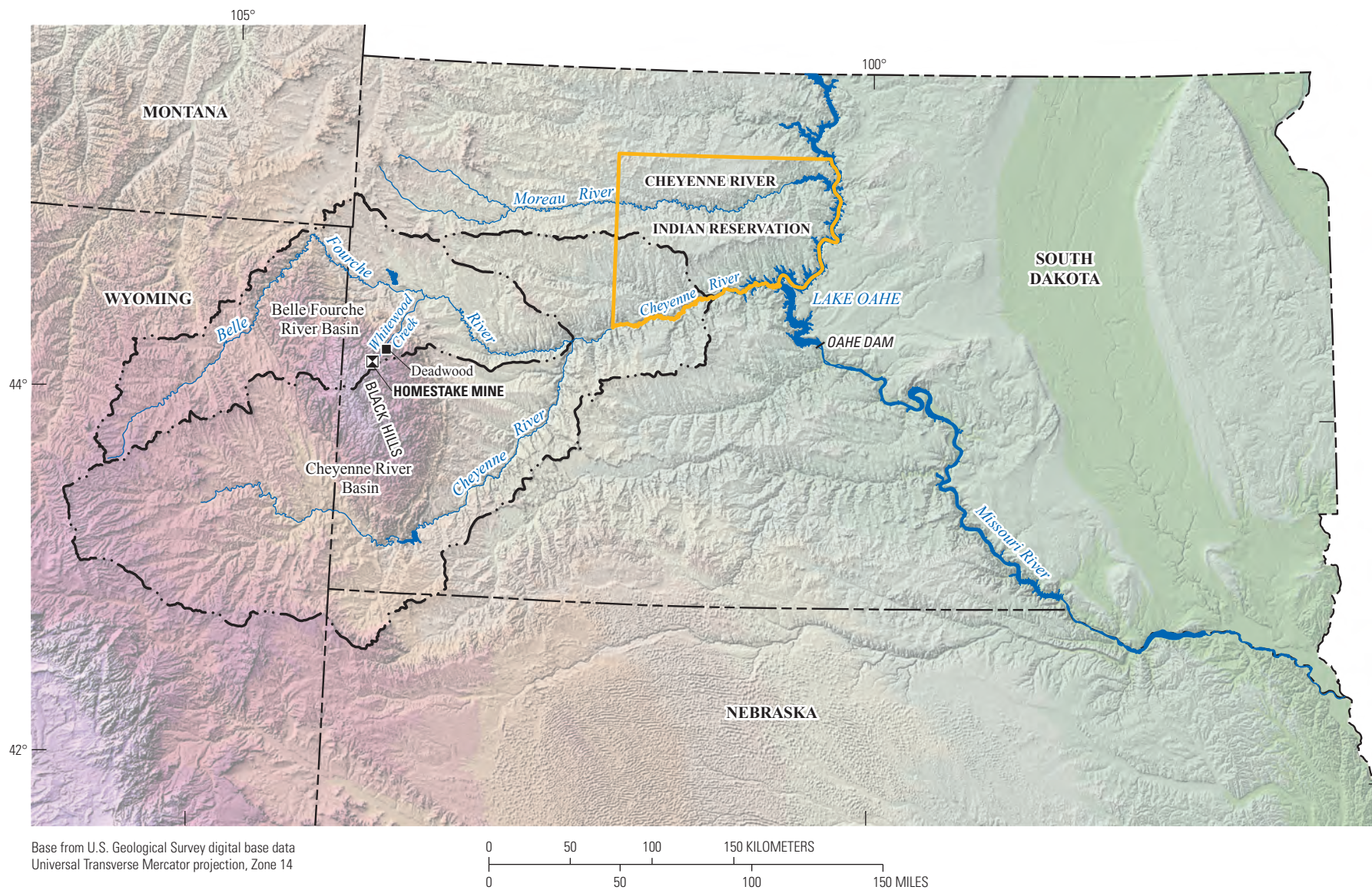


Figure 1. Location of the Cheyenne and Belle Fourche River Basins.

Title VI, authorized the Department of the Interior to hold in trust specified USACE lands and recreation areas around Lake Oahe for use in perpetuity by the Cheyenne River and Lower Brule Sioux Tribes. This public law is cited as the Water Resources Development Act (WRDA), which was amended in 2000 (U.S. Government, 2000).

Studies following the enactment of WRDA include ecological and human risk assessments by the U.S. Environmental Protection Agency (2005, 2006) for two exposure areas: the Cheyenne River arm of Lake Oahe, and a reach of the lower Cheyenne River extending downstream from its confluence with the Belle Fourche River to the Cheyenne River arm of Lake Oahe. Reference areas were the Moreau River, Moreau River arm of Lake Oahe, Lake Oahe north of the Cheyenne River arm, and upland stock ponds. The Moreau River flows approximately parallel to and 48 km (30 miles) north of the Cheyenne River (fig. 1). Ecological risk was identified for benthic organisms and semi-aquatic wildlife (birds and mammals), but not for fish, and was associated with selenium, arsenic, and methyl mercury. Human risk was identified for fishermen, particularly for subsistence fishermen. Toxic risk was associated with arsenic (but uncertainty was high) and with methyl mercury for subsistence fishermen. Moreau River sediment had a mean arsenic concentration of 7.3 mg/kg (U.S. Environmental Protection Agency, 2005) with a range from 4.0 to 20 mg/kg, similar to that present in previous studies (for example, U.S. Environmental Protection Agency, 1973; Goddard, 1989) of background concentrations of Cheyenne River sediment. Mercury was detected in less than one-half of all samples from reference and potentially contaminated sites for analyses with high reporting levels (90–280 micrograms per kilogram [$\mu\text{g/kg}$]). Sediment samples from the Cheyenne River and Cheyenne River arm (of Lake Oahe) was collected at seven locations (U.S. Environmental Protection Agency, 2005). The mean arsenic concentration of Cheyenne River sediment was 60 mg/kg with a range from 19 to 360 mg/kg, and mean arsenic concentration of Cheyenne River arm sediment was 24 mg/kg with a range from 8.7 to 62 mg/kg.

Engineering-Environmental Management, Inc. (2004) reported metal concentrations in fluvial sediment from USACE lands that were to be transferred to States and Tribes in response to the WRDA legislation. Reference sampling for that report included 10 samples on a terrace approximately 76 meters (m) above the submerged channel floor, and approximately 40 m above the lake surface. Both surface and subsurface sediment were analyzed for metals. Mean arsenic concentrations of fluvial sediment on terraces were 14 mg/kg for surface samples and 9.5 mg/kg for subsurface samples (Engineering-Environmental Management, Inc., 2004). Surface and subsurface concentrations of mercury were both 30 $\mu\text{g/kg}$. Potentially contaminated, valley-bottom deposits had mean arsenic concentrations of 60 mg/kg for surface samples and 85 mg/kg for subsurface samples, with maximum concentrations of 100 mg/kg for surface samples and 440 mg/kg for subsurface samples. The mean mercury

concentrations in valley-bottom deposits were 60 $\mu\text{g/kg}$ for surface samples and 70 $\mu\text{g/kg}$ for subsurface samples, with maximum concentrations of 84 $\mu\text{g/kg}$ for surface samples and 300 $\mu\text{g/kg}$ for subsurface samples.

In September 2008, the USACE requested that the USGS sample fluvial sediment along the Cheyenne River in response to section 606 (j), subsection 1(A) of the WRDA as amended in 2000 (U.S. Government, 2000). This amendment requires that the Secretary of the Army complete a study of sediment contamination in the Cheyenne River no later than 10 years after the date of enactment of that section of the WRDA. Based on the results from previous reports of sediment contamination from mining in the northern Black Hills (such as Goddard, 1989; Marron, 1992), the study of sediment contamination by the Secretary of the Army would include sites on both the Cheyenne and Belle Fourche Rivers. Field surveys and geochemical sampling by the USGS for that study were completed during the summers of 2009 and 2010. In the remainder of this report, the USGS study is referred to as the Cheyenne and Belle Fourche River sediment (CBFRS) study. This report was prepared in cooperation with the Cheyenne River Sioux Tribe.

Purpose and Scope

The purpose of this report is to describe study design, sample collection, analytical methods, quality control, locations and elevations of samples, and laboratory analyses used in the CBFRS study. The scope of this report does not include interpretation of data or findings, geomorphic maps, or estimates of bank-erosion or bar deposition.

The CBFRS study included two parts. The purpose and scope of Part I of the CBFRS study, completed in 2009, was to provide a “reference” for the concentration of metals in fluvial deposits that were not affected by mining activities in the northern Black Hills. Part I included sampling of fluvial deposits on high terraces, elevated well above the high stage recorded at nearby USGS streamgages. The purpose and scope of Part II of the CBFRS study, completed in 2010, was to characterize the concentration of metals in fluvial deposits potentially contaminated by mining activities in the northern Black Hills. Sediment samples collected for Part II of the CBFRS study are referred to as “potentially contaminated” samples in this report. In Parts I and II of the CBFRS study, sediment samples were analyzed for 23 metals, including arsenic and mercury.

The CBFRS study is distinguished from previous studies by Goddard (1989) in that samples were categorized in the framework of geomorphic setting. Geomorphic setting includes descriptors, such as active channel, active flood plain, back channel, or terraces. Multiple terraces were mapped in the study area. Some terraces were sufficiently elevated above the stream channels so that historical inundation by floodwaters may have been infrequent or unlikely. The extent of the channel, flood plain, and terraces along the middle

Belle Fourche and lower Cheyenne River were mapped at a 1:24,000 scale. Additional sites, not included in this report, were surveyed using ground-based Light Detection And Ranging (lidar) equipment following the 2010 spring flooding event to provide quantitative estimates of volumes of sediment eroded from banks or deposited on point bars during that period.

Study Design

Part I of the CBFRS study included the collection of samples from high terraces or channel sites that were not affected by discharges of mine tailings, which serve as a reference population. These sites are referred to as reference sites in this report. Part II of the study included the collection of sediment samples from sites that were potentially contaminated by discharges of mine tailings from the northern Black Hills. These sites are referred to as potentially contaminated sites in this report. Sediment samples from both reference and

potentially contaminated sites were analyzed for 23 metals listed in table 1.

Sampling Sites

The study design for reference sites included collecting samples from fluvial deposits that were not subject to influx of mine tailings or from terraces that were elevated well above historical streamflow stages, and sites on the Cheyenne River upstream from its junction with the Belle Fourche River (and therefore not affected by discharges from Whitewood Creek). Reference sites on terraces were located 9 to 85 m above the channel, and are best characterized as strath terraces with thin fluvial deposits capping bedrock that is exposed along the terrace riser (eroded edge of the terrace).

Fluvial deposits that were sampled at reference sites included gravel beds with lithologies that were consistent with a provenance in the Black Hills (Redden and DeWitt, 2008). Examples of consistent lithologies include limestone (such as Mississippian-age Madison Limestone in plateaus

Table 1. List of metals analyzed in sediment samples and reporting levels.

[USGS, U.S. Geological Survey; mg/kg, milligrams per kilogram; µg/kg, micrograms per kilogram]

Metal	USGS parameter code	Units	Minimum reporting level	Most common reporting level	Maximum reporting level
Antimony	29817	mg/kg	0.73	1.1	26
Arsenic	29819	mg/kg	0.97	1.3	32
Barium	29821	mg/kg	0.48	1.1	22
Beryllium	29823	mg/kg	0.24	0.26	5.6
Cadmium	29827	mg/kg	0.24	0.26	6.4
Calcium	29828	mg/kg	24	53	1,100
Chromium	29830	mg/kg	0.73	1.9	39
Cobalt	29831	mg/kg	0.47	0.53	11
Copper	29833	mg/kg	0.97	2.6	56
Iron	29835	mg/kg	7.3	42	1,000
Lead	29837	mg/kg	0.39	0.47	10
Magnesium	29838	mg/kg	9.7	16	330
Manganese	29840	mg/kg	0.48	2.4	58
Nickel	29846	mg/kg	1.9	2.1	44
Selenium	29848	mg/kg	0.63	1.6	33
Sodium	29851	mg/kg	240	260	5,600
Thallium	29852	mg/kg	0.58	1.6	33
Vanadium	29854	mg/kg	0.94	1.1	26
Zinc	29856	mg/kg	1.5	4.2	89
Mercury	62978	µg/kg	29	35	440
Aluminum	65196	mg/kg	4.8	26	560
Potassium	65198	mg/kg	140	160	3,300
Silver	65199	mg/kg	0.48	0.8	17

of the Black Hills), potassium-feldspar rich granite (such as Precambrian-age Harney Peak Granite in the core of the Black Hills), porphyritic rhyolite (as exposed in Tertiary-age intrusives in the northern Black Hills), red quartzite (present in the Cambrian- and Ordovician-age Deadwood Formation) and metamorphic rocks, such as schist and phyllite (present in the Precambrian-age core of the Black Hills). Ages of fluvial deposits on terraces were determined by radiocarbon or optically stimulated luminescence dating techniques. Duller (2008) provides an overview of field and laboratory techniques used for determining the age of sediments based on optically stimulated luminescence. Ages calculated from fluvial deposits on terraces were Quaternary age.

The study design for potentially contaminated sites included sediment sampling on transects that span the active flood plain, adjacent terraces, and bank exposures. Two sites downstream from Whitewood Creek were selected: (1) the middle Belle Fourche River site and (2) the lower Cheyenne River site. Field evidence for the designation of active flood plain included observations of inundation in 2008 and 2009, active backwater channels, loose sediment on the surface, blocks of ice on the surface, sediment deposited on top of vegetation (grass), material snagged in vegetation above the soil surface, and presence of driftwood on the surface.

Sediment Sampling at Reference Sites

Four sites on the lower Cheyenne River (Wasta, Trask Road, Bridger, and Hump Flat) and one site on the middle Belle Fourche River (Volunteer) were selected as reference sites (table 2; fig. 2). Multiple sediment samples were collected at reference sites from natural exposures (such as head scarps above slump blocks) or from pits excavated by hand shovel or trowel. Sampling locations are shown in figure 2; samples are identified by an abbreviation of the site name followed by other identification (for example, the Volunteer site has two sampling locations identified as VOLU-L1 and VOLU-L2). Locations of exposures or pits were randomly selected from a series of points along the terrace riser. A total of 10 random points were selected and evaluated for suitability in the field before sampling. Examples of attributes that would make a sample location unsuitable include (but were not limited to) the following:

- it was on or near a road or trail,
- it was over or near a utility line,
- it was near a previous sample site (within 7.6 m),
- excavation would affect a fence post, tree, woody brush, building, or other feature that should not be disturbed,
- the site was previously excavated (base of gravel pit or cattle pond),
- it was on an inaccessible scarp or has potential for collapse,

- the landowner requested excavation at a different location, or
- archaeological surveys indicated that the site was unacceptable.

Local utilities were contacted to determine that sampling would not threaten utility lines. Selected sampling locations were surveyed using high-precision global positioning system (GPS) equipment.

Samples also were collected from active channel bars on transects crossing the Cheyenne River at the Wasta and Trask Road sites (sampling locations TRAS-XS and WAST-XS on fig. 2). At both of those sampling locations, three pit locations on the transects were randomly selected and sampled. Locations had to be sufficiently elevated above stream level so that there would be no standing water in each excavated pit. Samples were collected from the surface (upper 10 centimeters [cm] of soil) and subsurface (generally an interval 20 to 40 cm deep), and sampling was completed during low streamflow. These samples were considered to be reference samples in this report because the channel is upstream from the confluence of the Cheyenne and the Belle Fourche Rivers, and therefore upstream from mine-tailing discharges.

Sediment Sampling at Potentially Contaminated Sites

Two sites were selected for sampling potentially contaminated fluvial deposits (table 3), one on the middle Belle Fourche River (figs. 3 and 4) and one on the lower Cheyenne River (fig. 5). Sediment sampling locations at potentially contaminated sites include those from multiple excavations on transects, subsurface cores (middle Belle Fourche River site only), and bank exposures. Sediment samples collected from excavations on transects included shallow samples (upper 10 cm of soil) at both the middle Belle Fourche River and lower Cheyenne River sites, and subsurface samples (generally an interval 20 to 40 cm deep) at only the middle Belle Fourche River site. Transects extended perpendicular from the river channel and included high terraces that were not necessarily contaminated by mine tailings. Locations of transects were selected to include lateral and point bar depositional environments on the active flood plain. Surfaces with evidence of recent flooding were of particular interest. Sampling locations are shown in figures 4 and 5; samples are identified by an abbreviation of the site name (“BF” for middle Belle Fourche River site or “CR” for the lower Cheyenne River site), followed by an abbreviation of the sample type (“GP” for subsurface core or “BK” for bank exposure), followed by other identification. For example, the lower Cheyenne River site (fig. 5) has four bank exposure sampling locations identified as CRBK1, CRBK2, CRBK3, and CRBK4, and three transects identified as CR1, CR2, and CR3.

On Belle Fourche River flood-plain transects, excavations were spaced approximately every 6 m, and a hand shovel was used to excavate each pit. At the lower Cheyenne River site,

Table 2. Reference site descriptions.

[USGS, U.S. Geological Survey; m, meters. Elevation, in meters, above North American Vertical Datum of 1988]

Site name (abbreviation)	Site characteristics	Site description
Wasta (WAST)	Name	Cheyenne River terrace above Wasta and channel at USGS streamgage.
	Elevation	Terrace at 77 m above channel and channel/flood plain near streamgage; elevation 774.2 m.
	Location	Terrace deposits exposed in gravel pit adjacent to Elm Springs Road and channel near USGS streamgage.
	Map description ¹	Wasta, T. 1 N., R. 14 E., NE¼ of section 5.
	Land use	Gravel mining.
Trask Road (TRAS)	Name	Cheyenne River terrace and channel near Trask Road.
	Elevation	Terrace at 77 m above channel and main channel; elevation 743.7 m.
	Location	West of Trask Road and adjacent channel sediment.
	Map description ¹	Wasta NW, T. 14 E., R. 3 N., SW¼ of section 25.
	Land use	Grazing.
Bridger (BRID)	Name	Cheyenne River terrace west of Bridger.
	Elevation	Terrace at 85 m above channel, elevation 658.4 m.
	Location	North of channel on Cheyenne River Indian Reservation land.
	Map description ¹	Bridger, T. 7 N., R. 18 E., SE½ of sections 28 and 29.
	Land use	Surface gravel mining, residence of landowner, grazing.
Hump Flat (HUMP)	Name	Cheyenne River terrace on Hump Flat.
	Elevation	Terrace at 85 m above channel, elevation 646.2 m.
	Location	North of channel, east of Route 73/34, 3 miles east of Bridger.
	Map description ¹	Bridger SE, T. 7 N., R. 19 E., S½ of sections 28 and 29.
	Land use	Nearby use includes crop production (hay).
Volunteer (VOLU)	Name	Belle Fourche River terrace near Bear Butte Creek and Volunteer.
	Elevation	Terrace at 12 m above channel, elevation 777.2 m.
	Location	South of Route 34, along 146th Avenue.
	Map description ¹	Rapid City 1 NE, T. 6 N., R. 8 E, SW¼ of section 11 and NE¼ of section 14.
	Land use	Crop production (hay).

¹Map descriptions based on USGS 7.5-minute series 1:24,000-scale topographical maps and Public Land Survey System designation by township (T), range (R), and section.

excavations were spaced approximately every 35 m on transects. A hand trowel was used for excavation. Elevation and coordinates of excavations at both potentially contaminated sites were surveyed using high-precision GPS equipment.

At the middle Belle Fourche River site, subsurface core samples (fig. 4) were collected from cores extracted using a direct push coring device on a transect parallel to, and offset approximately 10 m from, excavated pit transects. In general, cores were extracted to the depth of bedrock (Cretaceous-age Pierre Shale) or to a depth of 4.6 m, whichever was shallower (four subsurface cores were 1.15 m in length).

Sediment samples also were collected from bank exposures at both sites. Locations of bank-exposure samples were selected in the field on the basis of transect proximity and the availability of vertical bank exposure of 0.5 m or greater (to allow for vertical separation of samples). In general, exposures near transects and with underlying, exposed bedrock (Pierre Shale) were preferred, so that the complete fluvial sedimentary sequence could be described. Elevations and coordinates of bank exposures were surveyed using high-precision GPS equipment.

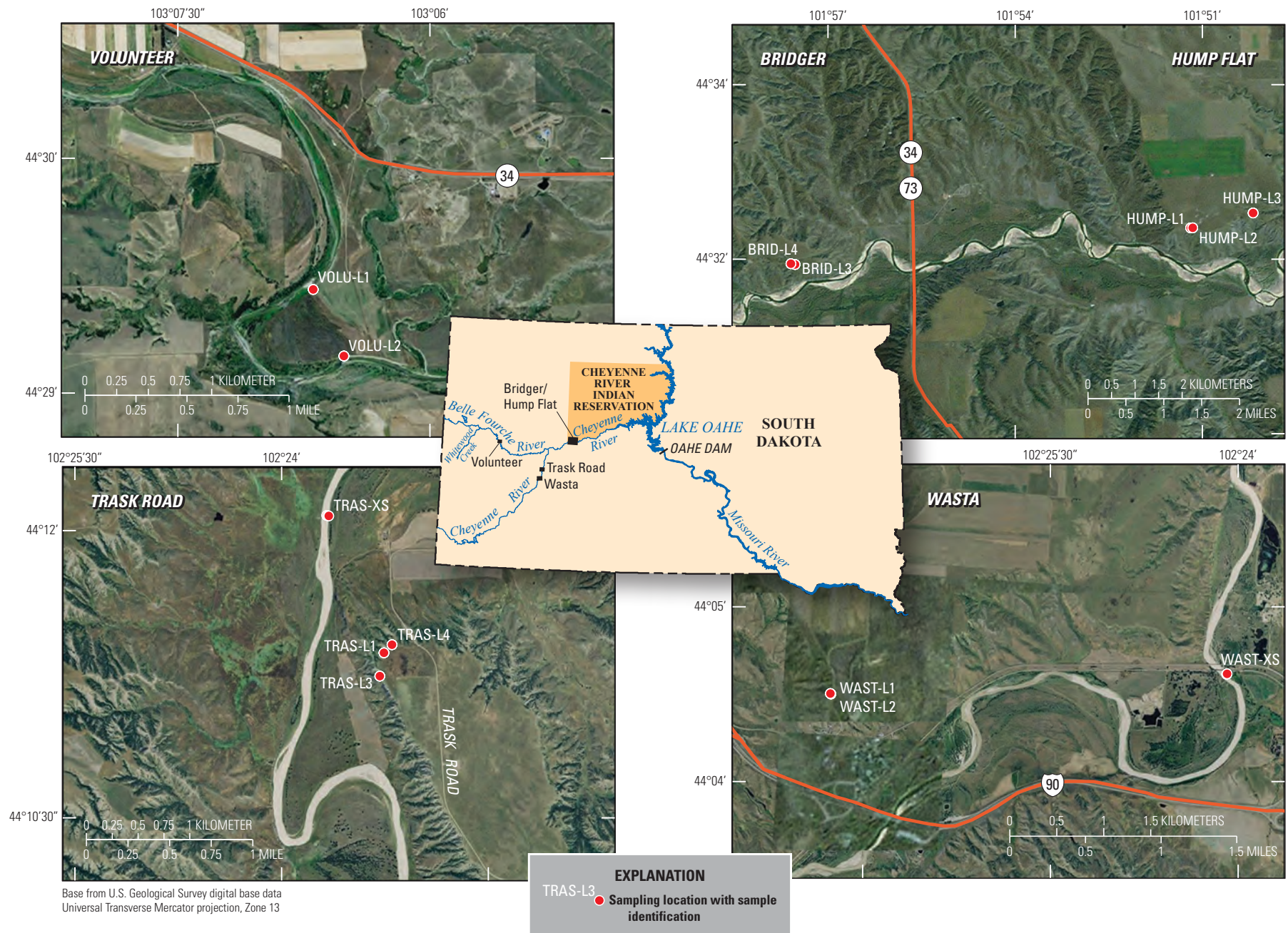


Figure 2. Location of reference sites and sampling locations.

Table 3. Potentially contaminated site descriptions.

[USGS, U.S. Geological Survey]

Site name (abbreviation)	Site characteristics	Site description
Cheyenne River (CR)	Name	Lower Cheyenne River.
	Location	Channel, flood plain, and terraces along the Cheyenne River, upstream from the Four Corners Road bridge.
	Map description ¹	Howes, T. 6 N., R. 17 E., sections 1, 2; T. 7 N., R. 17 E., section 36.
	Land use	Livestock grazing, surface gravel mining.
Belle Fourche River (BF)	Name	Middle Belle Fourche River.
	Location	Channel, flood plain, and terraces along the Belle Fourche River upstream from the South Dakota Highway 34 bridge.
	Map description ¹	Volunteer, T. 6 N., R. 8 E., sections 3, 4; T. 7 N., R. 8 E., sections 28, 33, 34.
	Land use	Livestock grazing.

¹Map descriptions based on USGS 7.5-minute series 1:24,000-scale topographical maps and Public Land Survey System designation by township (T), range (R), and section.

Sampling Equipment

Equipment used to collect samples included hand shovels, trowels, plastic bowls (for homogenizing samples), and 0.12-liter (L; 4-ounce) amber glass sample jars (supplied by the analytical laboratory, TestAmerica Laboratories). Shovels, trowels, and bowls used for pit excavation and sampling were cleaned using ALCONOX[®] liquid detergent and rinsed with distilled water before use. Sampling equipment was wrapped in clean plastic bags and placed in clean tarps in the field until needed for use. Equipment was cleaned after each use, before using on another pit excavation. When available, pre-sterilized and individually packaged (by the supplier) trowels were used for sample collection. Latex gloves and dust masks were used by sampling personnel throughout the sampling process. Sampling was avoided or terminated if winds were of sufficient strength to transport sediment.

The Geoprobe[®] direct-push coring device (Geoprobe Systems, 2012), lined with a 4-cm diameter by 115-cm length plastic sleeve, protected cores from contamination. New, clean plastic sleeves were used for each core segment. The bit of the coring device was cleaned by hand (with wire brush and water) to remove as much sediment as possible before each core extraction.

Sample Collection

Samples were collected at reference sites and potentially contaminated sites using similar sample-collection methods. Approximately 1 kg of sediment was collected using a clean trowel and placed into a clean mixing bowl. The sample was then homogenized in the field by stirring thoroughly with a clean trowel. The sample was then shaped into a cone, and the cone was quartered. Subsamples were collected from each

quarter until sufficient to fill a 0.12-L (4-ounce) amber glass container, supplied by the analytical laboratory (TestAmerica Laboratories, Denver, Colo.). The same number of subsamples was collected from each quarter so that no one quarter contributed more or less subsamples than another quarter. Once sufficient sample mass was collected (approximately 100 grams), sample jars were capped, labeled (paper label affixed to the jar), and double bagged in resealable bags. A metal tag with the sample number impressed on the tag was placed in the resealable bag. Samples were then stored in ice-filled coolers. Ice in coolers was double bagged to avoid leakage. Samples were shipped overnight with ice. A 0.12-L amber glass container filled with water was included with all ice-filled coolers. The analysis laboratory would measure the temperature of the water in this jar upon delivery of the ice-filled cooler. If the temperature of the water exceeded 6 degrees Celcius, the samples in the cooler would not be used for mercury analyses.

At reference sites (but not at potentially contaminated sites), surplus sediment collected (approximately 1 kg) to fill the 0.12-L (4-ounce), amber glass jar was stored in a resealable bag (double bagged) for possible particle-size analyses and estimate of arsenic concentration for size fractions. Surplus was retained to re-analyze arsenic concentration for particle-size fractions for samples previously identified as having the highest arsenic concentrations. Those samples were shipped to the analytical laboratory in coolers, but were not shipped on ice.

As previously described, samples from reference sites were collected from excavated pits along the terrace riser (eroded edge of the terrace) or from natural exposures. Excavations on the terrace riser were at times sufficiently large to consider replanting of vegetation. At those sites, vegetation was removed in such a manner to save the plant and roots so that it could be replanted upon completion of sample collection, which typically required 1 day. Upon completion of

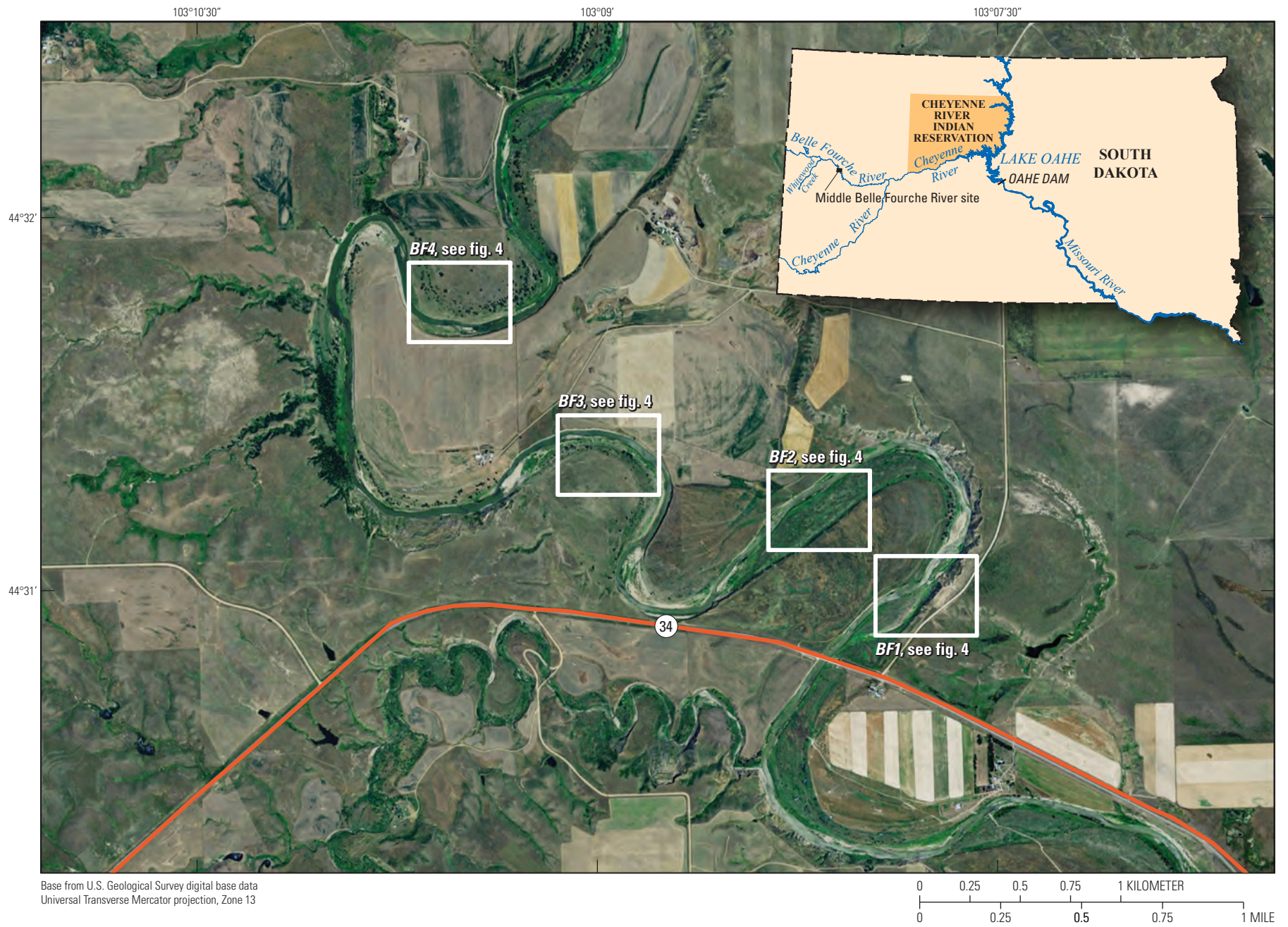


Figure 3. Location of the middle Belle Fourche River potentially contaminated site and sampling locations.

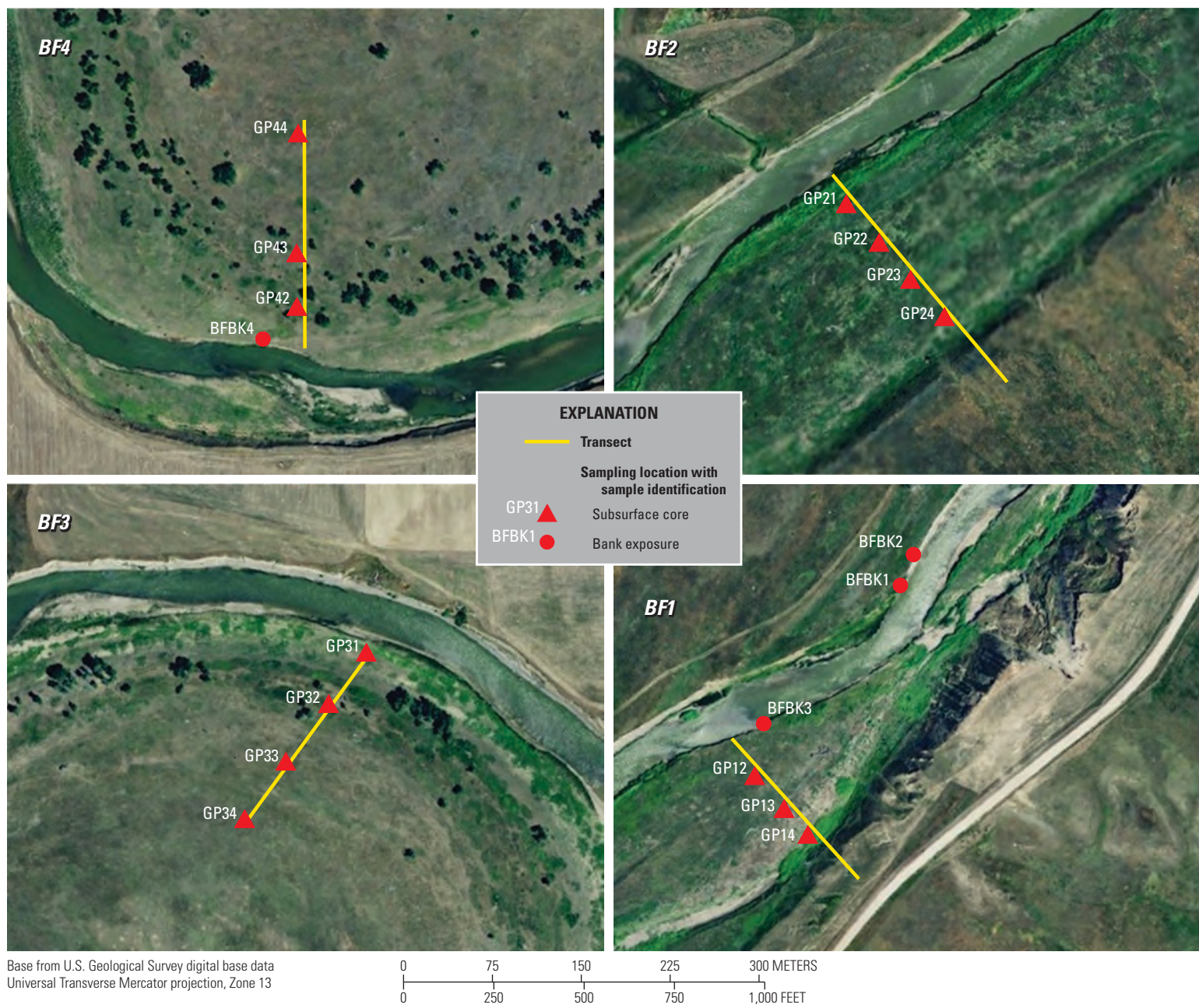


Figure 4. Sampling locations for transects, subsurface cores, and bank exposures at the middle Belle Fourche River potentially contaminated site.

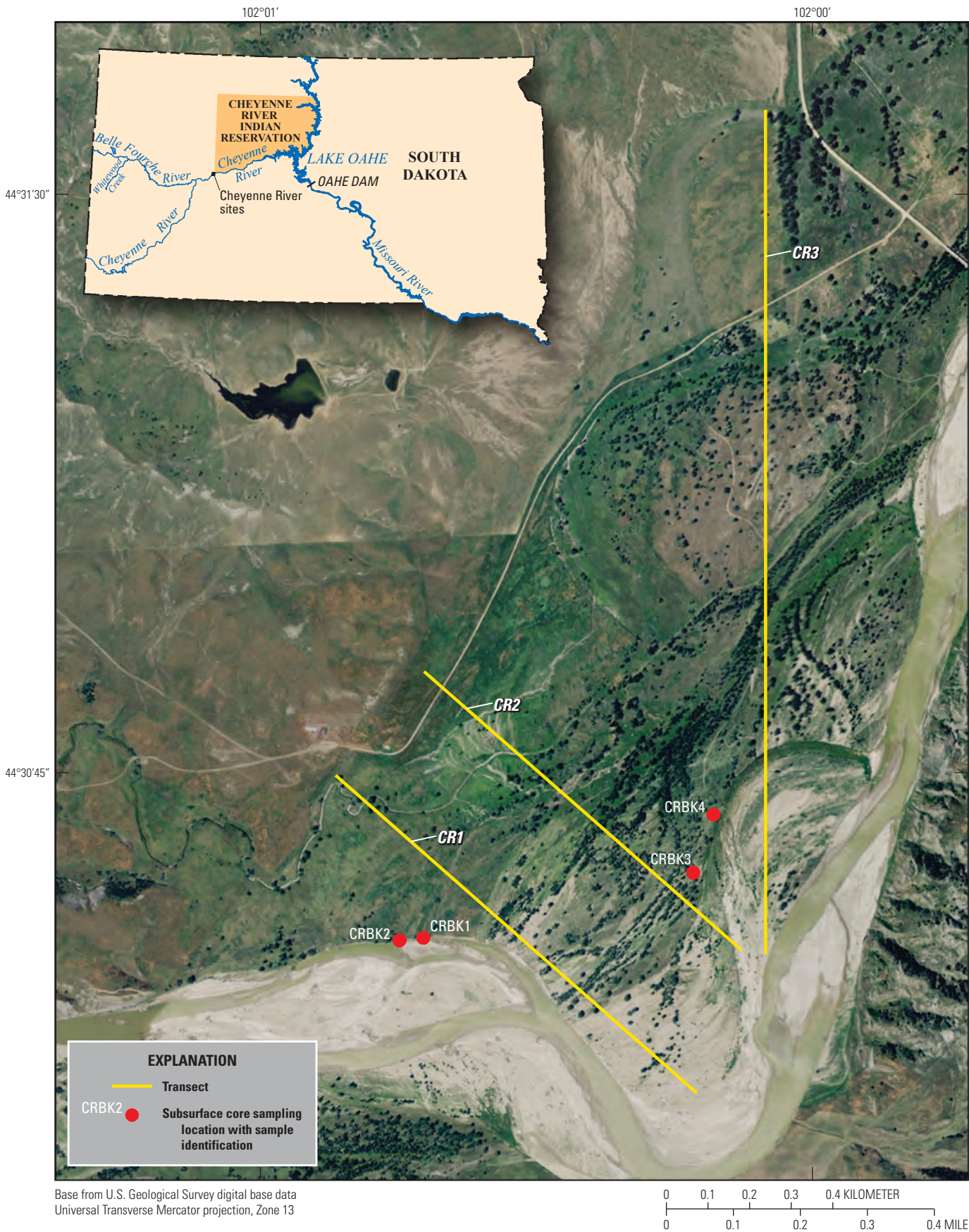


Figure 5. Sampling locations for transects and bank exposures at the lower Cheyenne River potentially contaminated site.

sampling, pits were refilled with the excavated material, vegetation was replanted, and the surface was watered. At natural exposures (such as scarps), the surface was scraped clean so that holes created by sampling were no longer apparent to the casual observer.

Methods used to collect samples from subsurface cores differed from those previously described. Subsurface cores were collected in the field using a Geoprobe® coring device. Cores were contained in a plastic sleeve (previously described), which was labeled, capped, sealed, and stored on ice in the field. Cores were transported to the USGS laboratory in Rapid City, S. Dak. At the laboratory, cores were split open using a clean splitter (sharp, hooked blade). Cores were photographed, described, and sampled. Five samples were collected from a set of cores for each subsurface core sampling location (which includes as many as four core lengths). Care was taken to collect samples from distinct sedimentary units described in cores. If less than five units were described, then the thickest unit was sampled multiple times. Samples were not homogenized because available sediment generally was less than the volume of the 0.12-L (4-ounce), amber glass jar. Samples were directly transferred to the amber glass jars, stored, and shipped on ice using procedures and protocols as previously described for storage and shipment of homogenized samples.

Sample Analysis

Sediment samples were submitted to TestAmerica Laboratories (Denver, Colo.) for analysis of metals. Analyses for the concentrations of 23 metals (table 1) were based on U.S. Environmental Protection Agency (2011b) standard methods for solids. Sample preparation and digestion followed USEPA method 3050B. Mercury was analyzed using cold vapor atomic absorption (USEPA method 7471A), and the remaining 22 metals were analyzed using inductively coupled plasma atomic-emission spectrometry (USEPA method 6010B). Moisture content of the samples was determined according to American Society for Testing and Materials (2011) standard D2216. Selected samples collected for Part I of the CBFRS study were sieved by personnel at TestAmerica Laboratories to separate sand (passing through a 2-millimeter mesh sieve but not passing through a 63-micrometer mesh sieve) from silt/clay fractions (passing through a 63-micrometer mesh sieve). Selected sieved samples were re-analyzed for arsenic concentrations using methods described previously for 22 metals.

Quality Assurance

Quality-assurance samples, which included sequential replicates, split duplicates, and control samples, were collected to assess the laboratory and environmental variability of metal concentrations. Sequential replicates were collected by resampling at the same location and depth of a previously collected sample. Sequential replicates are collected in the field and can

be used to assess environmental variability of metal concentrations. Split duplicates are collected in the field and consist of two sub-samples obtained from a sample after homogenization. Split duplicates can assess variability in a homogenized sample and variability associated with laboratory analyses. The relative percent differences (RPDs), which were calculated as the absolute difference in concentrations between the environmental and replicate (or duplicate) samples divided by mean concentration of the environmental/replicate (or duplicate) pair, are shown in table 4 for sequential replicate and split duplicate sample pairs. Large RPDs commonly were the result of small differences at low concentrations. For example, an environmental and replicate sample pair with arsenic concentrations of 14 and 19 mg/kg, respectively, would yield an RPD of 30 percent; however, the same absolute concentration difference (5 mg/kg) for a sample pair with an average arsenic concentration of 250 mg/kg would yield an RPD of only 2 percent.

Control samples are sediment from a stock container that has been independently analyzed for the suite of 23 metals by the USGS Crustal Imaging and Characterization Team, Denver, Colo. Control samples were from reference and potentially contaminated sediment on the flood plain along the Belle Fourche River near the Volunteer site (VOLU). Three 18.9-L (5-gallon) plastic buckets of sand-to-silt size sediment were collected from the upper 2 m of fluvial sediment on a terrace at site VOLU-L2 (fig. 2). At the height of the terrace (approximately 9 m above the channel), contamination from mine tailings would be unlikely (unless finer particles were transported by wind). Three 18.9-L (5-gallon) plastic buckets of potentially contaminated sediment were collected from red, sandy-silt deposits on the flood plain approximately 90 m upstream from sampling location VOLU-L2. The red color and silty texture is consistent with the color and texture of transported mine tailings (Goddard, 1989).

Control samples collected from fluvial sediment deposited on the terrace and on the flood plain were each separately homogenized by the USGS Crustal Imaging and Characterization Team to provide subsamples with consistent low and high arsenic concentrations, respectively. Subsamples of homogenized terrace and flood-plain samples then were mixed and homogenized to provide subsamples with consistent medium arsenic concentrations. Homogenized sediment was split and stored in plastic bags, each containing approximately 1 kg of sediment. Determination of concentrations of metals at that USGS laboratory were based on USEPA method 3050B digestion and USEPA method 6010B atomic emission spectrometry (U.S. Environmental Protection Agency, 2011b). Arsenic concentrations were determined to be 14.1 mg/kg, 1,575 mg/kg, and 715 mg/kg for the terrace, flood-plain, and mixed control samples, respectively.

Eight control samples were included with batches of reference and potentially contaminated sediment samples sent to TestAmerica Laboratories. Samples were labeled in such a way that they would not be distinguished as control samples. TestAmerica Laboratories was alerted that control samples

Table 4. Relative percent difference statistics for concentrations of selected metals for sequential replicate and split duplicate sediment samples.

[Count, number of replicate (duplicate)/environmental sample pairs]

Metal	Sequential replicates (potentially contaminated sites)					Split duplicates (potentially contaminated sites)					Sequential replicates (reference sites)				
	Minimum	Median	Mean	Maximum	Count	Minimum	Median	Mean	Maximum	Count	Minimum	Median	Mean	Maximum	Count
Aluminum	0	7	10	35	27	0	4	6	48	63	1	10	19	46	14
Antimony	0	5	8	84	27	0	4	9	137	63	0	0	0	0	14
Arsenic	0	8	14	60	45	0	5	7	38	63	0	17	30	114	14
Barium	0	8	10	27	27	0	5	7	70	63	5	25	36	113	14
Beryllium	0	7	8	26	27	0	3	5	30	63	0	6	23	83	14
Cadmium	0	12	40	156	27	0	4	14	198	63	0	24	39	145	14
Calcium	0	7	8	38	27	0	3	8	99	63	0	24	36	123	14
Chromium	0	8	10	29	27	0	4	6	32	63	3	10	20	68	14
Cobalt	0	6	8	30	27	0	3	5	29	63	1	16	29	136	14
Copper	0	5	9	33	27	0	4	5	26	63	0	9	22	87	14
Iron	0	4	9	32	27	0	3	5	59	63	0	11	25	93	14
Lead	0	8	8	62	27	0	0	5	26	63	1	13	17	65	14
Magnesium	0	10	11	37	27	0	4	5	51	63	0	19	23	96	14
Manganese	0	10	20	150	27	0	4	11	125	63	0	23	36	140	14
Mercury	0	10	12	63	27	0	14	23	178	63	0	21	27	71	14
Nickel	0	5	7	21	27	0	4	5	43	63	0	15	25	117	14
Potassium	0	10	10	32	27	0	4	6	67	63	4	11	19	48	14
Selenium	0	10	20	96	27	0	6	11	136	63	0	0	0	0	14
Silver	0	8	19	125	27	0	5	13	107	63	0	0	0	0	14
Sodium	0	10	14	43	27	0	5	7	95	63	0	6	21	120	14
Thallium	0	3	9	136	27	0	3	6	138	63	0	0	0	0	14
Vanadium	0	6	10	34	27	0	5	6	45	63	0	9	28	90	14
Zinc	0	4	5	16	27	0	2	4	15	63	0	6	20	84	14

were to be included with submitted sample batches, so that the laboratory could anticipate some samples to be outside the range of concentrations of other samples in a batch. Mean arsenic concentrations in control samples based on analyses by the USGS Crustal Imaging and Characterization Team laboratory and TestAmerica Laboratories were within 10 percent relative difference (table 5).

Concentrations of Selected Metals in Sediment

A total of 74 sediment samples were collected from fluvial deposits at reference sites (fig. 2), and 473 samples were collected from potentially contaminated sites on the middle Belle Fourche and lower Cheyenne Rivers. At the middle Belle Fourche River potentially contaminated site (figs. 3 and 4), 120 samples were collected from near the surface and 120 samples were collected from the subsurface in excavated pits on 4 transects. In addition, 20 samples were collected from four bank exposures, and 70 samples were collected from 14 subsurface cores collected on a transect parallel to, and offset approximately 10 m from, excavated pit transects. At the lower Cheyenne River potentially contaminated site (fig. 5), 123 samples were collected near the surface on three transects, and 20 samples were collected from 4 bank exposures. No samples were collected from the subsurface or cores at that site.

Metal concentrations in sediment samples and location information are presented in electronic format in the “Supplemental Data Tables” section for reference sites (table S1) and potentially contaminated sites (table S2). Some metal concentrations are reported as estimated values, meaning that either concentrations were greater than the instrument detection level but less than the lowest calibration standard, or there were discrepancies in meeting certain analyte-specific

quality-control criteria. Non-parametric summary statistics are presented in table 6 for the sediment samples from reference sites and in table 7 for sediment samples from potentially contaminated sites. Results for potentially contaminated samples are summarized according to the nearest transect (figs. 4 and 5; table S2) and relative depth (at or below the surface). Samples from bank exposures that were not near a transect are summarized separately. For context, table 8 presents mean arsenic and mercury concentrations for samples from reference and potentially contaminated sites reported in previous studies and the CBFRS. The mean arsenic concentration in reference sediment samples was 8 mg/kg, compared to 250, 650, and 76 mg/kg for potentially contaminated sediment samples at the surface of the middle Belle Fourche River site, the subsurface of the middle Belle Fourche River site, and the surface of the lower Cheyenne River site, respectively (table 8). The mean mercury concentration in reference sediment samples was 16 µg/kg, compared to 130, 370, and 71 µg/kg for potentially contaminated sediment samples at the surface of the middle Belle Fourche River site, the subsurface of the middle Belle Fourche River site, and the surface of the lower Cheyenne River site, respectively (table 8).

Cross-sectional profiles of land-surface elevations and arsenic concentrations in sediment samples from transects at the potentially contaminated sites are shown in figure 6 for the middle Belle Fourche River and in figure 7 for the lower Cheyenne River. Cross-sectional profiles of land-surface elevations and mercury concentrations in sediment samples are shown in figures 8 and 9 for the middle Belle Fourche River and lower Cheyenne River, respectively. Sample elevations as shown in figures 6–9 are listed in table S2. Cross-sectional profiles are oriented as if looking in the downstream direction. The cross-sectional profiles for the middle Belle Fourche River include arsenic concentrations from both surface and subsurface samples. A line indicating the maximum concentrations of arsenic (34 mg/kg) and mercury (66 µg/kg) at reference sites are included in the cross-sectional profiles.

Table 5. Comparison of mean arsenic concentrations in control samples analyzed by TestAmerica Laboratories and the U.S. Geological Survey Crustal Imaging and Characterization Team.

[Concentrations are in units of milligrams per kilogram. USGS, U.S. Geological Survey]

Control sample with relative arsenic concentration	Number of samples	Mean arsenic concentration		Mean relative percent difference
		TestAmerica	USGS	
Control 1—low	2	13	14.1	8.1
Control 2—medium	3	697	715	2.5
Control 3—high	3	1,533	1,575	2.7

16 Concentrations of Selected Metals in Fluvial Deposits along the Lower Cheyenne and Middle Belle Fourche Rivers

Table 6. Summary statistics for concentrations of selected metals in sediment samples from reference sites.

[Moisture content is in percent; concentrations for metals are in milligrams per kilogram except mercury is in micrograms per kilogram. <, less than; E, estimated value¹]

Property/metal	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples
Moisture content	1.0	2.1	3.5	7.4	35	74
Antimony	<1.8	<2	<2.1	<2.2	E0.8	74
Arsenic	2.6	4.9	7.2	10	E34	74
Barium	E48	95	145	245	940	74
Beryllium	E0.20	0.25	0.37	0.59	0.80	74
Cadmium	<0.51	E0.10	0.10	0.17	0.43	74
Calcium	4,300	8,600	14,000	18,000	86,000	74
Chromium	E1.5	3.2	4.3	8.1	21	74
Cobalt	1.6	2.9	4.0	5.9	11	74
Copper	E2	4.1	5.5	9.9	23	74
Iron	6,500	10,000	15,000	19,000	E52,000	74
Lead	2.2	3.7	4.7	7.8	13	74
Magnesium	570	1,100	1,400	2,850	7,300	74
Manganese	E120	250	375	495	E1,600	74
Nickel	E2.9	6.3	8.5	15	28	74
Selenium	<2.7	<3.1	<3.1	<3.2	0.97	74
Sodium	<510	<530	93.5	210	4,500	74
Thallium	<2.7	<3.1	<3.1	<3.2	<16	74
Vanadium	5.1	10	13	22	40	74
Zinc	9.5	19	27	39	130	74
Mercury	<31	6.0	12	18	66	74
Aluminum	1,200	1,900	2,750	5,675	E15,000	74
Potassium	250	353	565	1,075	6,000	74
Silver	<1.4	<1.5	<1.5	<1.6	<8	74

¹Some metal concentrations are reported as estimated values, meaning either concentrations were greater than the instrument detection level but less than the lowest calibration standard, or there were discrepancies in meeting certain analyte-specific quality-control criteria.

Table 7. Summary statistics for concentrations of selected metals in sediment samples from potentially contaminated sites, by location identification.[Location identification from table S2. Moisture content is in percent; concentrations are in milligrams per kilogram except mercury is in micrograms per kilogram. <, less than; E, estimated value¹]

Property/ metal	BF1						BF1-sub					
	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples
Moisture content	4.6	7.6	8.7	19	32	25	6.4	11	16	20	29	45
Antimony	<0.19	<0.20	<0.20	<0.20	<0.27	25	<0.19	<0.21	<0.22	<0.24	E0.53	45
Arsenic	15	38	58	130	310	25	9	110	290	1,500	4,200	45
Barium	74	130	170	200	230	25	100	140	160	180	250	45
Beryllium	0.41	0.51	0.53	0.57	0.70	25	E0.22	0.47	0.54	0.59	E0.87	45
Cadmium	E0.026	E0.075	E0.10	E0.13	E0.24	25	<0.024	E0.046	E0.18	0.66	5.9	45
Calcium	5,200	8,300	9,100	10,000	21,000	25	3,600	7,100	8,400	11,000	35,000	45
Chromium	9.8	13	14	15	19	25	6.6	14	16	17	24	45
Cobalt	6.1	7.8	8.5	8.9	9.3	25	7	8.5	9.3	10	14	45
Copper	15	19	22	23	29	25	13	25	27	53	73	45
Iron	17,000	23,000	25,000	26,000	30,000	25	17,000	26,000	33,000	69,000	110,000	45
Lead	9.2	10	11	11	12	25	6.6	11	12	13	16	45
Magnesium	3,300	4,600	5,100	5,300	6,300	25	1,900	5,300	5,800	6,600	17,000	45
Manganese	280	400	510	550	730	25	260	550	730	1,400	3,600	45
Nickel	16	19	21	23	27	25	7.4	19	22	26	37	45
Selenium	<0.46	E0.50	E0.61	E0.79	E1.2	25	<0.48	E0.67	E1.2	E2	6.7	45
Sodium	E90	E140	E170	E250	2,500	25	<330	E170	E220	400	2,000	45
Thallium	<0.32	<0.34	<0.34	<0.37	<0.46	25	<0.32	<0.36	<0.38	<0.40	E0.39	45
Vanadium	23	28	30	32	53	25	22	29	30	35	130	45
Zinc	52	61	65	69	81	25	44	66	70	77	89	45
Mercury	E19	41	58	78	210	25	E9.1	86	130	780	3,000	45
Aluminum	6,500	9,100	9,800	11,000	13,000	25	5,500	10,000	12,000	13,000	20,000	45
Potassium	1,100	1,500	1,600	1,900	2,300	25	830	1700	1,800	2100	2,900	45
Silver	<0.08	<0.08	<0.09	E0.11	E0.18	25	<0.08	<0.51	E0.16	E0.63	E1.2	45

Table 7. Summary statistics for concentrations of selected metals in sediment samples from potentially contaminated sites, by location identification.—Continued[Location identification from table S2. Moisture content is in percent; concentrations are in milligrams per kilogram except mercury is in micrograms per kilogram. <, less than; E, estimated value¹]

Property/ metal	BF2						BF2-sub					
	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples
Moisture content	5.6	10	12	14	33	35	3.4	6.3	8.8	13	27	55
Antimony	<0.19	<0.2	<0.21	<0.22	<0.26	35	<0.18	<0.19	<0.2	<0.21	E0.97	55
Arsenic	24	145	190	290	630	35	5.8	165	450	645	2,200	55
Barium	160	190	200	210	240	35	69	160	180	200	240	55
Beryllium	0.40	0.47	0.51	0.53	0.70	35	0.30	0.45	0.49	0.54	0.72	55
Cadmium	0.021	0.022	0.024	E0.036	E0.15	35	<0.02	<0.021	<0.023	E0.13	3.5	55
Calcium	2,600	6,600	9,100	9,650	20,000	35	1,500	4,350	7,600	12,000	19,000	55
Chromium	7	11	12	13	14	35	4.2	10	11	13	25	55
Cobalt	5	7.6	8.4	9.1	9.6	35	4.1	7.3	8.3	8.7	13	55
Copper	10	19.5	22	24	35	35	6.6	22	29	33	73	55
Iron	15,000	24,000	25,000	29,000	38,000	35	11,000	24,500	36,000	41,000	78,000	55
Lead	8.9	9.9	11	11	12	35	6.2	9.6	10	11	13	55
Magnesium	1,800	4,300	4,900	5250	5,900	35	2,700	3,800	4,500	5,400	13,000	55
Manganese	330	545	590	675	830	35	250	605	760	855	3,000	55
Nickel	10	17	19	20.5	22	35	8.9	15	17	20	25	55
Selenium	<0.48	E0.82	E0.94	E1.1	E1.6	35	<0.42	E0.51	1.1	1.5	2.8	55
Sodium	E42	E76	E100	E110	540	35	E52	E81	E100	E145	2,500	55
Thallium	<0.33	<0.35	<0.35	<0.37	<0.44	35	<0.32	<0.33	<0.34	<0.37	E0.5	55
Vanadium	16	18	20	22	25	35	12	17	19	23	46	55
Zinc	49	58	63	69	75	35	33	55	59	64	79	55
Mercury	E22	104	130	155	360	35	E8	105	210	285	2,400	55
Aluminum	5,300	7,800	8,600	9,950	11,000	35	2,700	7,100	8,100	9,800	19,000	55
Potassium	1,400	1,600	1,800	1,900	2,400	35	820	1,500	1,600	1,800	3,200	55
Silver	<0.08	E0.12	E0.16	E0.23	E0.34	35	<0.08	E0.14	E0.36	E0.45	0.81	55

Table 7. Summary statistics for concentrations of selected metals in sediment samples from potentially contaminated sites, by location identification.—Continued[Location identification from table S2. Moisture content is in percent; concentrations are in milligrams per kilogram except mercury is in micrograms per kilogram. <, less than; E, estimated value¹]

Property/ metal	BF3						BF3-sub					
	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples
Moisture content	4.2	7.9	9.0	12	16	30	5.2	7.8	11	15	32	50
Antimony	<0.19	<0.2	<0.2	<0.21	E0.33	30	<0.19	<0.2	<0.22	E0.33	1.2	50
Arsenic	100	140	215	390	610	30	11	60	445	730	3,100	50
Barium	160	203	230	240	260	30	68	130	170	210	280	50
Beryllium	0.45	0.49	0.51	0.55	0.65	30	E0.18	0.46	0.55	0.59	0.73	50
Cadmium	<0.021	<0.023	0.38	0.53	1.1	30	<0.022	E0.11	0.53	1.3	6.7	50
Calcium	2,300	6,725	8,250	8,800	11,000	30	2,500	6,000	8,050	11,000	44,000	50
Chromium	10	13	13	14	17	30	4.9	11	13	16	24	50
Cobalt	8.6	8.9	9.2	9.4	11	30	4.6	8.4	9	9.5	14	50
Copper	19	24	25	29	35	30	8.9	25	32	39	88	50
Iron	24,000	25,000	29,000	35,750	39,000	30	21,000	33,000	44,000	49,750	95,000	50
Lead	11	11	12	13	15	30	3.8	10	12	13	28	50
Magnesium	3,900	4,900	5,300	5,650	6,600	30	2,200	3,825	5,150	5,875	18,000	50
Manganese	510	605	670	775	880	30	190	673	865	980	4,000	50
Nickel	17	20	21	21	25	30	9.2	17	20	22	33	50
Selenium	<0.43	<0.45	<0.47	E1.0	1.9	30	<0.44	<0.48	E0.47	E0.87	4.6	50
Sodium	E67	E91	E100	E110	E200	30	E43	E110	E140	E245	1,100	50
Thallium	<0.32	<0.34	<0.35	<0.36	<0.38	30	<0.33	<0.34	<0.36	<0.37	E0.42	50
Vanadium	24	26	27	29	35	30	20	27	31	35	54	50
Zinc	59	67	69	72	82	30	35	58	65	71	83	50
Mercury	73	96	120	148	250	30	E12	68	150	240	2,400	50
Aluminum	6,700	9,025	9,900	10,000	14,000	30	3,600	7,925	9,650	12,000	20,000	50
Potassium	610	1,625	1,850	2,000	2,600	30	560	1,400	1,650	2,000	3,200	50
Silver	<0.08	E0.13	E0.18	E0.22	E0.34	30	<0.08	E0.14	E0.37	E0.52	E0.73	50

Table 7. Summary statistics for concentrations of selected metals in sediment samples from potentially contaminated sites, by location identification.—Continued

[Location identification from table S2. Moisture content is in percent; concentrations are in milligrams per kilogram except mercury is in micrograms per kilogram. <, less than; E, estimated value¹]

Property/ metal	BF4						BF4-sub					
	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples
Moisture content	7.7	8.9	10	14	16	30	1.7	4.0	6.0	8.5	22	50
Antimony	<0.19	<0.2	<0.2	<0.21	E0.24	30	<0.18	<0.19	<0.2	E0.22	1.1	50
Arsenic	230	300	375	475	590	30	7.2	77	490	648	3,200	50
Barium	160	190	200	210	220	30	80	130	170	190	220	50
Beryllium	0.52	0.56	0.59	0.60	0.67	30	0.28	0.41	0.50	0.57	0.65	50
Cadmium	E0.27	0.29	0.38	0.46	0.56	30	E0.047	E0.2	0.36	0.52	3.5	50
Calcium	1,400	8,000	9,150	10,750	14,000	30	1,700	5,025	8,650	11,000	21,000	50
Chromium	9.2	13	13	14	15	30	2.7	7.0	10	13	24	50
Cobalt	7.3	8.2	8.5	8.9	9.2	30	4.2	5.8	7.6	8.7	11	50
Copper	21	23	24	26	30	30	5.5	14	29	33	74	50
Iron	24,000	27,250	30,000	33,000	44,000	30	13,000	24,000	37,500	43,000	100,000	50
Lead	10	11	11	11	12	30	4.9	8.5	9.7	11	18	50
Magnesium	3,400	5,000	5,300	5,475	5,900	30	920	2,825	3,650	4,750	10,000	50
Manganese	570	642.5	690	737.5	880	30	350	485	815	888	2,500	50
Nickel	14	17	18	19	20	30	9.6	12	16	17	38	50
Selenium	E0.84	E1.1	E1.2	E1.4	2.1	30	<0.42	E0.48	E1.3	E1.6	3.1	50
Sodium	E49	E80	E92	E97	E180	30	E46	E72	E90	E100	1,300	50
Thallium	<0.33	<0.34	<0.35	<0.35	<0.37	30	<0.31	<0.32	<0.34	<0.35	<0.41	50
Vanadium	23	26	27	28	30	30	13	19	23	26	45	50
Zinc	62	67	70	71	74	30	33	47	57	65	85	50
Mercury	83	170	195	210	250	30	<5.3	75	235	318	2,800	50
Aluminum	7,300	11,000	11,000	12,000	13,000	30	1,300	4,900	7,900	9,950	16,000	50
Potassium	1,600	2,000	2,100	2,200	2,600	30	250	908	1,600	1,875	3,300	50
Silver	E0.21	E0.24	E0.29	E0.37	E0.55	30	<0.08	E0.22	E0.48	E0.58	0.95	50

Table 7. Summary statistics for concentrations of selected metals in sediment samples from potentially contaminated sites, by location identification.—Continued[Location identification from table S2. Moisture content is in percent; concentrations are in milligrams per kilogram except mercury is in micrograms per kilogram. <, less than; E, estimated value¹]

Property/ metal	BFBK1-2						CR1					
	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples
Moisture content	1	2.5	3	3.6	6.1	10	0.6	1.1	5.4	23	27	34
Antimony	<0.18	<0.19	<0.19	<0.2	E1.4	10	<0.18	<0.19	<0.22	<0.24	E0.88	34
Arsenic	7	348	945	1,675	3,000	10	8.5	24	42	83	140	34
Barium	120	123	140	183	260	10	150	193	275	310	470	34
Beryllium	E0.22	E0.39	E0.42	0.52	0.59	10	E0.21	0.35	0.49	0.66	0.96	34
Cadmium	E0.11	0.57	0.98	2.1	E4.5	10	E0.079	E0.14	E0.18	E0.23	0.62	34
Calcium	2,500	7,825	10,500	12,000	16,000	10	7,100	10,000	11,000	13,000	33,000	34
Chromium	E3	12	15	17	25	10	1.7	6.0	11	24	28	34
Cobalt	4.4	6.3	7.9	8.5	11	10	3.1	6.0	7.7	9.2	12	34
Copper	E 4.5	24	43	55	82	10	3.8	8.9	18	23	27	34
Iron	14,000	38,500	70,000	77,250	130,000	10	13,000	21,000	23,000	24,750	46,000	34
Lead	5.4	9.2	9.6	10	15	10	3.9	7.3	11	14	16	34
Magnesium	1,100	4,975	5,300	6,900	14,000	10	510	1,950	4,350	6,875	8,100	34
Manganese	310	575	1,350	1,575	3,500	10	320	472.5	580	710	4,100	34
Nickel	8.6	12	15	17	18	10	7.1	13	18	26	31	34
Selenium	<0.41	E1.4	E1.8	E2.6	3.2	10	<0.45	<0.53	E0.53	E0.76	2.9	34
Sodium	E57	E82	E160	993	1,600	10	E65	E110	E150	E198	310	34
Thallium	<0.31	<0.32	<0.33	<0.34	E0.62	10	<0.31	<0.32	<0.35	<0.4	3	34
Vanadium	14	24	31	38	56	10	10	16	25	34	39	34
Zinc	34	50.5	60	65	71	10	21	37	57	77	87	34
Mercury	E14	155	660	1,065	3,000	10	<5.2	E28	56	64	130	34
Aluminum	1,600	9,050	9,900	11,000	22,000	10	920	4,100	8,150	14,000	18,000	34
Potassium	320	1,850	2,050	2,600	3,600	10	180	845	1,800	2,700	3,200	34
Silver	<0.08	E0.26	E0.63	E0.83	E0.88	10	<0.08	<0.08	<0.09	<0.1	E0.57	34

Table 7. Summary statistics for concentrations of selected metals in sediment samples from potentially contaminated sites, by location identification.—Continued

[Location identification from table S2. Moisture content is in percent; concentrations are in milligrams per kilogram except mercury is in micrograms per kilogram. <, less than; E, estimated value¹]

Property/ metal	CR2						CR3					
	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples
Moisture content	2.1	18	21	23	32	30	1.3	9.9	14	18	35	59
Antimony	<0.20	<0.22	<0.23	<0.25	E0.82	30	<0.19	<0.20	<0.22	<0.23	E0.36	59
Arsenic	7.7	9.8	47	99	150	30	6.8	46.5	74	99	150	59
Barium	64	183	240	308	450	30	150	220	260	305	390	59
Beryllium	E0.11	0.53	0.58	0.68	0.88	30	0.28	0.48	0.58	0.67	0.78	59
Cadmium	E0.074	0.35	0.43	0.67	0.72	30	E0.15	0.26	0.34	0.4	0.58	59
Calcium	6,000	8,500	11,000	14,000	17,000	30	4,200	7,800	12,000	14,000	16,000	59
Chromium	1.3	13	14	23	26	30	4.5	12	15	19	25	59
Cobalt	1.6	8.2	8.8	9.4	10	30	4.1	7.4	8.2	9.0	9.7	59
Copper	2	19	21	22	24	30	7.9	18	20	23	25	59
Iron	6,900	22,000	23,000	24,000	27,000	30	12,000	20,000	22,000	24,500	28,000	59
Lead	2.5	12	13	14	14	30	6.9	12	13	14	15	59
Magnesium	440	5,050	5,900	6,675	7,500	30	1,600	4,400	5,800	6,400	7,800	59
Manganese	290	363	495	783	1,000	30	200	490	620	695	840	59
Nickel	3.3	20	22	25	27	30	9.5	17	21	22	26	59
Selenium	<0.42	<0.52	<0.57	E0.76	E1.2	30	<0.42	<0.46	<0.49	<0.52	E0.66	59
Sodium	E39	293	405	873	3,000	30	E64	E160	E230	400	2,400	59
Thallium	<0.31	<0.38	<0.39	<0.41	<0.46	30	<0.32	<0.35	<0.37	<0.39	<0.53	59
Vanadium	4.8	26	29	35	39	30	14	24	28	33	39	59
Zinc	11	65	71	74	82	30	36	57	67	76	87	59
Mercury	<5.2	55	60	85	110	30	E17	46	69	85	150	59
Aluminum	970	9,625	11,500	14,000	18,000	30	3,100	8,700	12,000	14,000	19,000	59
Potassium	220	2,200	2,500	2,775	3,400	30	720	2,050	2600	2,900	4,000	59
Silver	<0.08	<0.09	<0.10	<0.10	E0.12	30	<0.08	<0.09	<0.09	E0.1	E0.13	59

Table 7. Summary statistics for concentrations of selected metals in sediment samples from potentially contaminated sites, by location identification.—Continued[Location identification from table S2. Moisture content is in percent; concentrations are in milligrams per kilogram except mercury is in micrograms per kilogram. <, less than; E, estimated value¹]

Property/ metal	CRBK1-2						CRBK3-4					
	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples
Moisture content	0.1	1.6	2.0	2.4	2.7	10	5.5	6.5	7.5	8.7	13	10
Antimony	<0.17	<0.18	<0.19	<0.19	<0.19	10	<0.19	<0.20	<0.20	<0.21	<0.21	10
Arsenic	5.3	23	66	84	120	10	75	150	190	325	500	10
Barium	170	255	300	318	390	10	200	250	270	288	300	10
Beryllium	E0.16	E0.37	E0.42	E0.46	0.55	10	E0.38	E0.40	E0.46	E0.52	0.54	10
Cadmium	E0.096	E0.20	E0.28	E0.32	E0.36	10	E0.25	E0.32	E0.37	0.53	0.72	10
Calcium	9,900	11,250	13,000	13,000	16,000	10	13,000	14,000	15,000	15,750	20,000	10
Chromium	E2.5	8.7	9.6	12	12	10	8.2	9.3	11.5	15	16	10
Cobalt	2.8	5.6	6.1	6.5	7.8	10	5	6.1	6.9	7.6	8.8	10
Copper	E3.6	13	14	15	18	10	11	15	18	23	33	10
Iron	9,600	16,250	17,500	18,750	22,000	10	16,000	22,000	23,000	29,250	46,000	10
Lead	3.8	9.0	9.5	9.9	11	10	8.4	8.7	10	11	12	10
Magnesium	800	3,450	3,800	4,175	4,500	10	3,300	3,750	4,600	6,125	7,100	10
Manganese	280	442.5	470	545	670	10	510	625	650	815	1,200	10
Nickel	5.8	13	14	16	18	10	10	13	15	17	19	10
Selenium	<0.39	E0.44	E0.52	E0.59	E0.89	10	<0.46	E0.46	E0.62	E0.88	E1.5	10
Sodium	E90	465	540	565	850	10	E230	E315	E365	722.5	1,200	10
Thallium	<0.3	<0.3	<0.32	<0.32	<0.33	10	<0.33	<0.34	<0.35	<0.35	<0.37	10
Vanadium	9.2	20	21	24	24	10	17	20	23	27	27	10
Zinc	18	40	43	48	50	10	38	45	53	58	64	10
Mercury	E10	54	69	87	150	10	70	120	155	205	270	10
Aluminum	1,300	6,050	7,200	8,200	10,000	10	6,400	7,500	9,100	12,000	13,000	10
Potassium	300	1,425	1,750	1,875	2,200	10	1,400	1,725	2,300	2,450	2,900	10
Silver	<0.07	<0.07	<0.08	E0.08	E0.18	10	<0.08	E0.09	E0.11	E0.16	E0.30	10

¹Some metal concentrations are reported as estimated values, meaning either concentrations were greater than the instrument detection level but less than the lowest calibration standard, or there were discrepancies in meeting certain analyte-specific quality-control criteria.

Table 8. Mean concentrations of arsenic and mercury in sediment samples from reference and potentially contaminated sites reported in four different studies.

[mg/kg, milligrams per kilogram; µg/kg, micrograms per kilogram; BFR, Belle Fourche River; WWC, Whitewood Creek; --, not available; CR, Cheyenne River; CBFRS, Cheyenne and Belle Fourche River sediment study]

Study	Reference site	Potentially contaminated site	Surface / subsurface	Arsenic (mg/kg)		Mercury (µg/kg)	
				Reference	Potentially contaminated	Reference	Potentially contaminated
Goddard (1989)	BFR upstream from WWC	WWC	Surface and subsurface	9	1,600	--	--
Goddard (1989)	BFR upstream from WWC	BFR downstream from WWC	Surface and subsurface	9	550	--	--
Goddard (1989)	CR upstream from BFR	CR downstream from BFR	Surface and subsurface	8	78	--	--
U.S. Environmental Protection Agency (2005)	Moreau River	CR downstream from BFR	Surface	7	60	^{1,2} 70	^{1,2} 80
U.S. Environmental Protection Agency (2005)	Moreau River Arm of Lake Oahe	Cheyenne River arm of Lake Oahe	Surface	8	24	^{1,2} 90	^{1,2} 60
Engineering-Environmental Management, Inc. (2004)	Terraces above Lake Oahe	CR valley bottom upstream from Lake Oahe	Surface	14	60	30	60
Engineering-Environmental Management, Inc. (2004)	Terraces above Lake Oahe	CR valley bottom upstream from Lake Oahe	Subsurface	10	85	30	70
CBFRS (2009–10)	High terraces and CR upstream from BFR	BFR downstream from WWC	Surface	³ 8	250	^{1,3} 16	130
CBFRS (2009–10)	High terraces and CR upstream from BFR	BFR downstream from WWC	Subsurface	³ 8	650	^{1,3} 16	¹ 370
CBFRS (2009–10)	High terraces and CR upstream from BFR	CR downstream from BFR	Surface	³ 8	76	^{1,3} 16	¹ 71

¹Concentrations less than detection levels were evaluated as one-half the detection level.

²Mean concentration was less than the lowest detection level (90 µg/kg). Greater than one-half of all samples had concentrations less than the detection level.

³Mean concentration for all reference samples combined.

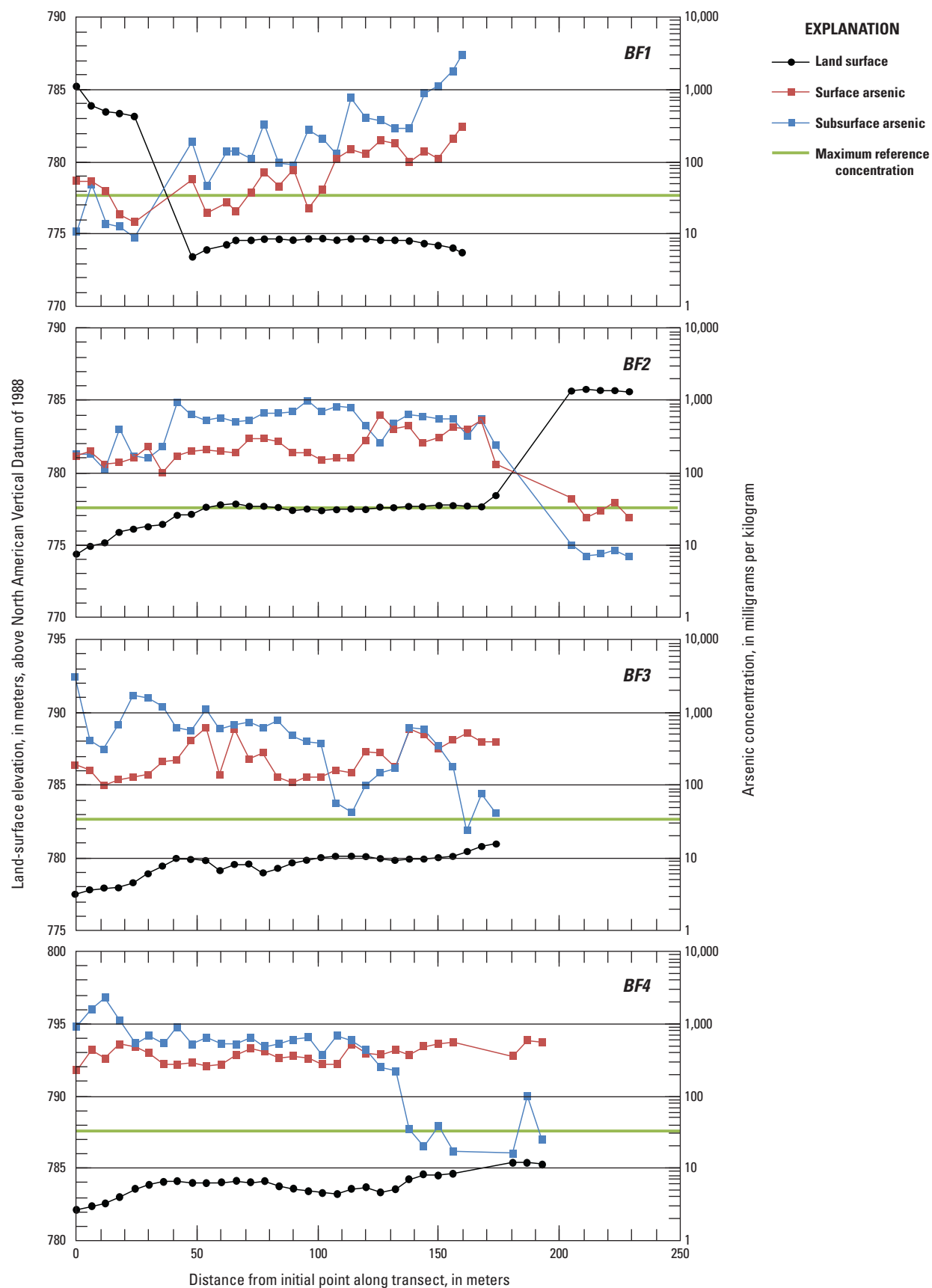


Figure 6. Cross-sectional profiles of land-surface elevations and arsenic concentrations in surface and subsurface sediment samples from transects on the middle Belle Fourche River.

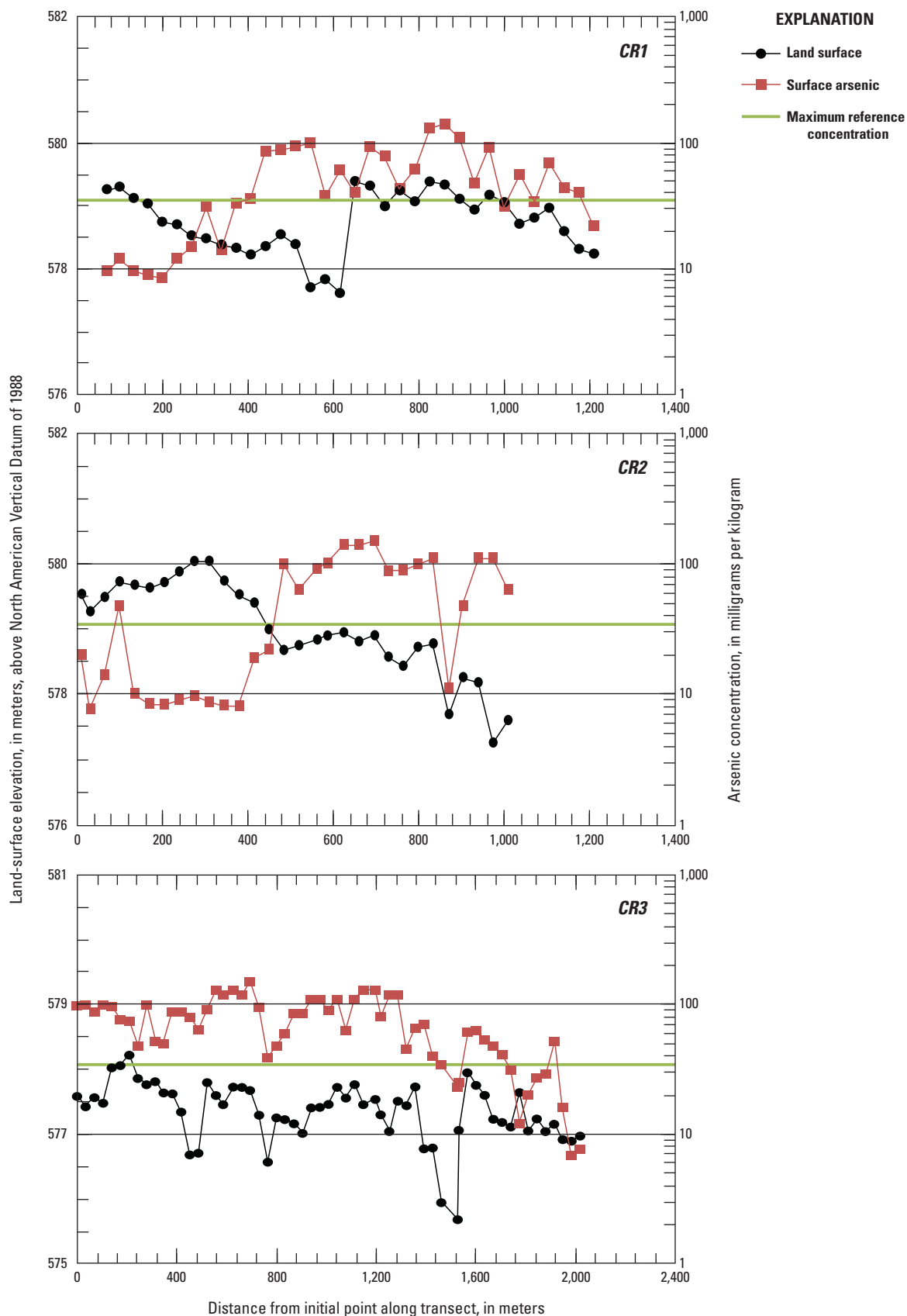


Figure 7. Cross-sectional profiles of land-surface elevations and arsenic concentrations in surface sediment samples from transects on the lower Cheyenne River.

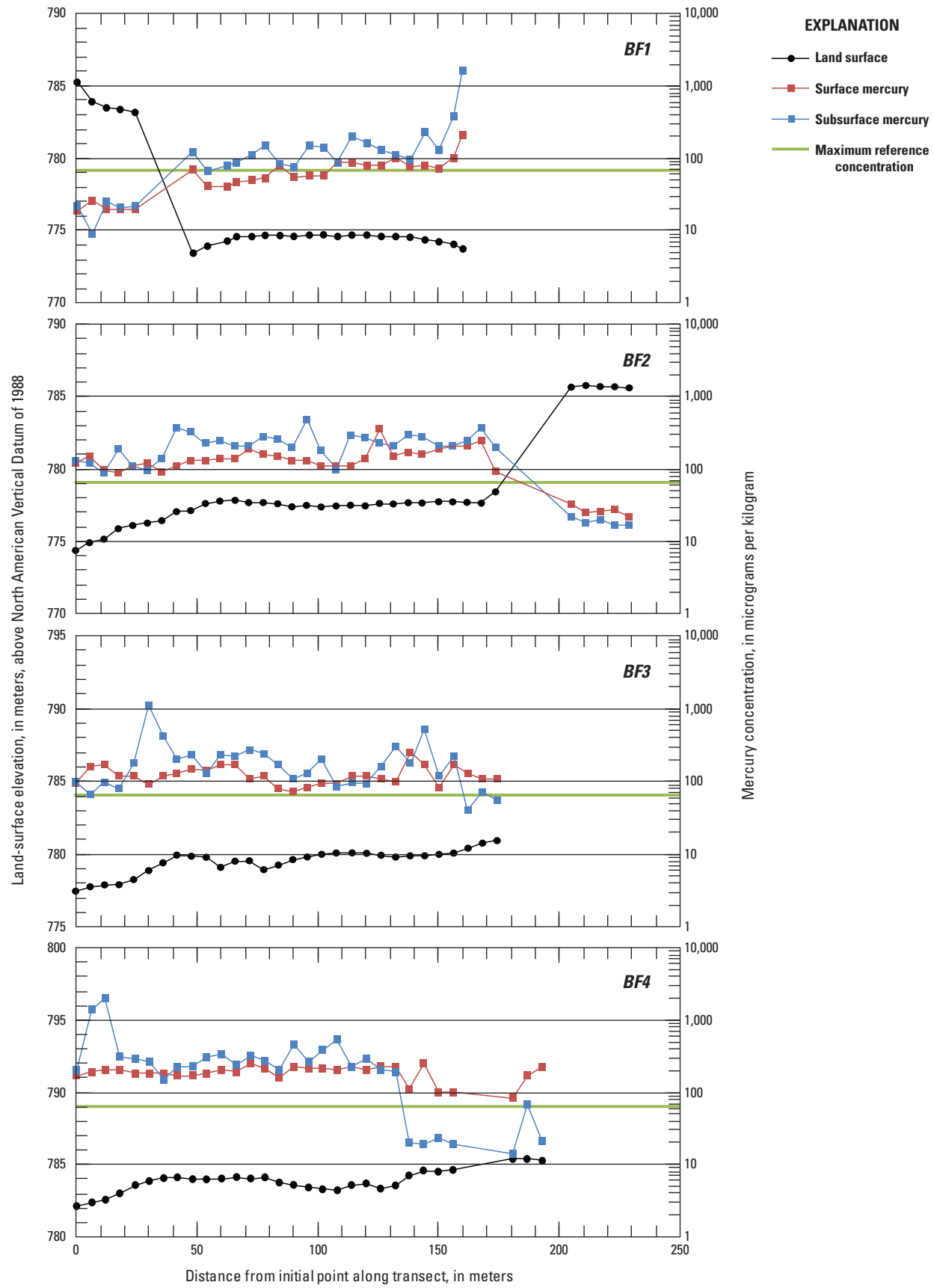


Figure 8. Cross-sectional profiles of land-surface elevations and mercury concentrations in surface and subsurface sediment samples from transects on the middle Belle Fourche River.

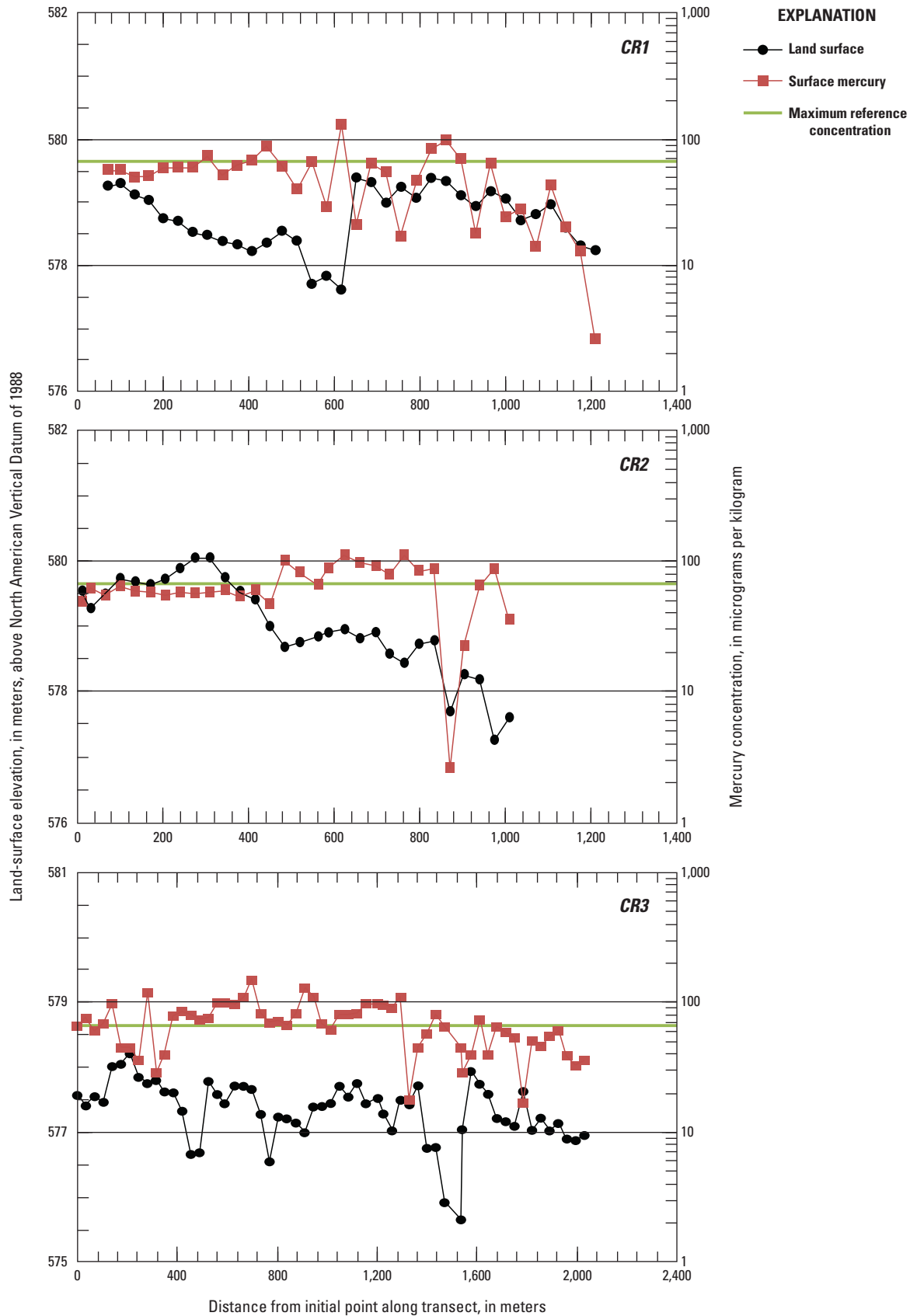


Figure 9. Cross-sectional profiles of land-surface elevations and mercury concentrations in surface sediment samples from transects on the lower Cheyenne River.

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Supplemental Data Tables

This supplemental section contains links to data tables that present the analytical results of selected metal concentrations in sediment samples from reference sites (table S1) and potentially contaminated sites (table S2). The Microsoft Excel spreadsheet ([Table_S1.xls](#)) contains a worksheet (worksheet: Intro) that describes the documentation and abbreviations used in table S1. The Microsoft Excel spreadsheet ([Table_S2.xls](#)) contains a worksheet (worksheet: Intro) that describes the documentation and abbreviations used in table S2.

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