

Prepared in cooperation with the U.S. Fish and Wildlife Service

Occurrence, Distribution, and Volume of Metals-Contaminated Sediment of Selected Streams Draining the Tri-State Mining District, Missouri, Oklahoma, and Kansas, 2011–12



Scientific Investigations Report 2016–5144

Cover. Miners in the Beaver Mine near Cardin, Oklahoma, around 1930. Photograph courtesy of Leona Atwood.

Occurrence, Distribution, and Volume of Metals-Contaminated Sediment of Selected Streams Draining the Tri-State Mining District, Missouri, Oklahoma, and Kansas, 2011–12

By D. Charlie Smith

Prepared in cooperation with the U.S. Fish and Wildlife Service

Scientific Investigations Report 2016–5144

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

U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Director

U.S. Geological Survey, Reston, Virginia: 2016

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment—visit <http://www.usgs.gov> or call 1–888–ASK–USGS.

For an overview of USGS information products, including maps, imagery, and publications, visit <http://store.usgs.gov>.

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this information product, for the most part, is in the public domain, it also may contain copyrighted materials as noted in the text. Permission to reproduce copyrighted items must be secured from the copyright owner.

Suggested citation:

Smith, D.C., 2016, Occurrence, distribution, and volume of metals-contaminated sediment of selected streams draining the Tri-State Mining District, Missouri, Oklahoma, and Kansas, 2011–12: U.S. Geological Survey Scientific Investigations Report 2016–5144, 86 p., <http://dx.doi.org/10.3133/sir20165144>.

ISSN 2328-0328 (online)

Contents

Abstract	1
Introduction.....	2
Description of Study Area and Mining History	2
Purpose and Scope	2
Previous Investigations.....	4
Methodology.....	6
Site Selection	6
Sample Collection	7
Stream Channel.....	7
Flood Plain.....	15
Sample Processing and Analysis.....	15
Stream Channel	20
Flood Plain.....	21
Laboratory Confirmation Samples	21
Estimation of the Volume of Contaminated Gravel Bar Deposits.....	22
Quality Control and Quality Assurance	23
Data Analysis Methods.....	23
Standard Reference Material	25
Blanks	29
Replicate X-Ray Fluorescence Analyses.....	29
Laboratory Confirmation Samples	29
Occurrence, Distribution, and Volume of Metals-Contaminated Sediment.....	33
Center Creek	33
Site Selection and Description	33
Depth and Concentration of Metals in Channel Sediments	33
Estimated Volume of Channel Sediment Contaminated by Mine Waste	37
Depth and Concentration of Metals in Flood-Plain Sediments	37
Turkey Creek	41
Site Selection and Description	41
Depth and Concentration of Metals in Channel Sediments	47
Estimated Volume of Channel Sediment Contaminated by Mine Waste	47
Depth and Concentration of Metals in Flood-Plain Sediments	47
Shoal Creek.....	50
Site Selection and Description	50
Depth and Concentration of Metals in Channel Sediments	50
Estimated Volume of Channel Sediment Contaminated by Mine Waste	55
Depth and Concentration of Metals in Flood-Plain Sediments	55
Tar Creek	55
Site Selection and Description	55
Depth and Concentration of Metals in Channel Sediments	58
Estimated Volume of Channel Sediment Contaminated by Mine Waste	58
Depth and Concentration of Metals in Flood-Plain Sediments	58

Spring River.....	62
Site Selection and Description	62
Depth and Concentration of Metals in Channel Sediments	62
Summary and Conclusions.....	64
References Cited.....	68

Figures

1. Map showing study sites in the Tri-State Mining District in Missouri, Oklahoma, and Kansas	3
2. Photograph showing freeze-core sampler with attached frozen sediment sample immediately after recovery and the freeze-core sampler with scale.....	13
3. Photograph showing liquid carbon dioxide injection tube inserted into the hollow driving rods during the injection of liquid CO ₂	14
4. Photograph showing removal of the rods and sample by hand using a fence-post puller	15
5. Photograph showing flood-plain core that has been prepared for analysis with the x-ray fluorescence instrument.....	21
6. Graphs showing relations of percent difference between mean concentration by x-ray fluorescence with the most-probable-value concentrations of cadmium, lead, and zinc in standard reference materials.....	28
7. Graphs showing relations between concentrations of cadmium, lead, and zinc in laboratory subsamples determined by x-ray fluorescence and laboratory methods, and between concentrations determined by x-ray fluorescence in original and split subsamples	31
8. Graphs showing comparison of relative percent difference between laboratory results for cadmium, lead, and zinc in the split samples, and the x-ray fluorescence results for either the original samples or the split sample before its submittal to the laboratory for stream channel sediment, Tri-State Mining District	32
9. Aerial photographs from 2013 and 1938 showing location of cores, samples, and tile probe soundings for sites C1 and C2 of intensive study on Center Creek, Missouri, 2011–12	34
10. Aerial photographs from 2013 and 1938 for site C3 and from 2013 and 1961 for site C4 showing location of cores, samples, and tile probe soundings on Center Creek, Missouri, 2011–12	35
11. Aerial photographs from 2013 and 1961 showing location of cores, samples, and tile probe soundings for sites C5 and C6 on Center Creek, Missouri, 2011–12	36
12. Boxplots showing frequency distributions of the concentrations of cadmium, lead, and zinc at specific sites in order from downstream to upstream.....	38
13. Graphs showing vertical concentration profiles for lead in the less than 2-millimeter size fraction of gravel bar-sediment samples scanned by x-ray fluorescence, Center Creek, Missouri, 2011–12	39
14. Graphs showing vertical concentration profiles for zinc in the less than 2-millimeter size fraction of gravel bar-sediment samples scanned by x-ray fluorescence, Center Creek, Missouri, 2011–12.....	40
15. Graphs showing vertical profiles by flood-plain core and sample location of lead concentrations analyzed by x-ray fluorescence in Center Creek, Turkey Creek, Shoal Creek, and Tar Creek, 2011–12	42

16.	Graphs showing vertical profiles by flood-plain core and sample location of zinc concentrations analyzed by x-ray fluorescence in Center Creek, Turkey Creek, Shoal Creek, and Tar Creek, 2011–12	43
17.	Aerial photographs from 2013 and 1938 showing location of bed-sediment cores, samples, and tile probe soundings for sites TC1, TC2, and TC3 in Turkey Creek, Missouri, 2012.....	44
18.	Aerial photographs from 2013 and 1938 showing location of bed-sediment cores, samples, and tile probe soundings for sites TC4 and TC5 in Turkey Creek, Missouri, 2012	45
19.	Aerial photographs from 2013 and 1961 showing location of bed-sediment cores, samples, and tile probe soundings for sites TC6 and TC7 in Turkey Creek, Missouri, 2012	46
20.	Graphs showing vertical profiles by core and sample location of lead concentrations in the less than 2-millimeter size fraction of gravel bar-sediment samples analyzed by x-ray fluorescence in Turkey Creek, Missouri, 2012.....	48
21.	Graphs showing vertical profiles by core and sample location of zinc concentrations in the less than 2-millimeter size fraction of gravel bar-sediment samples analyzed by x-ray fluorescence in Turkey Creek, Missouri, 2012.....	49
22.	Aerial photographs from 2013 and 1958 showing location of bed-sediment cores and sample locations for sites SFP1 and S1 in Shoal Creek, Missouri, 2012.....	51
23.	Aerial photographs from 2013 and 1938 showing location of bed-sediment cores and sample locations for sites S2 and SFP2 in Shoal Creek, Missouri, 2012.....	52
24.	Aerial photographs from 2013 and 1938 for sites S3 and S4, and from 2013 and 1958 for site S5 showing location of cores, samples, and tile probes in Shoal Creek, Missouri, 2012.....	53
25.	Graphs showing vertical profiles by core and sample location of lead concentrations in the less than 2-millimeter size fraction of stream channel samples analyzed by x-ray fluorescence in Shoal Creek, Missouri, 2012	54
26.	Graphs showing vertical profiles by core and sample location of zinc concentrations in the less than 2-millimeter size fraction of stream channel samples analyzed by x-ray fluorescence in Shoal Creek, Missouri, 2012	56
27.	Aerial photographs from 2013 and 1958 showing location of sediment cores, samples, and tile probe soundings for sites TR7, TR6, TR5, TRFP2, TR4, TR3, TR2, and TR1 on Tar Creek, Oklahoma, 2011	57
28.	Aerial photographs from 2013 and 1958 showing location of sediment cores, samples, and tile probe soundings for sites TR12, TR11, TRFP1, TR10, TR9, and TR8 on Tar Creek, Oklahoma, 2011	59
29.	Graphs showing vertical profiles by core and sample location of lead concentrations in the less than 2-millimeter size fraction of stream channel samples analyzed by x-ray fluorescence in Tar Creek, Oklahoma, 2011.....	60
30.	Vertical profiles by core and sample location of zinc concentrations in the less than 2-millimeter size fraction of stream channel samples analyzed by x-ray fluorescence in Tar Creek, Oklahoma, 2011	61
31.	Aerial photographs from 2013 and 1958 showing location of sediment cores and samples for sites SR1 and SR2 on Spring River, Kansas, 2012.....	63
32.	Graphs showing vertical profiles by core and sample location of lead and zinc concentrations in the less than 2-millimeter size fraction of gravel bar-sediment samples analyzed by x-ray fluorescence, Spring River, Kansas, 2012	64

Tables

1. Sediment core and sample locations, depth of water from the surface and maximum sample depth at each location, maximum depth of sediment exceeding the consensus probable effects concentration and the Tri-State Mining District specific probable effects concentration, and the percent depth of sediment exceeding the general probable effects concentration and the Tri-State Mining District specific probable effects concentration for Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and Spring River in the Tri-State Mining District, 2011–12.....	8
2. Flood-plain core and sample locations, maximum depth of core at each location, maximum depth of core exceeding the consensus probable effects concentration and the Tri-State Mining District-specific probable effects concentration, and the percent depth of core exceeding the general probable effects concentration and the Tri-State Mining District specific probable effects concentration for the flood plains of Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the Tri-State Mining District, 2011–12.....	12
3. Tile probe locations, depth of water from the surface, and maximum depth of refusal at each location for Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the Tri-State Mining District, 2011–12	16
4. Mean maximum proportional depth of sediment exceeding the consensus probable effects concentrations and the Tri-State Mining District specific probable effects concentrations, and mean total depth of boreholes and tile probes for each site, Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and Spring River in the Tri-State Mining District, 2011–12	24
5. Digitized gravel bar area, creek or river total drainage area, hydrologic unit code, mean thickness of sediments exceeding the consensus probable effects concentrations and the Tri-State Mining District specific probable effects concentration, and estimated total volume of sediment with concentrations of lead or zinc that exceed the consensus probable effects concentration and the Tri-State Mining District specific probable effects concentration for Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the Tri-State Mining District, 2011–12	26
6. Results of analyses of standard reference materials by the x-ray fluorescence unit....	27
7. Statistical summary of triplicate and septuplet x-ray fluorescence scans of intact flood-plain cores in the Tri-State Lead and Zinc Mining District, 2011–12	30
8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples	72

Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	4,047	square meter (m ²)
acre	0.4047	hectare (ha)
acre	0.4047	square hectometer (hm ²)
acre	0.004047	square kilometer (km ²)
square foot (ft ²)	929.0	square centimeter (cm ²)
square foot (ft ²)	0.09290	square meter (m ²)
square mile (mi ²)	259.0	hectare (ha)
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
cubic yard (yd ³)	0.7646	cubic meter (m ³)
Mass		
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)

International System of Units to U.S. customary units

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)
Area		
square meter (m ²)	0.0002471	acre
hectare (ha)	2.471	acre
square hectometer (hm ²)	2.471	acre
square kilometer (km ²)	247.1	acre
square centimeter (cm ²)	0.001076	square foot (ft ²)
square meter (m ²)	10.76	square foot (ft ²)
square hectometer (hm ²)	0.003861	section (640 acres or 1 square mile)
hectare (ha)	0.003861	square mile (mi ²)
square kilometer (km ²)	0.3861	square mile (mi ²)
Volume		
cubic meter (m ³)	1.308	cubic yard (yd ³)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

Datum

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

Abbreviations

ALA-D	enzyme-aminolevulinic acid dehydratase
CMERSC	Central Mineral and Environmental Resources Science Center
COC	chain of custody
CPEC	consensus probable effects concentration
DQO	data quality objective
ICP–AES	inductively coupled plasma-atomic emission spectrometry
ICP–MS	inductively coupled plasma-mass spectrometry
LOD	limit of detection
MPV	most probable value
MVT	Mississippi Valley-Type (metals)
NIST	National Institute of Standards and Technology
NRCS	Natural Resources Conservation Service
PEC	probable effects concentration
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
RSD	relative standard deviation
SLERA	screening level ecological risk assessment
SRM	standard reference material
SSURGO	Soil Survey Geographic Database
TPEC	Tri-State Mining District specific probable effects concentration
TSMD	Tri-State Mining District
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
XRF	x-ray fluorescence

Occurrence, Distribution, and Volume of Metals-Contaminated Sediment of Selected Streams Draining the Tri-State Mining District, Missouri, Oklahoma, and Kansas, 2011–12

By D. Charlie Smith

Abstract

Lead and zinc were mined in the Tri-State Mining District (TSMD) of southwest Missouri, northeast Oklahoma, and southeast Kansas for more than 100 years. The effects of mining on the landscape are still evident, nearly 50 years after the last mine ceased operation. The legacies of mining are the mine waste and discharge of groundwater from underground mines. The mine-waste piles and underground mines are continuous sources of trace metals (primarily lead, zinc, and cadmium) to the streams that drain the TSMD. Many previous studies characterized the horizontal extent of mine-waste contamination in streams but little information exists on the depth of mine-waste contamination in these streams. Characterizing the vertical extent of contamination is difficult because of the large amount of coarse-grained material, ranging from coarse gravel to boulders, within channel sediment. The U.S. Geological Survey, in cooperation with U.S. Fish and Wildlife service, collected channel-sediment samples at depth for subsequent analyses that would allow attainment of the following goals: (1) determination of the relation between concentration and depth for lead, zinc and cadmium in channel sediments and flood-plain sediments, and (2) determination of the volume of gravel-bar sediment from the surface to the maximum depth with concentrations of these metals that exceeded sediment-quality guidelines. For the purpose of this report, volume of gravel-bar sediment is considered to be distributed in two forms, gravel bars and the wetted channel, and this study focused on gravel bars. Concentrations of lead, zinc, and cadmium in samples were compared to the consensus probable effects concentration (CPEC) and Tri-State Mining District specific probable effects concentration (TPEC) sediment-quality guidelines.

During the study, more than 700 sediment samples were collected from borings at multiple sites, including gravel bars and flood plains, along Center Creek, Turkey Creek, Shoal

Creek, Tar Creek, and Spring River in order to characterize the vertical extent of mine waste in select streams in the TSMD. The largest concentrations of lead, zinc, and cadmium in gravel bar-sediment samples generally were detected in Turkey Creek and Tar Creek and the smallest concentrations were detected in Shoal Creek followed by the Spring River. Gravel bar-sediment samples from Turkey Creek exceeded the CPEC for cadmium (minimum of 70 percent of samples), lead (94 percent), and zinc (99 percent) at a slightly higher frequency than similar samples from Tar Creek (69 percent, 88 percent, and 96 percent, respectively). Gravel bar-sediment samples from Turkey Creek also contained the largest concentrations of cadmium (174 milligrams per kilogram [mg/kg]) and lead (7,520 mg/kg) detected; however, the largest zinc concentration (46,600 mg/kg) was detected in a gravel bar-sediment sample from Tar Creek. In contrast, none of the 65 gravel bar-sediment samples from Shoal Creek contained cadmium above the x-ray fluorescence reporting level of 12 mg/kg, and lead and zinc exceeded the CPEC in only 12 percent and 74 percent of samples, respectively. In most cases, concentrations of lead and zinc above the CPEC or TPEC were present at the maximum depth of boring, which indicated that nearly the entire thickness of sediment in the stream has been contaminated by mine wastes. Approximately 284,000 cubic yards of channel sediment from land surface to the maximum depth that exceeded the CPEC and approximately 236,000 cubic yards of channel sediment from land surface to the maximum depth that exceeded the TPEC were estimated along 37.6 of the 55.1 miles of Center Creek, Turkey Creek, Shoal Creek, and Tar Creek examined in this study. Mine-waste contamination reported along additional reaches of these streams is beyond the scope of this study. Flood-plain cores collected in the TSMD generally only had exceedances of the CPEC and TPEC for lead and zinc in the top 1 or 2 feet of soil with a few exceptions, such as cores in low areas near the stream or cores in areas disturbed by past mining.

Introduction

The Tri-State Mining District (TSMD) covers about 2,500 square miles (mi²) in southwest Missouri, northeast Oklahoma, and southeast Kansas (fig. 1) and has a rich history of lead and zinc mining beginning in the early 1800s and continuing through the mid-1900s. Most of the ore deposits were in Jasper and Newton Counties in Missouri, Ottawa County in Oklahoma, and Cherokee County in Kansas. More than 100 years of mining in the area has left a legacy of metal-contaminated mine-waste areas, contaminated soils and stream sediment, and contaminated groundwater in the region (Christenson, 1995; Barks, 1977; Feder and others, 1969).

Although a large amount of previous work has been done to characterize the spatial extent of surficial streambed sediments contaminated by mine waste in the TSMD (Pope, 2005; Juracek, 2009 and 2013; Andrews and others, 2009; MacDonald and others, 2010), little information is available on the depth or thickness of contaminated sediments in the streams. Based on surficial streambed-sediment samples compiled from various sources, maps by McDonald and others (2010) show that approximately 49 miles (mi) of Center Creek, Turkey Creek, Shoal Creek, and Tar Creek have streambed sediments that have moderate to high risk for toxicity to benthic invertebrates, as do sediments in the entire reach of the Spring River downstream from the mouth of Center Creek. Information on the depth of contamination is important to the U.S. Fish and Wildlife Service (USFWS) and other natural resource agencies entrusted with assessing damage to the ecosystem and evaluating restoration alternatives in the TSMD. Determining the depth of metal contamination is difficult in saturated streambed sediment because of the wide range of grain size of the sediments (silt and sand interspersed with coarse gravels and large cobbles) that are difficult to sample with traditional methods that are generally used to collect sands, silts, and clays. The USFWS requested assistance from the U.S. Geological Survey (USGS) to provide information on the depth of mine-waste contaminated sediments in selected streams in the TSMD. The USGS set the goals of (1) determination of the relation between concentration and depth for lead and zinc in channel sediments and flood-plain sediments, and (2) determination of the volume of channel sediments from the surface to the maximum depth with concentrations of lead and zinc that exceeded sediment-quality guidelines. Similar to previous studies, the extent of mine-waste contamination was determined using concentrations of Mississippi Valley-Type (MVT) metals, which include lead and zinc (Leach and others, 2010).

Description of Study Area and Mining History

The TSMD covers an area of about 2,500 mi² and spans three States (fig. 1). Lead and zinc ore are present in Mississippian-age rocks that are exposed at the surface in Missouri and buried by up to several hundred feet of younger

(Pennsylvanian-age) rocks in the Oklahoma and Kansas parts of the TSMD. Surface and near-surface deposits of lead ore were mined and smelted as early as 1820, but commercial mining of lead ore did not begin until about 1850 near Joplin, Missouri (Pope, 2005). Although zinc ore was about five times more common than lead ore, little zinc was produced from the district during the early years because of the difficulty in smelting zinc and the low price for the concentrate (Gibson, 1972). The lack of heavy machinery in the early years limited most mining to the shallow near-surface deposits in the Missouri part of the district. In the 1870s, the availability of railroads and steam machinery resulted in rapid expansion to other areas of the district, and by 1876, mines were opened at Galena, Kansas. In Oklahoma and Kansas, mine shafts as much as 480 feet (ft) deep allowed mining by the room and pillar method. The water from the deep underground mines was pumped into nearby streams to dewater the mine. Mining in the TSMD peaked in about 1920, after which most mining in Missouri ceased. Production from Kansas and Oklahoma gradually declined after World War II, with the last mine closing in 1970.

Ore was crushed during the milling process to extract the ore minerals. Waste rock from the milling process either was stored locally in large piles that often washed into nearby streams or was sold for use as agricultural lime, road aggregate, roof aggregate, or base rock for roads and railroads. The size to which the ore was crushed during milling decreased as milling methods improved and ranged from “chat” (medium to coarse sand) in the early years to silt-size material with the introduction of the floatation process around 1920.

Purpose and Scope

The purpose of this report is to present results of a USGS study to assess the depth of mine-waste contaminated sediments along selected reaches of streams along Center Creek, Turkey Creek, Shoal Creek, and Tar Creek (fig. 1) and two locations along the Spring River in the TSMD. In 2011, 22 stream channel cores and 13 flood-plain cores were collected in gravel bars, wetted channels, and the adjacent flood plain along a 7.4-mi stretch of Tar Creek in northeastern Oklahoma. In late 2011 and 2012, 24 stream channel cores and 7 flood-plain cores were collected in gravel bars, wetted channels, and the adjacent flood plain along a 11.1-mi stretch of Center Creek, 23 stream channel cores and 6 flood-plain cores were collected along a 10.1-mi stretch of Turkey Creek, 12 stream channel cores and 8 flood-plain cores were collected along a 9-mi stretch of Shoal Creek, and 5 stream channel cores were collected in 2 gravel bars on Spring River in southeastern Kansas and southwestern Missouri. For the purpose of this report, volume of gravel-bar sediment is considered to be distributed in two forms, gravel bars and the wetted channel, and this study focused on gravel bars.

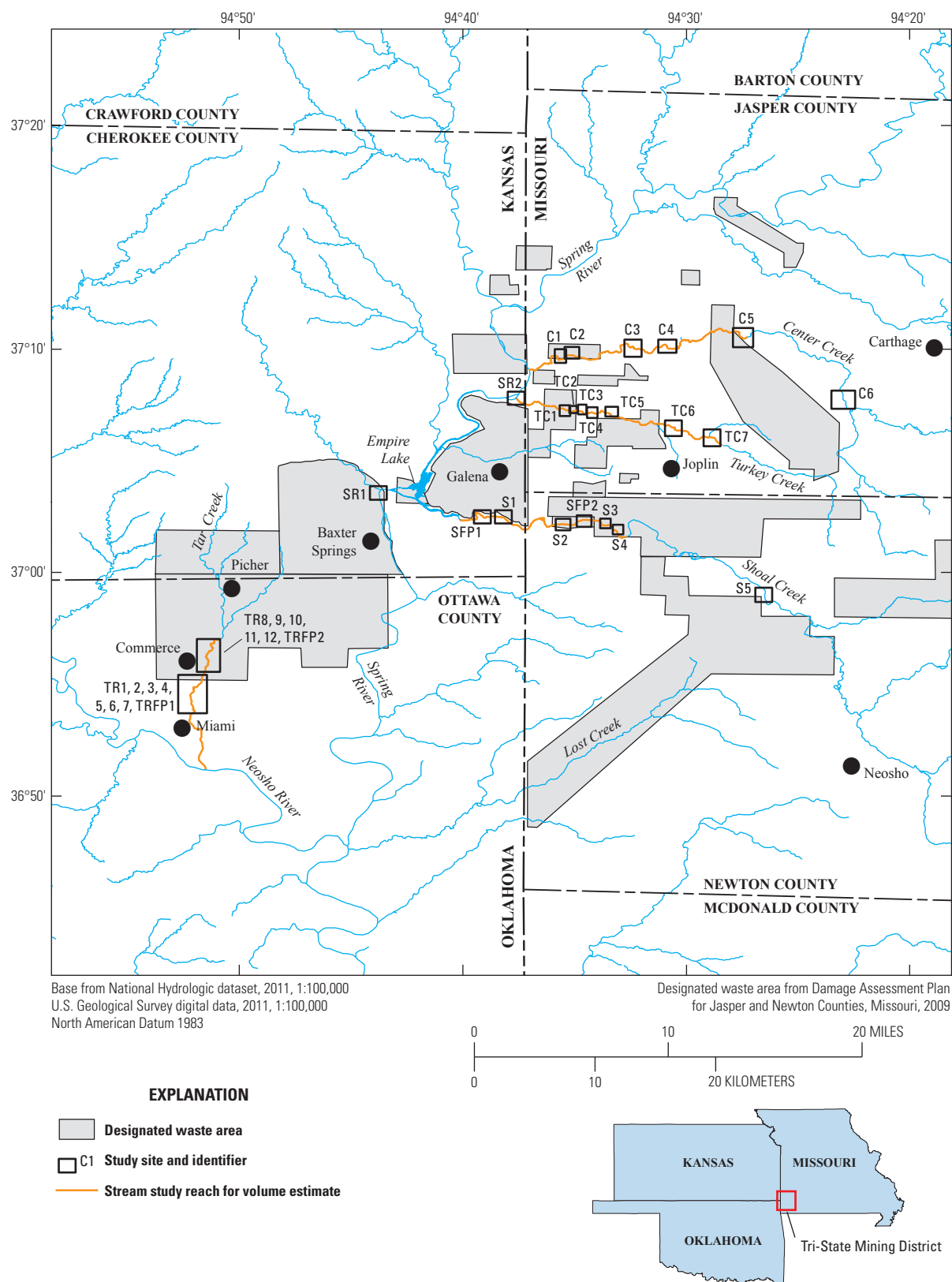


Figure 1. Study sites in the Tri-State Mining District in Missouri, Oklahoma, and Kansas.

Previous Investigations

Previous studies have sought to determine the lasting effects of more than 100 years of mining in the TSMD. Pope (2005) points out that hundreds of books, reports, articles, pamphlets, circulars, and abstracts have been written about the TSMD. This highlights the vast amount of work and research that has been done that ranges from geologic aspects to the environmental effects of the mining. Some of the earliest research examined the geologic nature of TSMD. Schmidt and Leonhard (1874) give one of the earliest accounts of the TSMD and describe in great detail the ore, geological conditions, and the mining activities at the time.

The TSMD is an MVT deposit that was first characterized by Bastin (1939). MVT deposits are sulfide mineral deposits and are generally dominated by zinc (sphalerite) and lead (galena) ores that are hosted in carbonate rocks. They also may contain silver and copper, which can be mined for profit. Other MVT-related metals include arsenic, barium, cadmium, nickel, and cobalt (Leach and others, 2010). These types of deposits are found throughout the world, but the largest and most studied deposits are in North America. Many large MVT deposits are found in the drainage basin of the Mississippi River in the central United States and include those found in the Viburnum Trend and the Old Lead Belt in southeast Missouri, the Upper Mississippi Valley District in Illinois, Wisconsin, and Iowa, and in northern Arkansas, and central Tennessee.

One of the earliest studies on the environmental effects of mining in the district was done by Bailey (1911), who collected surface-water samples from the Spring River and select tributaries that drain the TSMD. A water sample collected from a tributary of Spring River just north of Galena, Kans., had a zinc concentration of 732 milligrams per liter (mg/L). Bailey (1911) also sampled water directly from select mine discharge and storage ponds. Concentrations of zinc in those samples ranged from 677 mg/L to 1,852 mg/L.

Barks (1977) determined that mine-waste runoff and mine-water discharge were contributing to high concentrations of zinc and lead in Center Creek and Turkey Creek. Barks (1977) determined that groundwater from abandoned lead and zinc mines had a mean zinc concentration of 9.4 mg/L, but was limited to the immediate mine area and had little effect on the deep aquifer. The mean dissolved zinc concentration in runoff from mine-waste areas was 16 mg/L but was as large as 200 mg/L in one summer runoff sample that also had a lead concentration of 0.4 mg/L and cadmium concentration of 1.4 mg/L. Barks (1977) also determined that mine-water discharge had increased the dissolved zinc concentrations in receiving streams from a background concentration of 0.04 mg/L to about 0.5 mg/L during low-flow conditions and that the higher concentrations were sustained during high-flow conditions by runoff from mine-waste piles. The deposition of mine waste in the streambed increased concentrations of lead and zinc in the bed material from background concentrations of 20 milligrams per kilogram (mg/kg) to 450 mg/kg for lead and from 100 mg/kg to 2,500 mg/kg for zinc (Barks, 1977).

Barks (1977) estimated that the runoff from mine-waste piles contributed to a 25-fold increase in concentrations of lead and zinc in the stream bed sediments.

Exposure to contaminants in an aquatic environment can cause adverse effects on the health of various aquatic species, and the contaminant concentrations at which adverse effects can occur vary widely and depend on exposure time, species, life stage, and many other factors. In an effort to establish a guideline for aquatic exposure to various contaminants, sediment toxicity tests, commonly using *Hyalella azteca* (a freshwater amphipod), are done to determine acute and chronic exposures to contaminants (Wang and others, 2004). The results of toxicity tests are used to obtain the probable effects concentration (PEC) values for the various contaminants, above which adverse effects are more likely. MacDonald and others (2000) developed consensus-based PEC values (referred to as consensus probable effects concentration [CPEC] values in this report) for some trace metals that were based on several published sediment-quality guidelines obtained from observed effects that elevated concentrations of mining related metals had on aquatic wildlife. CPEC values were determined to be 33 mg/kg for arsenic, 4.98 mg/kg for cadmium, 111 mg/kg for chromium, 149 mg/kg for copper, 128 mg/kg for lead, 48.6 mg/kg for nickel, and 459 mg/kg for zinc (MacDonald and others, 2000). Ingersoll and others (2009), using sediments from the TSMD, developed PEC values for cadmium, lead, and zinc concentrations that were predicted to reduce the survival rate of *Hyalella azteca* by 10 percent relative to reference sediments that were natural background concentrations and not enriched from mineralized areas. The Tri-State specific PEC (referred to as Tri-State Mining District specific probable effects concentration [TPEC] in this report) values of Ingersoll and others (2009) were determined to be 11.1 mg/kg for cadmium, 150 mg/kg for lead, and 2,083 mg/kg for zinc. The TPECs were developed using sediment samples collected from the Grand Lake O' the Cherokees (Grand Lake) in Oklahoma. The TSMD lies in the watersheds of the Spring River and the Neosho River. The Spring River flows into the Neosho River upstream from Grand Lake. The TSMD encompasses streams with varying levels of lead- and zinc-mining effects. For this reason, the CPEC or TPEC may not be an appropriate metric in all parts of the TSMD. In this report the general term PEC is used to represent both the CPEC and TPEC.

Pope (2005) studied surficial sediments from the Spring River and Tar Creek watersheds in Kansas and determined that the sediments were particularly enriched in cadmium, lead, and zinc compared to other trace elements. The median concentrations for cadmium, lead, and zinc were 13, 180, and 1,800 mg/kg, respectively. Pope (2005) determined that the maximum concentrations of cadmium, lead, and zinc were several hundred times higher than the minimum values for those respective metals, whereas the majority of maximum concentrations of other trace metals were less than (<) 10 times the minimum value. Pope (2005) determined that samples in most mine-affected individual watersheds had

concentrations of cadmium, lead, and zinc that exceeded their respective CPEC. Concentrations exceeded the CPEC in 64 percent of cadmium samples, 56 percent of lead samples, and 75 percent of zinc samples.

Schmitt and others (2005) collected 74 fish, representing 6 different species, from 6 different sites on the Spring and Neosho Rivers in northeast Oklahoma in the TSMD. These six sites had varying degrees of mining influence, including non-mined reference sites. Schmitt and others (2005) analyzed the blood from each fish for cadmium, lead, zinc, iron, hemoglobin, and the activity of the enzyme δ -aminolevulinic acid dehydratase (ALA-D), which is involved in heme synthesis and is inhibited by lead. Fish from the sites that were most heavily affected by mining had elevated cadmium, lead, and zinc concentrations in their blood and generally exhibited a decrease in activity of ALA-D. Enzyme activity was greatest in fish from the reference sites. Schmitt and others (2005) also determined a negative correlation between lead concentrations and ALA-D activity in most species collected for the study. Their results indicated that lead was bioavailable and active biochemically in the Spring/Neosho River system.

Spring River flows through Empire Lake in Kansas, which traps much of the river's sediment load. Juracek (2006) collected cores of bottom sediments from Empire Lake to determine the history of sediment deposition in the lake—a history that reflects the land use changes in the TSMD. Juracek (2006) was able to identify pre-1954 and post-1954 layers of sediment based on the activity of cesium-137. The overall concentrations of metals in sediments decreased as sediments got younger and have leveled off since 1954. Despite the concentrations remaining constant, cadmium concentrations exceeded the CPEC by 440 to 640 percent, lead by 40 to 80 percent, and zinc by 580 to 970 percent in the most recently deposited (2005) sediments. The total volume and mass of sediment in Empire Lake was estimated to be 44 million cubic feet (about 1.6 million cubic yards) and 2,400 million pounds, respectively. Juracek (2006) also estimated the total mass of cadmium (78,000 pounds), lead (650,000 pounds), and zinc (12 million pounds) in sediment contained within Empire Lake. Sediment is deposited in Empire Lake during low-inflow periods; however, the ability of the reservoir to act as a sediment trap may have decreased over time and during periods of high-inflow most sediment may be transported through the reservoir and deposited farther downstream (Juracek, 2006).

Angelo and others (2007) studied mussels in the Spring River and determined that the number of species downstream from the heavily mined areas in the TSMD was considerably less than the number of species upstream from the mining areas. This decrease in species richness also corresponded to elevated concentrations of cadmium, lead, and zinc in the water, sediment, and tissue samples.

Tar Creek, a tributary to the Neosho River, drains the historically most productive mining area of the TSMD near Picher, Oklahoma (Andrews and others, 2009). Andrews and others (2009) collected lakebed, streambed, and flood-plain

sediments and (or) stream water samples at 30 sites in the Spring and Neosho River Basins and the Grand Lake O' the Cherokees from 2000 to 2006. Of all the water samples collected from the study, samples from Tar Creek had the highest concentrations of cadmium, lead, manganese, and zinc. Tar Creek also had the highest concentrations of cadmium, iron, lead, manganese, and zinc in streambed-sediment samples collected for the study.

Juracek and Becker (2009) collected cores from five locations in the Grand Lake O' the Cherokees to look at trends in the deposition of lead, zinc, cadmium, and other selected constituents. Concentrations of cadmium and lead in the core samples were typically less than the CPEC (MacDonald and others, 2000). Concentrations were also less than the TPECs (Ingersoll and others, 2009) of 11.1 mg/kg for cadmium and 150 mg/kg for lead. In contrast, zinc concentrations typically exceeded the CPEC of 459 mg/kg but were less than the TPEC of 2,083 mg/kg. Using the activity of cesium-137, Juracek and Becker (2009) were able to identify layers of sediment deposited earlier than 1954 and noticed an initial spike in concentrations of lead and zinc after 1964 and then a general decrease in concentrations in the depositional material beginning in the 1980s.

McDonald and others (2010) conducted an advanced screening level ecological risk assessment (SLERA) of aquatic habitats in streams within and draining the TSMD. The SLERA consisted of a screening level ecological risk assessment to aquatic organisms and a detailed ecological risk assessment to benthic invertebrates to provide risk managers with additional information for identifying contaminant sources in streams, evaluating candidate source control measures, and assessing other risk management options. Of the 1,162 sampling sites, 566 (49 percent) posed moderate or high risks to benthic invertebrate communities from contaminants of potential concern (COPCs) in the TSMD. The primary COPCs identified in sediment were metals, polycyclic aromatic hydrocarbons (PAHs), and butyl benzyl phthalate. Most sediment samples that posed moderate to high risk to benthic invertebrates were identified along about the lower 20 mi of Center Creek, the lower 18 mi of Turkey Creek, the lower 20 mi of Shoal Creek, and the lower 8–10 mi of Tar Creek. Sediments with moderate risk to benthic invertebrates also were present along most of the Spring River from its mouth at the Neosho River upstream to at least the mouth of Center Creek.

The effect of past mining activities is not limited to aquatic animals. Van der Merwe and others (2011) determined that migratory Canada geese (*branta canadensis*) collected in the TSMD had elevated concentrations of lead and zinc in their tissue. In their study, four to eight apparently healthy Canada geese, primarily young of the year goslings and adults, were collected from four sites with known mine-waste contamination and one reference site with no known contamination and were examined for metal poisoning. The geese from the mine-waste contaminated sites showed decreased activity of ALA-D that corresponded with elevated lead concentrations

in tissue samples. Geese at one of the contaminated sites also demonstrated signs of zinc poisoning in the form of fibrosis and vacuolization of the pancreas, which also corresponded with elevated pancreatic zinc concentrations.

Juracek (2013) expanded upon his 2009 study by focusing on the presence of mining related lead and zinc in the flood plains of the Spring River and its tributaries in Cherokee County, Kans. Juracek (2013) identified the flood plain using USGS 1:24,000-scale topographic quadrangle maps. The 2013 study indicated that surficial soils in the Spring River flood plain generally had lead and zinc concentrations that were less than the CPECs, and the concentrations that exceeded the CPECs were restricted to the flood plain of tributary streams. Concentrations that exceeded the CPEC or the TPEC were generally within the upper 2 ft of soil, or more frequently within the upper 6 inches (in.) of soil. Concentrations of lead and zinc in the surficial soil samples in the Spring River flood plain tended to decrease with increasing distance downstream and with increasing distance from the channel—the largest concentrations were generally present near the stream channel. Surficial soils in tributaries with very little mined areas had concentrations of lead and zinc that were substantially less than the CPEC and TPEC. Tributaries with extensive lead- and zinc-mined areas had concentrations of lead and zinc in surficial soils that frequently or typically exceeded the CPEC and TPEC.

Methodology

The large area of the TSMD required an array of methods for collecting samples from the stream channels along selected stream reaches and adjacent flood plains. The initial approach was to identify a representative reach along each stream that would be studied, and this selected reach would include several geomorphic channel units such as riffle, run, and pool. Several possible study sites along each stream were identified, but during an initial field reconnaissance of the area, land-owner permission to access was not granted at most proposed study sites. Alternative study sites were selected that often were shorter in length and contained fewer geomorphic channel features. In an effort to provide more spatial data on depth of mine-waste contaminated sediments along each stream, additional study locations focusing on gravel bars were added along each stream. Collection of channel sediments focused primarily on gravel bars, and the thickness of sediments was determined using various coring techniques and a tile probe.

Site Selection

Five streams in the TSMD were selected for study: Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and the Spring River. These streams were selected because they drain mined areas, are spatially distributed across the TSMD, and have a range of drainage areas—Turkey Creek (46 mi²),

Tar Creek (53 mi²), Shoal Creek (251 mi²), and Center Creek (300 mi²). The Spring River has a drainage area of about 2,422 mi² at the downstream-most sampling site near Baxter Springs, Kans., but the overall drainage area at its mouth at the Grand Lake O' the Cherokees is 2,590 mi².

Study reaches, flood plains, and gravel bar sites were identified using Natural Resources Conservation Service (NRCS [1938]), U.S. Department of Agriculture (2010), and Google Earth™ (2011) aerial imagery and NRCS Soil Survey Geographic Database [SSURGO (NRCS, 2003)] maps. After possible study reaches (overall length of stream that was studied) and sites (sections of the stream consisting of 1 or 2 gravel bars and [or] an adjacent flood plain) were chosen, the corresponding flood plain was identified using SSURGO maps by identifying soils that were classified as “frequently flooded,” where the probability of flooding in any year is greater than 50 percent, or “occasionally flooded,” where the probability of flooding in any year is 5 to 50 percent (Natural Resources Conservation Service, 2003). Flood-plain sites along Spring River and its tributaries selected by Juracek (2010) were also located in soils that were classified as “frequently flooded” or “occasionally flooded,” indicating that both methods were comparable. Once these sites were identified, landowner permission to access the gravel bars and flood plains was pursued. Site identifiers were chosen for locations on the streams that had 1 to 2 gravel bars in proximity to one another. In the case of Center Creek and Turkey Creek, the flood-plain samples were near site C2 (Center Creek) and sites TC2 and TC3 (Turkey Creek; fig. 1). The site identifiers used the first letter of the stream and the number of its order from downstream in relation to other sites on the stream. Two letters from the stream name were used in case the first letters of the two stream names were identical. For example, site C2 is on Center Creek and it is the second upstream site from the mouth of Center Creek. Site TR1 is the first upstream site on Tar Creek from the mouth. Site identifiers with “FP” in the identifier indicated flood-plain cores with the exception of Center Creek and Turkey Creek, which were both intensive study areas and the flood-plain transects were part of the gravel bar transects. For example, site C2 contained gravel bar-sediment samples and flood-plain samples. Flood-plain samples were collected from several cores located along one or two transects approximately perpendicular to the stream either on one side of the stream or on both sides depending on the flood-plain location and accessibility. Transects were used to describe the linear placement of core holes across the flood plain and gravel bar used to characterize the metal concentrations spatially both at depth and horizontally across the flood plain from the lowest elevation near the stream channel to its highest elevation based on flooding frequency. Additional cores were collected in locations that were not along the flood-plain transects but were at features of interest, such as old channels or low-lying areas, that could be areas of preferential deposition. These additional flood-plain samples were given the prefix “FB” to indicate a possibly biased flood-plain boring. Because the Spring River flood plain had already been

sampled by Juracek (2013), no flood-plain cores were collected from the Spring River flood plain.

Two stream sites, one on the lower part of the reach of Center Creek and one on the lower part of the reach of Turkey Creek, were selected for more intensive study. These were sites C1 and C2 on Center Creek and sites TC1, TC2, and TC3 on Turkey Creek (fig. 1). A greater number of cores within the channel and on the adjacent flood plain were collected at these intensive sites compared to other sites along the streams. Also, additional gravel bars were sampled upstream from these two intensive study sites to provide further information on the spatial variability of metal concentrations within the stream channel. Because of difficulty obtaining access, intensive study sites were not located along Tar Creek, Shoal Creek, or Spring River. A complete list of channel-sediment sample and flood-plain sample locations can be found in tables 1 and 2, respectively.

Sample Collection

This section presents the details of the sampling methods used to collect both channel-sediment samples and flood-plain sediment samples. A detailed field log was made for each flood plain and channel sediment core and sample by a hydrologist during the sample collection. The general sedimentological description of sample, method description, general remarks, and core recovery was noted on each log. Each log also included a detailed field sketch of the gravel bar, wetted channel, and (or) flood plain. A chain of custody (COC) was filled out for every flood-plain core and channel-sediment sample collected. The COC noted the general handling procedures, location, and persons in custody of the samples as they were transported from the field to the USGS Rolla, Mo., office or USFWS office for handheld x-ray fluorescence (XRF) analysis by USFWS personnel.

Stream Channel

Gravel bar-sediment samples required different methods based on cohesion, depth, and grain-size distribution of the sediments. Shallow samples on gravel bars (<2 ft deep and above the water surface) were collected using a shovel and a small hand scoop. A hole was typically dug to the target depth with a shovel. The disturbed sediment on the sides of the hole was carefully cleared away to expose the undisturbed sediment. A plastic hand scoop was then used to scoop up a sample of undisturbed sediment from the all exposed 1-ft intervals. Care was taken to avoid sampling near areas that could contain float from shallower depths. The channel-sediment sample was then placed directly in double plastic bags that were marked with the date, time, depth interval, and coring location identifier. The plastic scoop was rinsed with deionized water after each use to prevent cross contamination between the samples. Gravel bars with a surface 3 to 6 ft above the water level of the stream were typically excavated to the maximum depth above

the saturation zone with a tractor-mounted bucket if the gravel bar was accessible by heavy equipment, and then samples were collected as described above. If the gravel bar was not accessible by heavy equipment, then samples from above the water surface were collected by digging a hole with a shovel as described above.

A traditional method for sediment sampling is to collect core samples using a heavy walled sampler such as the split-spoon sampler or the piston sampler (Coduto, 1999). Loose, saturated sediment may fall from these samplers as they are removed from the subsurface (Murphy and Herkelrath, 1996). Further difficulties are encountered when sampling in coarse-grained sediments. Because of its high friction, sand and fine gravel can create a plug within the sampler during collection, which can prevent material from completely feeding into the sampler. Granular material larger than the opening of the sampler can block the opening and prevent sediment from feeding into to tube (Zapico and others, 1987). Zapico and others (1987) used a piston sampler to collect saturated cohesionless sands and gravels to depths up to approximately 110 ft and reported a mean recovery rate of 88 percent. The researchers suspected that the presence of cobble-sized material may have been responsible for the reduced recovery rate. Because of the great volume of coarse-grained material found in streams of the TSMD, this study used a combination of traditional and experimental methods to obtain gravel bar-sediment samples.

Most of the gravel bar-sediment samples were collected by using the freeze-core method (Smith and Barr, USGS, written commun., 2015; Smith, 2013; Smith and Elmore, 2013) with a truck- or tractor-mounted Geoprobe™ direct-push soil probe to mechanically force the freeze-core sampler into the subsurface and retrieve it. Many of the gravel bars in the TSMD are fine grained material mixed with cobble and boulder-size material, which can cause poor core recovery with traditional core methods. The saturated sediment in TSMD streams has little or no cohesion and can quickly fall from the traditional sampler as it is removed from the subsurface.

A freeze-core bit was fabricated at the USGS Missouri Water Science Center (fig. 2) and has been successfully used to collect vertical profiles of sediments from other mine-waste contaminated streams (Smith and Barr, USGS, written commun., 2015). Early designs used by Lisle and Eads (1991) recommended a simple hand-driven hollow rod to freeze sediments in gravels used by salmon spawning. The design used for the TSMD study was a 1-ft long freeze-core sampler fabricated from Geoprobe™ 1.25-in. drive rods with ½-in. vertical steel fins along the outside, which has a gross diameter of 2.25 in. (fig. 2). Large material is pushed aside by the sampler as it is driven to the desired depth. Fine grain material is then frozen alongside the sampler between the fins. The fins also protect the frozen sample from scraping against large material as the rods are pulled from the subsurface. Performance and quality assurance testing of the freeze-core sampler were discussed in Smith (2013) and Smith and Elmore (2013).

The freeze-core sampler was attached to a 4-ft section of hollow drive rod and driven into the sediment mechanically

Table 1. Sediment core and sample locations, depth of water from the surface and maximum sample depth at each location, maximum depth of sediment exceeding the consensus probable effects concentration and the Tri-State Mining District specific probable effects concentration, and the percent depth of sediment exceeding the general probable effects concentration and the Tri-State Mining District specific probable effects concentration for Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and Spring River in the Tri-State Mining District, 2011–12.

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; h:mm, hours, minutes; ft, foot; CPEC, probable effects concentration (MacDonald and others, 2000); TPEC, Tri-State Mining District specific probable effects concentration (Ingersoll and others, 2009); GB, gravel bar; —, no data; WC, wetted channel; all coordinates are referenced in the World Geodetic System 1984]

Coring or sample identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Time (hhmm)	Gravel bar or wetted channel	Site identifier	Depth of water below the surface at coring or sample location (ft)	Maximum sediment depth ^a (ft)	Maximum depth of sediment exceeding the CPEC (ft)	Maximum depth of sediment exceeding the TPEC (ft)	Percent depth of sediment exceeding the CPEC	Percent depth of sediment exceeding the TPEC
Center Creek												
CTR-CH-1	370943	943519	11/02/2011	0800	GB	C1	2.0	8.0	8.0	7.0	100.0	87.5
CTR-CH-2	370941	943521	11/02/2011	1310	GB	C1	1.0	9.5	9.5	7.5	100.0	78.9
CTR-CH-3	370937	943523	11/02/2011	1415	GB	C1	1.0	8.5	8.5	6.0	100.0	70.6
CTR-CH-4	370935	943521	11/03/2012	1055	GB	C1	2.0	7.0	6.0	2.0	85.7	28.6
CTR-GB-1	370934	943524	11/03/2011	—	GB	C1	1.0	0.2	0.2	0.2	100.0	100.0
CTR-WC-1	370937	943523	11/02/2012	1445	WC	C1	-0.5	6.5	6.5	3.0	100.0	46.2
CTR-WC-2	370939	943523	11/02/2012	1600	WC	C1	-1.0	7.0	7.0	0.0	100.0	0.0
CTR-CH-5	370942	943503	11/04/2011	1050	GB	C2	1.0	6.5	6.5	5.5	100.0	84.6
CTR-CH-6	370934	943503	11/04/2011	1320	GB	C2	1.0	1.0	1.0	1.0	100.0	100.0
CTR-CH-7	370933	943501	11/04/2011	1340	GB	C2	1.0	1.0	1.0	1.0	100.0	100.0
CTR-WC-3	370944	943506	11/04/2011	1315	WC	C2	-1.5	0.2	0.2	0.2	100.0	100.0
CTR-WC-4	370941	943459	11/04/2011	1340	WC	C2	-2.5	0.2	0.2	0.2	100.0	100.0
CC-A-HD1	371002	943220	05/12/2012	1437	GB	C3	0.0	4.0	4.0	4.0	100.0	100.0
CC-A-HD2	371002	943219	05/12/2012	1700	GB	C3	0.0	6.0	6.0	6.0	100.0	100.0
CC-D-HD1	371006	943052	06/07/2012	1447	GB	C4	0.0	3.5	3.5	3.5	100.0	100.0
CC-D-HD2	371006	943052	06/07/2012	1559	GB	C4	1.0	4.0	4.0	4.0	100.0	100.0
CC-D-WC1	371006	943052	06/07/2012	1200	GB	C4	-2.0	0.5	0.5	0.5	100.0	100.0
CC-C-HD1	371027	942727	06/05/2012	0830	GB	C5	1.0	4.3	4.3	4.3	100.0	100.0
CC-C-HD2	371028	942725	06/05/2012	—	GB	C5	1.0	2.0	2.0	2.0	100.0	100.0
CC-C-WC1	371028	942725	06/07/2012	1200	GB	C5	-2.5	0.5	0.5	0.5	100.0	100.0
CC-B-HD1	370743	942257	05/15/2012	1043	GB	C6	0.0	2.0	0.0	0.0	0.0	0.0
CC-B-HD2	370744	942258	05/15/2012	1130	GB	C6	0.0	3.0	0.0	0.0	0.0	0.0
CC-B-HS1	370743	942257	05/15/2012	—	GB	C6	1.0	2.0	0.0	0.0	0.0	0.0
CC-B-HS2	370744	942258	05/15/2012	—	GB	C6	0.0	2.0	0.0	0.0	0.0	0.0

Table 1. Sediment core and sample locations, depth of water from the surface and maximum sample depth at each location, maximum depth of sediment exceeding the consensus probable effects concentration and the Tri-State Mining District specific probable effects concentration, and the percent depth of sediment exceeding the general probable effects concentration and the Tri-State Mining District specific probable effects concentration for Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and Spring River in the Tri-State Mining District, 2011–12.—Continued

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; h:mm, hours, minutes; ft, foot; CPEC, probable effects concentration (MacDonald and others, 2000); TPEC, Tri-State Mining District specific probable effects concentration (Ingersoll and others, 2009); GB, gravel bar; —, no data; WC, wetted channel; all coordinates are referenced in the World Geodetic System 1984]

Coring or sample identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Time (h:mm)	Gravel bar or wetted channel	Site identifier	Depth of water below the surface at coring or sample location (ft)	Maximum sediment depth ^a (ft)	Maximum depth of sediment exceeding the CPEC (ft)	Maximum depth of sediment exceeding the TPEC (ft)	Percent depth of sediment exceeding the CPEC	Percent depth of sediment exceeding the TPEC
Turkey Creek												
TKC-CH-5	370715	943516	06/21/2012	1300	GB	TC1	0.9	4.3	4.3	4.3	100.0	100.0
TKC-CH-5P	370715	943518	06/20/2015	1640	GB	TC1	2.0	2.0	2.0	2.0	100.0	100.0
TKC-CH-6	370717	943517	06/21/2012	1140	GB	TC1	5.0	8.5	8.5	8.5	100.0	100.0
TKC-CH-7	370718	943515	06/20/2012	1630	GB	TC1	1.0	4.5	4.5	4.5	100.0	100.0
TKC-WC-3	370718	943516	06/21/2012	1030	WC	TC1	-0.3	3.0	3.0	3.0	100.0	100.0
TKC-CH-4	370713	943507	06/20/2012	1330	GB	TC2	7.0	11.5	11.5	11.5	100.0	100.0
TKC-CH-1	370715	943459	06/19/2012	1015	GB	TC3	3.6	6.5	6.5	6.5	100.0	100.0
TKC-CH-2	370715	943501	06/19/2012	1230	GB	TC3	3.3	8.2	8.2	7.0	100.0	85.4
TKC-CH-3	370714	943500	06/19/2012	1640	GB	TC3	6.2	13.0	13.0	13.0	100.0	100.0
TKC-WC-1	370715	943501	06/19/2012	1530	WC	TC3	-1.6	4.6	2.0	2.0	43.5	43.5
TC-D-HD1	370709	943413	06/06/2012	0925	GB	TC4	1.9	8.5	8.5	8.5	100.0	100.0
TC-D-HD2	370708	943411	06/06/2012	1200	GB	TC4	2.2	5.1	5.1	5.1	100.0	100.0
TC-B-HD1	370625	943031	05/16/2012	1020	GB	TC6	0.5	6.0	6.0	6.0	100.0	100.0
TC-B-HD2	370625	943030	05/16/2012	1045	GB	TC6	0.4	6.4	1.0	1.0	15.6	15.6
TC-C-HD1	370627	943029	05/16/2012	1415	GB	TC6	0.7	3.0	3.0	3.0	100.0	100.0
TC-C-HD2	370627	943029	05/16/2012	1420	GB	TC6	0.4	3.0	3.0	3.0	100.0	100.0
TC-C-HS1	370627	943029	05/16/2012	1425	GB	TC6	1.2	2.0	2.0	2.0	100.0	100.0
TC-E-HD1	370704	943323	06/06/2012	1630	GB	TC5	0.3	2.0	2.0	2.0	100.0	100.0
TC-E-HD2	370702	943323	06/06/2012	1620	GB	TC5	1.0	4.5	4.5	4.5	100.0	100.0
TC-E-HD3	370704	943323	06/06/2012	1235	GB	TC5	0.3	1.0	1.0	1.0	100.0	100.0
TC-E-WC1	370702	943323	06/07/2012	1140	WC	TC5	-2.8	0.7	0.7	0.7	50.0	50.0
TC-A-HD1	370601	942844	05/15/2012	1555	GB	TC7	0.0	1.3	1.3	0.0	100.0	0.0
TC-A-HD2	370601	942846	05/15/2012	1635	GB	TC7	0.0	1.8	1.8	0.0	100.0	0.0

Table 1. Sediment core and sample locations, depth of water from the surface and maximum sample depth at each location, maximum depth of sediment exceeding the consensus probable effects concentration and the Tri-State Mining District specific probable effects concentration, and the percent depth of sediment exceeding the general probable effects concentration and the Tri-State Mining District specific probable effects concentration for Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and Spring River in the Tri-State Mining District, 2011–12.—Continued

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; h:mm, hours, minutes; ft, foot; CPEC, probable effects concentration (MacDonald and others, 2000); TPEC, Tri-State Mining District specific probable effects concentration (Ingersoll and others, 2009); GB, gravel bar; —, no data; WC, wetted channel; all coordinates are referenced in the World Geodetic System 1984]

Coring or sample identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Time (hhmm)	Gravel bar or wetted channel	Site identifier	Depth of water below the surface at coring or sample location (ft)	Maximum sediment depth ^a (ft)	Maximum depth of sediment exceeding the CPEC (ft)	Maximum depth of sediment exceeding the TPEC (ft)	Percent depth of sediment exceeding the CPEC	Percent depth of sediment exceeding the TPEC
Shoal Creek												
SH-CH-11	370230	943824	07/09/2012	1430	GB	S1	3.0	9.0	9.0	0.0	100.0	0.0
SH-WC-3	370228	943824	07/09/2012	1200	WC	S1		4.0	4.0	0.0	100.0	0.0
SH-CH-8	370210	943528	07/30/2012	1640	GB	S2	1.0	9.0	3.0	1.0	33.3	11.1
SH-CH-9	370211	943529	07/30/2012	1508	GB	S2	5.1	11.9	8.0	6.0	67.2	50.4
SH-CH-7	370206	943331	07/11/2012	0855	GB	S3	4.0	7.9	7.9	0.0	100.0	0.0
SH-CH-5	370207	943322	07/12/2012	1300	GB	S3	2.0	1.0	1.0	0.0	100.0	0.0
SH-WC-2	370206	943323	07/12/2012	0820	WC	S3	-2.2	2.0	2.0	0.0	100.0	0.0
SH-CH-1	370156	943315	07/31/2012	0805	GB	S4	1.0	6.0	6.0	0.0	100.0	0.0
SH-CH-2	370159	943318	07/31/2012	0920	GB	S4	3.0	7.1	2.0	0.0	28.2	0.0
SH-WC-1	370158	943319	07/12/2012	1030	WC	S4	-1.2	2.8	1.0	0.0	35.7	0.0
SC-A-HD1	365859	942628	05/17/2012	0910	GB	S5	2.2	3.5	2.0	0.0	57.1	0.0
SC-A-HD2	365859	942628	05/17/2012	0940	GB	S5	0.9	2.0	2.0	0.0	100.0	0.0
Tar Creek												
TAR-12-HC1	365554	945124	07/28/2011	1345	WC	TR1	-2.0	0.2	0.2	0.2	100.0	100.0
TAR-11-HC1	365413	945209	07/27/2011	1300	GB	TR2	3.0	4.0	4.0	4.0	100.0	100.0
TAR-TR-11	365413	945209	07/14/2011	1510	GB	TR2	-1.8	1.6	1.0	1.0	62.5	62.5
TAR-TR-5	365426	945212	07/13/2011	1750	GB	TR3	-0.3	0.5	0.5	0.0	100.0	0.0
TAR-4-HC1	365438	945206	07/28/2011	1100	GB	TR4	1.0	2.2	2.2	2.2	100.0	100.0
TAR-TR-4	365438	945206	07/13/2011	1715	GB	TR4	1.0	1.0	1.0	1.0	100.0	100.0
TAR-3-HP1	365442	945203	07/28/2011	1000	GB	TR5	0.0	3.0	3.0	3.0	100.0	100.0
TAR-TR-3	365442	945202	07/13/2011	1610	GB	TR5	0.0	0.7	0.7	0.7	100.0	100.0
TAR-TR-3A	365442	945204	07/12/2011	1500	GB	TR5	1.0	2.0	2.0	2.0	100.0	100.0
TAR-TR-2	365453	945154	07/13/2011	1520	GB	TR6	0.1	0.3	0.3	0.3	100.0	100.0

Table 1. Sediment core and sample locations, depth of water from the surface and maximum sample depth at each location, maximum depth of sediment exceeding the consensus probable effects concentration and the Tri-State Mining District specific probable effects concentration, and the percent depth of sediment exceeding the general probable effects concentration and the Tri-State Mining District specific probable effects concentration for Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and Spring River in the Tri-State Mining District, 2011–12.—Continued

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; h:mm, hours, minutes; ft, foot; CPEC, probable effects concentration (MacDonald and others, 2000); TPEC, Tri-State Mining District specific probable effects concentration (Ingersoll and others, 2009); GB, gravel bar; —, no data; WC, wetted channel; all coordinates are referenced in the World Geodetic System 1984]

Coring or sample identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Time (hhmm)	Gravel bar or wetted channel	Site identifier	Depth of water below the surface at coring or sample location (ft)	Maximum sediment depth ^a (ft)	Maximum depth of sediment exceeding the CPEC (ft)	Maximum depth of sediment exceeding the TPEC (ft)	Percent depth of sediment exceeding the CPEC	Percent depth of sediment exceeding the TPEC
Tar Creek—Continued												
TAR-TR-1	365500	945147	07/13/2011	1450	GB	TR7	-0.8	0.3	0.3	0.3	100.0	100.0
TAR-TR-10 ^b	365554	945124	07/14/2011	1370	GB	TR8	0.2	2.9	1.0	1.0	34.5	34.5
TAR-6-VC1	365426	945212	07/27/2011	1400	GB	TR9	1.0	3.5	3.5	3.5	100.0	100.0
TAR-TR-6 ^b	365605	945125	07/14/2011	1000	GB	TR9	0.2	3.5	1.0	1.0	28.6	28.6
TAR-TR-7 ^b	365609	945127	07/14/2011	1035	GB	TR10	0.0	3.3	1.0	1.0	30.3	30.0
TAR-9-PT1	365625	945123	07/27/2011	1110	GB	TR11	2.0	4.0	4.0	4.0	100.0	100.0
TAR-9-VC1	365626	945123	07/27/2011	1030	GB	TR11	2.0	6.6	6.0	5.0	90.9	78.5
TAR-9-VC1A	365626	945123	07/27/2011	1230	GB	TR11	2.0	6.6	6.6	6.0	100.0	90.9
TAR-BAR-1	365625	945123	08/10/2011	0845	GB	TR11	1.0	6.0	5.0	5.0	83.3	83.3
TAR-TR-9 ^b	365626	945123	07/14/2011	1230	GB	TR11	0.5	4.3	1.0	1.0	23.3	23.3
TAR-8-VC1	365630	945116	07/27/2011	1300	GB	TR12	0.5	3.8	3.8	3.8	100.0	100.0
TAR-TR-8 ^b	365630	945116	07/14/2011	1140	GB	TR12	0.0	3.3	1.0	1.0	30.3	30.3
Spring River												
SR-CH-1	370331	944344	08/01/2012	0955	GB	SR1	6.0	15.0	13.0	0.0	86.7	0.0
SR-CH-2	370333	944344	08/01/2012	1215	GB	SR1	4.0	19.1	19.1	0.0	100.0	0.0
SR-CH-3	370335	944343	08/01/2012	1650	GB	SR1	1.0	14.0	6.0	0.0	42.9	0.0
SR-CH-4	370749	943735	08/02/2012	1238	GB	SR2	1.0	5.3	5.3	5.0	100.0	94.3
SR-CH-5	370748	943737	08/02/2012	1340	GB	SR2	1.2	8.0	8.0	2.0	100.0	25.0

^aThe maximum depth of recovery, which is equal to the refusal of the sampler.

^bThe maximum depth of the core or sample and the maximum depth differ due to the collection of shallow core or samples paired with tile probe sounding to determine the maximum depth at these locations.

12 Occurrence, Distribution, and Volume of Metals-Contaminated Sediment of Selected Streams, Tri-State Mining District

Table 2. Flood-plain core and sample locations, maximum depth of core at each location, maximum depth of core exceeding the consensus probable effects concentration and the Tri-State Mining District-specific probable effects concentration, and the percent depth of core exceeding the general probable effects concentration and the Tri-State Mining District specific probable effects concentration for the flood plains of Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the Tri-State Mining District, 2011–12.

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; hhmm, hours, minutes; ft, foot; CPEC, consensus probable effects concentration (MacDonald and others, 2000); TPEC, Tri-State Mining District specific probable effects concentration (Ingersoll and others, 2009); —, no data; all coordinates are referenced in the World Geodetic System 1984]

Coring or sample identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Time (hhmm)	Site identifier	Maximum depth of core (ft)	Maximum depth of core exceeding the CPEC (ft)	Maximum depth of core exceeding the TPEC (ft)	Percent depth of core exceeding the CPEC	Percent depth of core exceeding the TPEC
Center Creek										
CTR-FB-1	370940	943519	11/05/2011	1530	C1	9.0	4.0	3.0	44.4	33.3
CTR-FB-2	370939	943507	11/05/2011	1145	C2	9.0	0.0	0.0	0.0	0.0
CTR-FP-1	370952	943500	11/08/2011	1415	C2	12.0	11.0	8.0	91.7	66.7
CTR-FP-2	370949	943501	11/08/2011	1300	C2	16.0	16.0	16.0	100.0	100.0
CTR-FP-3	370946	943502	11/08/2011	1140	C2	9.5	1.0	1.0	10.5	10.5
CTR-FP-4	370939	943503	11/01/2011	1220	C2	8.0	0.0	0.0	0.0	0.0
CTR-FP-5	370936	943504	11/01/2011	—	C2	14.0	0.0	0.0	0.0	0.0
Turkey Creek										
TKC-FB-1	370715	943501	06/18/2012	1620	TC3	14.5	12.0	1.0	82.8	6.9
TKC-FB-2	370711	943510	06/19/2012	0905	TC1	13.6	1.0	1.0	7.4	7.4
TKC-FP-1	370721	943506	06/18/2012	1410	TC2	9.0	7.0	1.0	77.8	11.1
TKC-FP-2	370719	943505	06/18/2012	1500	TC2	13.0	10.0	10.0	76.9	76.9
TKC-FP-3	370717	943503	06/18/2012	1545	TC2	11.0	9.0	2.0	81.8	18.2
TKC-FP-4	370713	943459	06/19/2012	0820	TC3	11.0	9.0	1.0	81.8	9.1
Shoal Creek										
SH-FB-1	370158	943310	07/10/2012	1245	S4	6.0	0.0	0.0	0.0	0.0
SH-FB-2	370218	943426	07/10/2012	1200	SFP2	9.0	0.0	0.0	0.0	0.0
SH-FB-3	370217	943435	07/10/2012	1245	SFP2	16.0	12.0	0.0	75.0	0.0
SH-FB-4	370159	943318	07/31/2012	0920	S4	9.0	9.0	8.0	100.0	88.9
SH-FP-1	370234	943855	07/10/2012	1545	SFP1	9.6	0.0	0.0	0.0	0.0
SH-FP-2	370239	943855	07/10/2012	1515	SFP1	8.8	0.0	0.0	0.0	0.0
SH-FP-3	370244	943855	07/10/2012	1435	SFP1	10.0	0.0	0.0	0.0	0.0
SH-FP-4	370249	943855	07/10/2012	1400	SFP1	11.0	10.0	0.0	90.9	0.0
Tar Creek										
TAR-FB-1	365449	945217	08/09/2011	1405	TRFP2	10.0	0.0	0.0	0.0	0.0
TAR-FB-2	365440	945204	08/09/2011	1455	TRFP2	11.0	6.0	3.0	54.5	27.3
TAR-FB-3	365440	945205	08/09/2011	1430	TRFP2	10.0	10.0	1.0	100.0	10.0
TAR-FB-4	365625	945124	08/10/2011	1200	TR11	11.0	1.0	1.0	9.1	9.1
TAR-FP1-1	365613	945128	08/09/2011	1735	TRFP1	8.5	7.0	5.0	82.4	58.8
TAR-FP1-2	365613	945126	08/09/2011	1715	TRFP1	13.0	1.0	1.0	7.7	7.7
TAR-FP1-3	365613	945123	08/09/2011	1650	TRFP1	11.5	1.0	1.0	8.7	8.7
TAR-FP1-4	365613	945120	08/09/2011	1625	TRFP1	9.0	0.0	0.0	0.0	0.0
TAR-FP2-1	365440	945207	08/09/2011	1315	TRFP2	13.0	1.0	1.0	7.7	7.7
TAR-FP2-2	365441	945210	08/09/2011	1250	TRFP2	11.0	0.0	0.0	0.0	0.0

Table 2. Flood-plain core and sample locations, maximum depth of core at each location, maximum depth of core exceeding the consensus probable effects concentration and the Tri-State Mining District-specific probable effects concentration, and the percent depth of core exceeding the general probable effects concentration and the Tri-State Mining District specific probable effects concentration for the flood plains of Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the Tri-State Mining District, 2011–12.—Continued

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; hhmm, hours, minutes; ft, foot; CPEC, consensus probable effects concentration (MacDonald and others, 2000); TPEC, Tri-State Mining District specific probable effects concentration (Ingersoll and others, 2009); —, no data; all coordinates are referenced in the World Geodetic System 1984]

Coring or sample identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Time (hhmm)	Site identifier	Maximum depth of core (ft)	Maximum depth of core exceeding the CPEC (ft)	Maximum depth of core exceeding the TPEC (ft)	Percent depth of core exceeding the CPEC	Percent depth of core exceeding the TPEC
Tar Creek—Continued										
TAR-FP2-3	365443	945212	08/09/2011	1200	TRFP2	13.5	0.0	0.0	0.0	0.0
TAR-FP2-4	365444	945215	08/09/2011	1110	TRFP2	10.0	0.0	0.0	0.0	0.0
TAR-FP2-5	365446	945221	08/09/2011	1135	TRFP2	7.9	0.0	0.0	0.0	0.0



Figure 2. Freeze-core sampler with attached frozen sediment sample immediately after recovery and the freeze-core sampler with scale (Smith and Elmore, 2013).

by the Geoprobe™ hammer or by hand using a 15-pound (lb) fence-post driver at locations not accessible to heavy equipment. Once the sampler was driven to the required depth, 0.125-in. stainless steel tubing was inserted into the driving rods until the opening of the tubing was even with the center of the freeze-core sampler. The tubing was attached to a tank of liquid carbon dioxide (CO_2). The tank had an internal siphon tube that draws liquid from the bottom of the tank, ensuring that liquid CO_2 was released and not gaseous CO_2 . This was also accomplished using a tank without a siphon tube by inverting the tank. It was important to release the liquid CO_2 near the center of the sampler because the evaporation of the liquid was instantaneous. The endothermic reaction absorbed heat energy, which cooled the sampler and the surrounding saturated sediment. Liquid CO_2 was injected into the sampler for 0.5–4 minutes (min) (fig. 3). The injection of CO_2 was either continuous or divided up into two to three pulses with 15- to 30-second breaks. The length of time that CO_2 was injected was varied based on conditions in the field and sample recovery of previous samples. The rods and sampler were removed mechanically by the Geoprobe™ or by hand using a fence-post puller (fig. 4).

Once the frozen sample was removed, it was quickly rinsed with deionized water to remove loose particles that may have attached from shallower depths while the sampler was pulled upward. This rinse left a frozen core that was a representative channel-sediment sample at the depth that it was frozen. The sampler with frozen sediment was placed over a steel pan (fig. 2) and the frozen sediment was scraped into the pan with a plastic scraping tool. If needed, any remaining attached sediment was then melted by rinsing into the pan

using deionized water. The sample was then placed in double plastic bags and labeled with the date, time, depth interval, and core identification.

Tar Creek lacked the cobble and boulder sized material present at the other streams and the freeze-core method often was not necessary. Shallow samples (<2 ft deep and above the water surface) were collected using a shovel and a small hand scoop similar to the other streams. Deeper channel-sediment samples were collected using the vibra-core method as described by Lanesky and others (1979) to collect continuous cores from the surface to bedrock. The vibra-core method involved vibrating a 4-in. aluminum tube into the sediment with an attached concrete mixer. Aluminum alloys generally contain trace amounts of copper, magnesium, manganese, silicon, tin, and zinc. These amounts are generally <1 percent. The sample for analysis was taken from about a 2-in. diameter core in the center of the aluminum tube to reduce the probability of contamination of the sample. The vibra-core method tended to work well for sampling at Tar Creek because the sediment thickness was generally a few feet or less. Once the cores were removed from the subsurface, the excess core tube was cut off using a reciprocating saw and the ends covered in plastic and sealed with tape. The core was marked with the date, time, depth interval, core identification, and orientation. The last method used for gravel-bar sediment was a steel Geoprobe™ core barrel sampler with plastic liner, typically used for collecting flood-plain samples (described in methodology subsection, “Flood plain”), was hammered into the gravel-bar sediment in gravel bars with an intermediate sediment thickness of 1 to 2 ft.



Figure 3. Liquid carbon dioxide (CO_2) injection tube inserted into the hollow driving rods during the injection of liquid CO_2 .



Figure 4. Removal of the rods and sample by hand using a fence-post puller.

The depth of refusal at each borehole (traditional core, freeze core, or vibra core) location was recorded. Refusal was assumed to be the lower vertical extent of the channel sediments. A tile probe was also used to verify the depth of refusal at the borehole locations as well as at other locations within the channel to provide additional information on the thickness distribution of channel sediments. The height of the gravel bar deposits above the water level of the stream at each borehole location and tile probe location was determined by measuring the depth to water that was visible in the borehole or by measuring the height with a hand level and surveyor's rod. A complete list of tile probe locations can be found in table 3.

Flood Plain

Flood-plain cores were collected using a truck-mounted Geoprobe™ direct-push soil sampling unit. Traditional coring used a 4-ft long, 2.25-in. outside diameter core barrel to collect a 1.125-in. diameter core. After collection of each 4-ft increment, the sampler was mechanically removed from the soil. It was opened to retrieve the soil core that was inside of a clear plastic sleeve that prevented contact with the steel core barrel. Once a core was retrieved, it was measured to determine the percent recovery, which is computed by dividing the length of recovered core by the length of the run. Plastic caps were placed on both ends of the plastic sleeve and secured with tape. The plastic sleeve was labeled with the date, time, depth interval, core identification, and orientation.

A measurement was made in the open hole to verify the depth between runs and ensure that the hole did not collapse. An insert was used in the drive shoe of the core barrel to prevent soil from entering until the core barrel reached the previous sampling depth in the event that the hole collapsed. Measuring the depth of the hole ensured that the sample was representative of the target depth. This process was repeated after each run until the sampler met refusal.

Sample Processing and Analysis

The following describes the handling and processing procedures including the storage, sieving, and XRF analysis of more than 700 stream and flood-plain samples collected during this study. An XRF instrument was used to analyze all samples for the concentration of arsenic, cadmium, barium, cobalt, copper, manganese, nickel, lead, and zinc. The 2007 Thermo Niton™ XL3t 600 XRF instrument was owned by the USFWS and analyses were conducted by USFWS personnel at the USFWS office in Columbia, Missouri and the USGS office in Rolla, Missouri. The XRF instrument analyzed concentrations for these nine MVT-related metals; however, the primary metals of concern for the project were cadmium, lead, and zinc. The XRF analysis was conducted following the U.S. Environmental Protection Agency Method 6200 (EPA, 2007) which can be used in the determination of elemental concentrations in soils and must be used with confirmatory analysis using other techniques.

Table 3. Tile probe locations, depth of water from the surface, and maximum depth of refusal at each location for Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the Tri-State Mining District, 2011–12.

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; ft, foot; GB, gravel bar; WC, wetted channel; --, no data]

Tile probe identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Site identifier	Gravel bar or wetted channel	Depth of water below the surface (ft)	Maximum depth of refusal (ft)
Center Creek							
CC-A-TP-1	371002	943220	5/14/2012	C3	GB	0.0	6.3
CC-B-TP-1	370743	942258	5/15/2012	C6	GB	0.0	3.4
CC-B-TP-2	370744	942258	5/15/2012	C6	GB	0.0	2.1
CC-B-TP-3	370744	942258	5/15/2012	C6	GB	0.0	3.0
CC-C-WC-TP-1	371028	942727	6/5/2012	C5	WC	-3.8	0.2
CC-C-WC-TP-2	371028	942726	6/5/2012	C5	WC	-2.5	1.7
CC-D-TP-1	371008	943052	6/7/2012	C4	GB	0.0	2.0
CC-D-WC-TP-2	371007	943053	6/7/2012	C4	WC	-2.0	1.0
CRT-GP-1	370943	943522	11/3/2011	C1	GB	0.0	9.0
CRT-GP-10	370944	943518	11/3/2011	C1	GB	0.0	5.0
CRT-GP-11	370940	943522	11/3/2011	C1	GB	6.0	13.5
CRT-GP-2	370940	943523	11/3/2011	C1	GB	0.5	8.5
CRT-GP-3	370938	943524	11/3/2011	C1	GB	0.0	8.4
CRT-GP-4	370936	943524	11/3/2011	C1	GB	0.0	6.2
CRT-GP-5	370937	943523	11/3/2011	C1	GB	1.0	8.0
CRT-GP-6	370937	943523	11/3/2011	C1	GB	1.0	10.0
CRT-GP-7	370938	943523	11/3/2011	C1	GB	0.5	8.5
CRT-GP-8	370940	943523	11/3/2011	C1	GB	0.5	9.5
CRT-GP-9	370943	943522	11/3/2011	C2	GB	0.0	7.0
CTR-GP-13	370943	943502	11/4/2011	C2	GB	2.0	7.2
CTR-GP-14	370942	943501	11/4/2011	C1	GB	7.0	8.8
CTR-TP-1	370933	943525	11/3/2011	C1	GB	--	1.0
CTR-TP-2	370932	943529	11/3/2011	C1	GB	--	2.0
Turkey Creek							
TC-A-TP-1	370601	942845	5/15/2012	TC7	GB	1.1	1.6
TC-A-TP-2	370601	942846	5/15/2012	TC7	GB	2.6	4.0
TC-A-TP-3	370601	942844	5/15/2012	TC7	GB	0.0	1.0
TC-B-TP-1	370625	943032	5/16/2012	TC6	GB	0.1	4.6
TC-B-TP-2	370625	943031	5/16/2012	TC6	GB	0.2	2.4
TC-B-TP-3	370627	943031	5/16/2012	TC6	GB	1.3	4.4
TC-B-TP-4	370627	943030	5/16/2012	TC6	GB	0.6	5.3
TC-D-WC-TP-1	370709	943413	6/6/2012	TC4	WC	-1.7	3.0
TC-D-WC-TP-2	370708	943412	6/6/2012	TC4	WC	-1.7	2.0
TC-E-TP-2	370705	943324	6/6/2012	TC5	GB	0.0	4.7
TC-E-WC-TP-1	370703	943323	6/6/2012	TC5	WC	-2.8	1.8
TKC-TP-1	370716	943459	6/19/2012	TC3	GB	3.6	8.7
TKC-TP-2	370715	943501	6/19/2012	TC3	GB	3.3	8.2
TKC-TP-3	370716	943502	6/19/2012	TC3	GB	-1.6	3.0
TKC-TP-4	370718	943517	6/20/2012	TC1	WC	-0.3	2.9

Table 3. Tile probe locations, depth of water from the surface, and maximum depth of refusal at each location for Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the Tri-State Mining District, 2011–12.—Continued

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; ft, foot; GB, gravel bar; WC, wetted channel; --, no data]

Tile probe identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Site identifier	Gravel bar or wetted channel	Depth of water below the surface (ft)	Maximum depth of refusal (ft)
Shoal Creek							
SC-A-TP-1	365900	942628	5/17/2012	S5	GB	2.2	3.5
SC-A-TP-2	365860	942628	5/17/2012	S5	GB	0.1	3.6
SC-A-TP-3	365859	942628	5/17/2012	S5	GB	0.5	3.1
SC-A-TP-4	365859	942628	5/17/2012	S5	GB	0.0	3.2
SH-WC-TP-1	370158	943320	7/12/2012	S4	WC	-1.2	2.8
Tar Creek							
TAR-TP-7-0	365610	945127	7/14/2011	TR10	WC	-1.2	0.2
TAR-TP-7-1	365610	945127	7/14/2011	TR10	WC	-1.2	0.2
TAR-TP-7-2	365610	945127	7/14/2011	TR10	WC	-1.5	1.0
TAR-TP-7-3	365610	945127	7/14/2011	TR10	WC	-1.7	1.4
TAR-TP-7-4	365610	945127	7/14/2011	TR10	WC	-1.2	2.0
TAR-TP-7-5	365610	945127	7/14/2011	TR10	WC	-1.0	2.3
TAR-TP-7-6	365610	945127	7/14/2011	TR10	WC	-0.7	3.3
TAR-TP-7-7	365610	945127	7/14/2011	TR10	GB	0.0	3.5
TAR-TP-9-1	365626	945124	7/14/2011	TR11	GB	3.0	5.2
TAR-TP-9-2	365626	945124	7/14/2011	TR11	GB	2.0	4.7
TAR-TP-9-3	365626	945124	7/14/2011	TR11	GB	1.0	4.5
TAR-TP-9-4	365626	945124	7/14/2011	TR11	GB	0.5	4.3
TAR-TP-9-5	365626	945124	7/14/2011	TR11	WC	-0.3	3.7
TAR-TP-9-6	365626	945124	7/14/2011	TR11	WC	-0.5	3.5
TAR-TP-9-7	365626	945124	7/14/2011	TR11	WC	-0.9	3.3
TAR-TP-9-8	365626	945124	7/14/2011	TR11	WC	-1.5	2.8
TAR-TP-9-9	365626	945124	7/14/2011	TR11	WC	-1.5	2.5
TAR-TP-8-0	365630	945116	7/14/2011	TR12	GB	0.5	3.1
TAR-TP-8-1	365630	945116	7/14/2011	TR12	GB	0.5	3.0
TAR-TP-8-10	365630	945116	7/14/2011	TR12	GB	1.0	4.0
TAR-TP-8-11	365630	945116	7/14/2011	TR12	GB	1.3	4.1
TAR-TP-8-12	365630	945116	7/14/2011	TR12	GB	2.0	4.8
TAR-TP-8-2	365630	945116	7/14/2011	TR12	GB	0.1	2.8
TAR-TP-8-3	365630	945116	7/14/2011	TR12	WC	-0.1	2.4
TAR-TP-8-4	365630	945116	7/14/2011	TR12	WC	-0.2	2.8
TAR-TP-8-5	365630	945116	7/14/2011	TR12	WC	-0.2	2.9
TAR-TP-8-6	365630	945116	7/14/2011	TR12	GB	0.0	3.3
TAR-TP-8-7	365630	945116	7/14/2011	TR12	GB	0.3	3.7
TAR-TP-8-8	365630	945116	7/14/2011	TR12	GB	0.3	3.7
TAR-TP-8-9	365630	945116	7/14/2011	TR12	GB	0.3	3.7
TAR-TP-11-1	365414	945208	7/14/2011	TR2	WC	-0.5	0.2
TAR-TP-11-10	365414	945208	7/14/2011	TR2	WC	-1.2	0.8
TAR-TP-11-11	365414	945208	7/14/2011	TR2	WC	-1.5	0.4

Table 3. Tile probe locations, depth of water from the surface, and maximum depth of refusal at each location for Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the Tri-State Mining District, 2011–12.—Continued

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; ft, foot; GB, gravel bar; WC, wetted channel; --, no data]

Tile probe identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Site identifier	Gravel bar or wetted channel	Depth of water below the surface (ft)	Maximum depth of refusal (ft)
Tar Creek—Continued							
TAR-TP-11-12	365414	945208	7/14/2011	TR2	WC	-1.7	0.2
TAR-TP-11-13	365414	945208	7/14/2011	TR2	WC	-1.7	0.1
TAR-TP-11-14	365414	945208	7/14/2011	TR2	WC	-1.6	0.1
TAR-TP-11-15	365414	945208	7/14/2011	TR2	WC	-1.5	2.0
TAR-TP-11-2	365414	945208	7/14/2011	TR2	WC	-1.9	0.9
TAR-TP-11-3	365414	945208	7/14/2011	TR2	WC	-1.8	2.3
TAR-TP-11-4	365414	945208	7/14/2011	TR2	WC	-1.8	1.6
TAR-TP-11-5	365414	945208	7/14/2011	TR2	WC	-2.0	2.3
TAR-TP-11-6	365414	945208	7/14/2011	TR2	WC	-2.0	2.7
TAR-TP-11-7	365414	945208	7/14/2011	TR2	WC	-1.9	2.3
TAR-TP-11-8	365414	945208	7/14/2011	TR2	WC	-0.9	1.2
TAR-TP-11-9	365414	945208	7/14/2011	TR2	WC	-1.1	0.8
TAR-TP-5-0	365427	945212	7/13/2011	TR3	GB	0.0	0.3
TAR-TP-5-1	365427	945212	7/13/2011	TR3	WC	-0.1	0.7
TAR-TP-5-10	365427	945212	7/13/2011	TR3	WC	-1.5	0.1
TAR-TP-5-11	365427	945212	7/13/2011	TR3	WC	-1.2	0.1
TAR-TP-5-12	365427	945212	7/13/2011	TR3	WC	-1.1	0.1
TAR-TP-5-13	365427	945212	7/13/2011	TR3	WC	-0.9	0.1
TAR-TP-5-14	365427	945212	7/13/2011	TR3	WC	-0.9	0.1
TAR-TP-5-15	365427	945212	7/13/2011	TR3	WC	-0.8	0.5
TAR-TP-5-16	365427	945212	7/13/2011	TR3	WC	-0.2	3.2
TAR-TP-5-2	365427	945212	7/13/2011	TR3	WC	-0.3	0.5
TAR-TP-5-3	365427	945212	7/13/2011	TR3	WC	-0.9	0.3
TAR-TP-5-4	365427	945212	7/13/2011	TR3	WC	-1.1	0.1
TAR-TP-5-5	365427	945212	7/13/2011	TR3	WC	-1.3	0.2
TAR-TP-5-6	365427	945212	7/13/2011	TR3	WC	-1.5	0.1
TAR-TP-5-7	365427	945212	7/13/2011	TR3	WC	-1.5	0.1
TAR-TP-5-8	365427	945212	7/13/2011	TR3	WC	-1.7	0.1
TAR-TP-5-9	365427	945212	7/13/2011	TR3	WC	-1.6	0.1
TAR-TP-4-0	365438	945206	7/13/2011	TR4	GB	0.1	1.7
TAR-TP-4-1	365438	945206	7/13/2011	TR4	GB	0.2	1.9
TAR-TP-4-10	365438	945206	7/13/2011	TR4	WC	-1.2	0.1
TAR-TP-4-11	365438	945206	7/13/2011	TR4	WC	-0.3	0.1
TAR-TP-4-12	365438	945206	7/13/2011	TR4	WC	-0.3	0.7
TAR-TP-4-2	365438	945206	7/13/2011	TR4	GB	0.2	1.8
TAR-TP-4-3	365438	945206	7/13/2011	TR4	GB	0.0	1.0
TAR-TP-4-4	365438	945206	7/13/2011	TR4	WC	-0.3	1.0
TAR-TP-4-5	365438	945206	7/13/2011	TR4	WC	-0.7	1.0
TAR-TP-4-6	365438	945206	7/13/2011	TR4	WC	-1.0	1.2

Table 3. Tile probe locations, depth of water from the surface, and maximum depth of refusal at each location for Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the Tri-State Mining District, 2011–12.—Continued

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; ft, foot; GB, gravel bar; WC, wetted channel; --, no data]

Tile probe identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Site identifier	Gravel bar or wetted channel	Depth of water below the surface (ft)	Maximum depth of refusal (ft)
Tar Creek—Continued							
TAR-TP-4-7	365438	945206	7/13/2011	TR4	WC	-1.7	0.3
TAR-TP-4-8	365438	945206	7/13/2011	TR4	WC	-1.7	0.1
TAR-TP-4-9	365438	945206	7/13/2011	TR4	WC	-1.5	0.1
TAR-TP-3-0	365443	945201	7/13/2011	TR5	GB	0.7	0.7
TAR-TP-3-1	365443	945201	7/13/2011	TR5	GB	0.0	0.7
TAR-TP-3-2	365443	945201	7/13/2011	TR5	WC	-0.5	0.2
TAR-TP-3-3	365443	945201	7/13/2011	TR5	WC	-0.1	0.1
TAR-TP-3-4	365443	945201	7/13/2011	TR5	WC	-0.5	0.4
TAR-TP-3-5	365443	945201	7/13/2011	TR5	WC	-0.2	0.1
TAR-TP-3-6	365443	945201	7/13/2011	TR5	WC	-0.0	0.1
TAR-TP-3-7	365443	945201	7/13/2011	TR5	GB	0.1	0.1
TAR-TP-2-1	365453	945154	7/13/2011	TR6	WC	-0.1	0.1
TAR-TP-2-10	365453	945154	7/13/2011	TR6	WC	-0.8	0.1
TAR-TP-2-11	365453	945154	7/13/2011	TR6	WC	-0.5	0.1
TAR-TP-2-12	365453	945154	7/13/2011	TR6	WC	-0.3	0.1
TAR-TP-2-13	365453	945154	7/13/2011	TR6	WC	-0.3	0.1
TAR-TP-2-14	365453	945154	7/13/2011	TR6	WC	-0.1	0.1
TAR-TP-2-15	365453	945154	7/13/2011	TR6	WC	-0.1	0.1
TAR-TP-2-2	365453	945154	7/13/2011	TR6	GB	0.1	0.1
TAR-TP-2-3	365453	945154	7/13/2011	TR6	GB	0.3	0.7
TAR-TP-2-4	365453	945154	7/13/2011	TR6	GB	0.3	0.5
TAR-TP-2-5	365453	945154	7/13/2011	TR6	GB	0.1	0.3
TAR-TP-2-6	365453	945154	7/13/2011	TR6	WC	-0.2	0.1
TAR-TP-2-7	365453	945154	7/13/2011	TR6	WC	-0.6	0.1
TAR-TP-2-8	365453	945154	7/13/2011	TR6	WC	-0.3	0.1
TAR-TP-2-9	365453	945154	7/13/2011	TR6	WC	-0.7	0.1
TAR-TP-1-1	365500	945148	7/13/2011	TR7	WC	-0.8	0.1
TAR-TP-1-10	365500	945148	7/13/2011	TR7	WC	-0.8	0.1
TAR-TP-1-11	365500	945148	7/13/2011	TR7	WC	-1.1	0.1
TAR-TP-1-12	365500	945148	7/13/2011	TR7	WC	-1.0	0.1
TAR-TP-1-13	365500	945148	7/13/2011	TR7	WC	-1.3	0.1
TAR-TP-1-14	365500	945148	7/13/2011	TR7	WC	-1.2	0.1
TAR-TP-1-15	365500	945148	7/13/2011	TR7	WC	-1.5	0.1
TAR-TP-1-16	365500	945148	7/13/2011	TR7	WC	-1.8	0.1
TAR-TP-1-17	365500	945148	7/13/2011	TR7	WC	-2.0	0.1
TAR-TP-1-18	365500	945148	7/13/2011	TR7	WC	-1.9	0.1
TAR-TP-1-19	365500	945148	7/13/2011	TR7	WC	-2.0	0.1
TAR-TP-1-2	365500	945148	7/13/2011	TR7	WC	-0.8	0.1
TAR-TP-1-3	365500	945148	7/13/2011	TR7	WC	-0.8	0.1

Table 3. Tile probe locations, depth of water from the surface, and maximum depth of refusal at each location for Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the Tri-State Mining District, 2011–12.—Continued

[DDMMSS, degrees, minutes, seconds; mm/dd/yyyy, month, day, year; ft, foot; GB, gravel bar; WC, wetted channel; --, no data]

Tile probe identifier	Latitude (DDMMSS)	Longitude (DDMMSS)	Date (mm/dd/yyyy)	Site identifier	Gravel bar or wetted channel	Depth of water below the surface (ft)	Maximum depth of refusal (ft)
Tar Creek—Continued							
TAR-TP-1-4	365500	945148	7/13/2011	TR7	WC	-0.7	0.1
TAR-TP-1-5	365500	945148	7/13/2011	TR7	WC	-0.6	0.1
TAR-TP-1-6	365500	945148	7/13/2011	TR7	WC	-0.5	0.3
TAR-TP-1-7	365500	945148	7/13/2011	TR7	WC	-0.3	0.1
TAR-TP-1-8	365500	945148	7/13/2011	TR7	WC	-0.8	0.1
TAR-TP-1-9	365500	945148	7/13/2011	TR7	WC	-0.8	0.1
TAR-TP-10-0	365554	945124	7/14/2011	TR8	GB	0.0	2.8
TAR-TP-10-1	365554	945124	7/14/2011	TR8	GB	0.0	3.0
TAR-TP-10-10	365554	945124	7/14/2011	TR8	GB	0.5	3.3
TAR-TP-10-2	365554	945124	7/14/2011	TR8	GB	0.2	2.9
TAR-TP-10-3	365554	945124	7/14/2011	TR8	WC	-0.1	3.0
TAR-TP-10-4	365554	945124	7/14/2011	TR8	WC	-0.1	3.4
TAR-TP-10-5	365554	945124	7/14/2011	TR8	WC	-0.3	3.0
TAR-TP-10-6	365554	945124	7/14/2011	TR8	WC	-1.0	2.3
TAR-TP-10-7	365554	945124	7/14/2011	TR8	WC	-0.8	2.3
TAR-TP-10-8	365554	945124	7/14/2011	TR8	WC	-1.0	2.2
TAR-TP-10-9	365554	945124	7/14/2011	TR8	GB	0.5	3.7
TAR-TP-6-0	365605	945125	7/14/2011	TR9	WC	-0.5	3.7
TAR-TP-6-1	365605	945125	7/14/2011	TR9	WC	-0.3	4.0
TAR-TP-6-2	365605	945125	7/14/2011	TR9	WC	-0.3	0.9
TAR-TP-6-3	365605	945125	7/14/2011	TR9	WC	-0.2	3.2
TAR-TP-6-4	365605	945125	7/14/2011	TR9	GB	0.0	3.7
TAR-TP-6-5	365605	945125	7/14/2011	TR9	GB	0.2	3.4
TAR-TP-6-6	365605	945125	7/14/2011	TR9	GB	0.5	5.0
TAR-TP-6-7	365605	945125	7/14/2011	TR9	GB	1.0	5.4

Stream Channel

After collection, channel-sediment samples were allowed to air dry for several days at the USGS office in Rolla, Mo. Once the samples were dry, they were disaggregated using a stainless steel mortar and pestle. Stainless steel is an iron, chromium, and nickel alloy that may be a source of contamination into the sample for these three elements; however, nickel varied in a manner consistent with other metal contamination derived from the sediment, whereas contamination from the probe would tend not to vary from sample to sample. In addition, sediment sampled using other hardware also contained these elements. Vibra-core samples were opened to expose the sediment and allowed to air dry. Samples were collected from the vibra-core tube by scooping the sediment from each 1-ft interval using a plastic scoop, placed in plastic

bags, and weighed. The weights were generally greater than 200 grams (g), and these samples did not require disaggregation. All samples were then sieved using a single 2-millimeter (mm) mesh-size stainless steel sieve (U.S. Number 10). This divided the sample into two size fractions, <2 mm and >2 mm. The two fractions were placed in separate plastic bags, labeled, and weighed. The <2-mm size fraction of each sample was analyzed three times using the XRF instrument. Before each individual scan, the bag was thoroughly mixed to ensure a representative scan. Each analysis was 60 seconds in duration, which was sufficient time to determine concentrations of the MVT-related metals (arsenic, cadmium, barium, cobalt, copper, manganese, nickel, lead, and zinc). The arithmetic mean of the three individual analyses was reported as the concentration in the sample for each constituent.

Flood Plain

The plastic sleeves containing flood-plain cores were cut lengthwise in the laboratory with a special core cutting knife to expose an area of the core about 1 in. wide. The outside of the core is typically disturbed during the coring process as it slides against the steel cutting head and into the core barrel. A steel knife was then used to remove a 0.25-in. thick section to expose the undisturbed core (fig. 5). This created a flat surface for the XRF that was relatively undisturbed and would be representative of the metal concentrations at that location. The core recovery was measured and the depths were marked to guide the XRF analysis. Then the core was cut into 2-ft lengths and placed in core boxes to air dry. Metal concentrations were determined using an XRF placed on the flat surface of the core previously exposed with the knife. Each 1-ft section of core was generally analyzed three times by USFWS using the XRF at the USGS office in Rolla, Mo. The original protocol was to collect XRF measurements using a 60-second analysis at three equally spaced intervals within each foot of the core and then compute the mean of these three measurements. For example, the mean of measurements at 0.25, 0.50, and 0.75 ft would represent the metal concentrations in the 0- to 1-ft depth interval and was assigned the mean depth of 0.50 ft. After several days of XRF analysis, it was determined that metal concentrations in flood-plain cores tended to be largest in the upper few feet then decreased to much smaller concentrations throughout most of the lower sections of the cores. To expedite the analyses of hundreds of feet of core, three analyses were made each foot for the upper 3 to 5 feet of each core, and at depths greater than 5 ft, a single analysis was first done at the even foot mark. As long as the single analysis at the even foot mark indicated relatively low concentrations of zinc (less than about

one-half the CPEC), analysis proceeded at 1-ft intervals down the core. If, for example, the single analysis indicated a zinc concentration greater than one-half the CPEC at 6 ft, then three analyses at the 6.25-, 6.50-, and 6.75-ft intervals were done and the mean calculated to represent the metals concentrations in the 6- to 7-ft intervals. Such a mean concentration was reported for the assigned mean depth of 6.5 ft.

Additional measures were taken during the analysis of the 379 core sections to expedite the results for the flood-plain cores. A 60-second analysis using the XRF is required to determine the concentrations for arsenic, cadmium, barium, cobalt, copper, manganese, nickel, lead, and zinc. A 30-second analysis can be used determine the concentrations of the same metals with the exception of cadmium and barium. During the analysis of the flood-plain cores, the analysis time was reduced from 60 seconds to 30 seconds for 211 core sections (samples).

Laboratory Confirmation Samples

Eighty-five stream channel and flood-plain sediment samples were split and submitted for laboratory analysis to evaluate the accuracy of the concentrations obtained by the XRF instrument which is required when using EPA method 6200 (EPA, 2007). Samples sent to the laboratory were selected to ensure spatial coverage of each stream segment and to represent a range of lead and zinc concentrations. Of the 355 stream channel samples, 76 were sent for laboratory confirmation. Nine samples from the 34 flood-plain borings (379 total samples) were selected for laboratory confirmation. Most of the flood-plain samples selected were within the top few feet of the boreholes where the XRF detected larger concentrations of lead and zinc.

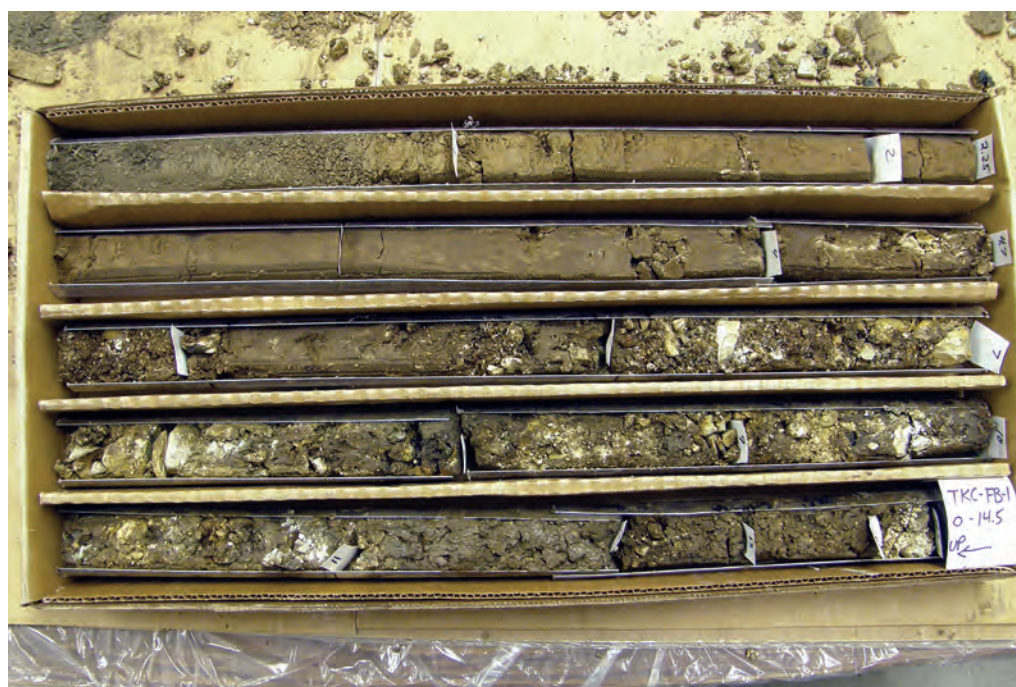


Figure 5. Flood-plain core that has been prepared for analysis with the x-ray fluorescence instrument.

Laboratory splits from the <2-mm size fraction of stream channel samples that had been previously prepared and analyzed by the XRF were prepared by removing 3 to 5 g of sample from the original sample using a plastic spatula and placing it in a separate bag. Before the split sample was collected, the sample bag was mixed by turning the sample bag over 10 to 15 times then opening the bag and passing the spatula through the entire thickness of the mixed sample. Only one to three passes through the original sample were required to obtain the split sample.

The laboratory confirmatory samples for the flood-plain core samples required additional processing because the original XRF analyses were made on the intact core. The 1-ft interval selected for laboratory confirmation was removed from the plastic liner, disaggregated and sieved using a 2-mm stainless steel sieve, and the material finer than 2 mm was weighed before placing in a plastic bag. The laboratory confirmatory samples were then split from the bagged material in the same manner as described above for stream channel samples. Before submitting the split samples to the laboratory, each split sample (stream channel or flood-plain core) was analyzed again using the XRF to provide a more direct comparison between the XRF and laboratory analytical results.

Split samples were shipped to the USGS Central Mineral and Environmental Resources Science Center (CMERSC) laboratory in Denver, Colorado. The laboratory analyzed the split samples using inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) methods on samples that were completely digested (Taggart, 2002). The laboratory reported concentrations for 43 constituents, 9 of which were also analyzed by XRF for this study.

Concentration of metals in a sample detected through laboratory analysis through the complete digestion of the sample does not completely reflect the typical digestion process in aquatic organisms or the true bioavailability of the metals found in the sediment. The strength of stomach acids tend to vary based on diet. Beasley and others (2015) have shown that stomach acid pH lowers with the risk of food-borne pathogen exposure. Scavengers tend to have lower stomach pH than carnivores, and carnivores tend to have lower stomach acid pH than herbivores. Lower stomach acid pH can result in greater metal bioavailability by increasing metal solubility (Luoma, 1989). Beasley and others (2015) reported scavenger birds with stomach acid pH ranging from 1.1 to 1.7. There are also many other factors that affect the bioavailability of metals, including metal concentrations, solute metal speciation, metal concentration in food, metal partitioning among ligands within food, influence of other cations, temperature, and redox potential (Luoma, 1983).

Estimation of the Volume of Contaminated Gravel Bar Deposits

Sullivan and others (1987) indicate that most of the readily available sediment is found in gravel bars for large to moderate streams and characterization of gravel-bar sediments in this study focused on gravel bars with some additional samples collected from the wetted channel. Estimates of the volume of contaminated gravel bar deposits were computed relative to two benchmarks of contamination (that is, for both PEC values [CPEC and TPEC]) because of the importance of such information to the USFWS and other natural resource agencies of the TSMD for assessing damage to the ecosystem and evaluating restoration alternatives. The maximum depth of contamination was determined as the maximum depth where either the lead or zinc concentration exceeded the respective PEC values. The data files showing maximum sample depth at each location are listed in the Stream channel sediment samples dataset (Smith, 2016). Cadmium concentrations were not used to determine contaminated sediment depths because the limit of detection (LOD) for cadmium from the XRF analysis (12 mg/kg) was larger than the cadmium PECs: CPEC (4.98 mg/kg) and TPEC (11.1 mg/kg). Thus, no sample analyzed by XRF could be determined with certainty from any depth to have a cadmium concentration below either PEC value.

Occasionally, the concentration of lead or zinc would exceed either the CPEC or the TPEC at one depth, but not exceed either at the next depth (or several subsequent depths), and then would exceed again at an even greater depth. For example, the concentration of lead exceeds both the CPEC and the TPEC at 4–5 ft. The concentration of lead then does not exceed either the CPEC or the TPEC at 5–8 ft but then does exceed the CPEC and the TPEC at 8–9 ft. The maximum depth of contamination was reported as the deepest CPEC or TPEC exceedance in this case 9 ft, and it was assumed that the distance between the land surface and the maximum contaminated depth represented the depth of excavation required to remediate the contaminated sediment, despite the fact that part or all of the sediment above may not actually have been classified as contaminated per the CPEC or TPEC.

Two measures were required to estimate the volume of contaminated sediment in Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the reaches studied: (1) the depth of contaminated sediment in the study reach and (2) the areal extent of contaminated sediment in the study reach. Estimates of the volume of contaminated sediment along the Spring River could not be made because of the small number of locations sampled. To determine the depth of contaminated sediment in the study reach, a six-step procedure was used:

- D1. Determine the maximum depth for each borehole that exceeded either the CPEC or the TPEC, or both, for lead and zinc (Smith, 2016; Stream channel sediment samples; table 1)
- D2. Express the maximum depth (from D1 above) of contamination (relative to each PEC type) as a proportion

of the investigation depth in each borehole (maximum contaminated sediment depth in core divided by total depth represented by recovered core), expressed as a percentage. The investigation sample depth at each location is listed in the Flood-plain cores dataset (Smith, 2016).

- D3. Determine the mean depth of the sediment at each individual site (mean value of borehole refusal depths and tile probe refusal depths for each site; table 4)
- D4. Determine the mean maximum proportional depth of contamination for each site (compute the mean of D2 above), expressed as a percentage, for the CPEC and TPEC (table 4)
- D5. Determine the mean maximum depth of sediment exceeding the CPEC or TPEC for each site (multiply mean maximum proportional depth of contamination [from D4 above] by the mean depth of sediment in each gravel bar [from D3 above]) (table 4)
- D6. Determine the overall mean of the site-mean depths of contaminated sediment for each study site (tables 4 and 5, mean value for stream)

To determine the areal extent of contaminated sediment sampled in the study reach, a two-step procedure was followed:

- A1. Determine the planimetric area of each gravel bar within the studied reach. Google Earth™ aerial georeferenced orthophotography from 2012 (Center Creek, Turkey Creek, and Shoal Creek) and 2015 (Tar Creek) was used to identify and delineate the gravel bars that were digitized at the nominal scale of 1:2000 into a geographic information system (GIS). Comparison of more recent aerial photographs to 1930s aerial photographs also was done to identify persistent bars, areas of stream channel migration, and bars that were partially vegetated on the more recent photographs. For example, a gravel bar may experience recent growth of vegetation, which can hide the overall size of the bar. This can be identified using older aerial photography.
- A2. Determine the total area of contaminated sediment by summing the areas of each individual gravel bar for the selected study reach of each stream (fig. 1). There were sites located outside of the reaches selected for the estimation of the volume of contaminated sediment (site C6 in Center Creek and site S5 in Shoal Creek; fig. 1). These sites had distances of 7.5 mi (Center Creek) and 10 mi (Shoal Creek) between these sites and the closest downstream site so volume estimates were not calculated for these reaches.

The volume of contaminated gravel bar sediment along the sampled reaches of Center Creek, Turkey Creek, Shoal Creek, and Tar Creek was estimated by multiplying the total areal extent of gravel bars along each studied reach by the

mean maximum depth of contaminated sediment in gravel bars along that studied reach that exceeded the CPEC or the TPEC (D6 times A2 above; table 4).

Estimated volumes of sediment in gravel bars in the study reaches exceeding the CPEC and TPEC presented in this report should be considered minimum volumes because they are only based on lead and zinc concentrations in the sampled gravel bars. Because the XRF LOD was greater than the PECs for some other constituents, particularly cadmium and nickel concentrations, other constituents could have exceeded the PECs, which could potentially have changed the maximum depths of contaminated sediment that were determined from the lead and zinc concentrations. In addition, there are many other gravel bars within the study reaches that were not sampled, in addition to sediment beneath other channel features such as in pools and riffles, which were not sufficiently characterized. Finally, the estimated volume of contaminated sediment is only for the 37.6 mi of selected reaches along Center Creek, Turkey Creek, Shoal Creek, and Tar Creek that were examined in this study. The total length of these streams that are contaminated by mine waste is approximately 49 mi (MacDonald and others, 2010).

Quality Control and Quality Assurance

To efficiently analyze the large number of samples collected (357 stream channel samples [Smith, 2016; Stream channel sediment samples]; 379 flood-plain samples [Smith, 2016; Flood-plain cores]) in this study, all samples were analyzed using the XRF. Although samples were collected during 2011 to 2012, samples were analyzed during five periods between October 2012 and June 2014 as samples were processed and the XRF operated by the USFWS became available. Several quality control and quality assurance procedures were implemented to ensure the quality of the data acquired using the XRF. A series of standards and blanks were analyzed at the beginning, end, and several times throughout the day when environmental samples were analyzed. In addition to standards, triplicate and septuplet analyses of the selected flood-plain cores were done during the analysis. These were replicate analyses (3 or 7) at the same location in the core without moving the XRF instrument. Analyzing the same location of the core multiple times determines the variability in precision of the XRF on samples that are often more heterogeneous in both grain size and metals distribution than prepared standards. In addition, split samples from 85 channel sediment and flood-plain samples were analyzed by the XRF instrument and also analyzed by the CMERSC laboratory to allow comparison of the XRF results to the laboratory results.

Data Analysis Methods

Data analysis was completed using a combination of graphical methods and basic statistics to interpret and to better

24 Occurrence, Distribution, and Volume of Metals-Contaminated Sediment of Selected Streams, Tri-State Mining District

Table 4. Mean maximum proportional depth of sediment exceeding the consensus probable effects concentrations and the Tri-State Mining District specific probable effects concentrations, and mean total depth of boreholes and tile probes for each site, Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and Spring River in the Tri-State Mining District, 2011–12.

[CPEC, consensus probable effects concentration (MacDonald and others, 2000); TPEC, Tri-State Mining District specific probable effects concentration (Ingersoll and others, 2009); ft, foot; --, not applicable]

Site identifier	Maximum proportional depth exceeding the CPEC	Maximum proportional depth exceeding the TPEC	Average total depth of coring and tile probes from site (ft)	Average depth of sediment exceeding the CPEC (ft)	Average depth of sediment exceeding the TPEC (ft)
Center Creek					
C1	98.0	58.8	7.3	7.1	4.3
C2	100.0	96.9	3.3	3.3	3.2
C3	100.0	100.0	5.4	5.4	5.4
C4	100.0	100.0	2.2	2.2	2.2
C5	100.0	100.0	1.7	1.7	1.7
C6	0.0	0.0	2.5	0.0	0.0
Mean, excluding gravel bar C6	--	--	--	4.0	3.4
Turkey Creek					
TC1	100.0	100.0	4.2	4.2	4.2
TC2	100.0	100.0	11.5	11.5	11.5
TC3	85.9	82.2	7.5	6.4	6.1
TC4	100.0	100.0	4.7	4.7	4.7
TC5	83.1	83.1	4.1	3.4	3.4
TC6	87.5	87.5	2.6	2.2	2.2
TC7	100.0	0.0	1.5	1.5	0.0
Mean	--	--	--	4.9	4.6
Shoal Creek					
S1	100.0	0.0	6.5	6.5	0.0
S2	50.3	30.8	10.5	5.3	3.2
S3	100.0	0.0	3.6	3.6	0.0
S4	54.6	0.0	4.7	2.6	0.0
S5	78.5	0.0	3.1	2.5	0.0
Mean, excluding gravel bar S5	--	--	--	4.5	0.8
Tar Creek					
TR1	100.0	100.0	0.2	0.2	0.2
TR2	81.3	81.3	1.4	1.1	1.1
TR3	100.0	0.0	0.4	0.4	0.0
TR4	100.0	100.0	0.9	0.9	0.9
TR5	100.0	100.0	0.7	0.7	0.7
TR6	100.0	100.0	0.2	0.2	0.2
TR7	100.0	100.0	0.1	0.1	0.1
TR8	34.5	34.5	2.9	1.0	1.0
TR9	64.3	64.3	3.6	2.3	2.3
TR10	30.3	30.0	1.9	0.6	0.6
TR11	79.5	74.6	4.4	3.6	3.5

Table 4. Mean maximum proportional depth of sediment exceeding the consensus probable effects concentrations and the Tri-State Mining District specific probable effects concentrations, and mean total depth of boreholes and tile probes for each site, Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and Spring River in the Tri-State Mining District, 2011–12.—Continued

[CPEC, consensus probable effects concentration (MacDonald and others, 2000); TPEC, Tri-State Mining District specific probable effects concentration (Ingersoll and others, 2009); ft, foot; --, not applicable]

Site identifier	Maximum proportional depth exceeding the CPEC	Maximum proportional depth exceeding the TPEC	Average total depth of coring and tile probes from site (ft)	Average depth of sediment exceeding the CPEC (ft)	Average depth of sediment exceeding the TPEC (ft)
Tar Creek —Continued					
TR12	65.2	65.2	3.4	2.2	2.2
Mean	--	--	--	1.1	1.1
Spring River					
SR1	76.5	0.0	16.0	12.3	0.0
SR2	100.0	59.7	6.7	6.7	4.0
Mean	--	--	--	9.5	2.0

understand the data. Graphical examination included bar graphs, scatterplots, and boxplots. Basic statistics given in this report include the number of cases, means, standard deviations, lower and upper 95th percentiles, and RSDs. Medians and upper and lower quartiles were displayed graphically in boxplots.

Left censored data were common in the XRF results due to the high LOD of the XRF compared to laboratory results. The mean was calculated from the results of three individual scans using the XRF for each sample. Constituents for a sample that were below the LOD for the XRF for all three scans were reported as the LOD value. The LOD for the constituents of interest in this report are 11 mg/kg for arsenic, 12 mg/kg for cadmium, 100 mg/kg for barium, 260 mg/kg for cobalt, 35 mg/kg for copper, 85 mg/kg for manganese, 65 mg/kg for nickel, 13 mg/kg for lead, and 25 mg/kg for zinc. If one or two of the three scans were below the LOD then that particular LOD value would be used to calculate the mean. For example, the mean of three individual scans of a sediment sample with reported copper concentrations of 38 mg/kg, 34 mg/kg, and “< LOD” (less than the LOD) would be the mean of 38, 35, and 35 mg/kg. Means that were less than their respective LOD were reported as less than their respective LOD using the less than sign. For, example a sample with three individual scans that reported all concentrations less than the LOD, the reported concentration in the tables would be <35 mg/kg. Concentrations below the LOD were not used to calculate RPDs and were not used in any scatterplots. The LOD values were used only in the bar charts showing the vertical concentration of lead and zinc and in the creation of boxplots because the distribution shown by boxplots is better represented by using the reported values and concentrations below the LOD. The distribution of data would be skewed if LODs were not used.

Standard Reference Material

Standards included National Institute of Standards and Technology (NIST) high standard [standard reference material (SRM) 2710a Montana I Soil], NIST medium standard (SRM 2711a Montana I Soil), NCS DC 73308 standard, and the U.S. Environmental Protection Agency Resource Conservation and Recovery Act (RCRA) standard. Standards were used to ensure the instrument was within daily calibration requirements and to assess the general accuracy and precision of the XRF measurements on known materials. The overall mean concentration, standard deviation, upper and lower 95th percentiles, and percent difference were calculated for six MVT-related metals measured by XRF in each standard and compared to the standard’s most probable value (MPV; table 6). Accuracy of the XRF allowed a percent difference within 30 percent of the standard’s MPV concentration of target elements to be the data quality objective (DQO) for this project.

The precision of the XRF measurements was assessed by calculating the relative standard deviation (RSD) of XRF measurements for each of the standards. The RSD was calculated for target elements in each standard by dividing the standard deviation of the XRF results by the mean XRF result for each standard. The DQO for the precision of XRF measurements for this study was that the RSD would be <20 percent for all target elements measured in the standard materials. The standards were also used to ensure that the XRF was calibrated properly on a daily basis before and during the analysis of environmental samples. The concentrations of the measured target elements were to be within plus or minus 20 percent of the standard’s MPV or the instrument would be recalibrated.

Mean concentrations of arsenic, lead, manganese, and zinc from more than 30 analyses of standard reference materials by the XRF attained the accuracy goal of being within

Table 5. Digitized gravel bar area, creek or river total drainage area, hydrologic unit code, mean thickness of sediments exceeding the consensus probable effects concentrations and the Tri-State Mining District specific probable effects concentration, and estimated total volume of sediment with concentrations of lead or zinc that exceed the consensus probable effects concentration and the Tri-State Mining District specific probable effects concentration for Center Creek, Turkey Creek, Shoal Creek, and Tar Creek in the in the Tri-State Mining District, 2011–12.

[ft², square foot; mi, mile; mi², square mile; USGS, U.S. Geological Survey; CPEC, consensus probable effects concentration (MacDonald and others, 2000); ft, foot; TPEC, Tri-State Mining District specific probable effects concentration (Ingersoll and others, 2009); yd³, cubic yard; --, data not calculated]

Creek or river name	Area of all digitized gravel bars along reach from mouth to most upstream site ^a used in volume estimate (ft ²)	Area of all digitized gravel bars along reach from mouth to most upstream site ^a used in volume estimate (acre)	Length of stream used for volume estimate ^b (mi)	Length of stream studied ^c (mi)	Drainage area (mi ²)	USGS hydrologic unit code	Average maximum depth to sediment exceeding the CPEC (ft)	Average maximum depth to sediment exceeding the TPEC (ft)	Minimum volume of sediment exceeding CPEC that could be excavated (yd ³)	Minimum volume of sediment exceeding TPEC that could be excavated (yd ³)
Center Creek	916,000	21.0	11.1	18.6	300	1107020706	4.0	3.4	136,000	115,000
Turkey Creek	632,000	14.5	10.1	10.1	46	110702070901	4.9	4.6	115,000	108,000
Shoal Creek	146,000	3.4	8.5	18.5	251	1107020708	4.5	0.8	24,000	4,000
Tar Creek	230,000	5.28	7.4	7.4	53	110702060106	1.1	1.1	9,000	9,000
Spring River	--	--	--	--	2,590	11070207	9.5	2.0	--	--
Total	1,924,000	--	37.1	54.6	--	--	--	--	284,000	236,000

^aThe farthest upstream site used in the volume estimate was not the farthest upstream site in the length of the studied stream due to stretches of stream (Center Creek and Shoal Creek) with little or no data.

^bThe length of the stream used in the volume estimate was shorter than the overall length of the stream studied due to stretches of stream (Center Creek and Shoal Creek) with little or no data.

^cThe overall length of the studied stream reach from the farthest upstream site to its mouth at the Spring River (Center Creek, Turkey Creek, and Shoal Creek) or Neosho River (Tar Creek).

Table 6. Results of analyses of standard reference materials by the x-ray fluorescence unit.

[mg/kg; milligram per kilogram; n, sample size; XRF, x-ray fluorescence; LCL, lower 95-percent confidence limit; UCL, upper 95-percent confidence limit; RSD, relative standard deviation; NIST, National Institute of Standards and Technology; NCS, NCS Testing Technology Co., Ltd.; <, less than; --, not calculated; RCRA, Resource Conservation and Recovery Act; shaded value indicates value outside project goal of mean XRF value more than 30 percent different from standard or precision as measured by RSD of less than 20 percent; analysis was conducted using an x-ray fluorescence instrument owned and operated by the U.S. Fish and Wildlife Service personnel following the U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office]

Constituent	Standard most probable value (mg/kg)	n	Number of left censored values ^a	XRF mean (mg/kg)	XRF standard deviation (mg/kg)	LCL (mg/kg)	UCL (mg/kg)	Percent difference between XRF mean and standard (mg/kg)	RSD (percent)	Overall average RSD ^b (percent)
NIST high standard										
Arsenic	626	33	0	722	48.95	704.7	739.4	15.3	6.78	14.2
Barium	707	32	0	615.2	53.81	595.8	634.6	-13.0	8.75	16.8
Cadmium	21.8	32	0	29	6.09	26.8	31.2	33.0	21.00	14.1
Lead	5,532	33	0	5,430	203.8	5,358	5,502	-1.8	3.75	8.9
Manganese	10,100	33	0	9,887	588.2	9,678	10,096	-2.1	5.95	8.6
Zinc	6,952	33	0	6,885	291.2	6,781	6,988	-1.0	4.23	11.3
NIST medium standard										
Arsenic	105	31	1	104.5	24.08	95.71	113.4	-0.5	23.0	--
Barium	726	30	0	601.7	46.599	584.3	619.1	-17.1	7.74	--
Cadmium	41.7	30	0	45.96	7.7	43.09	48.84	10.2	16.8	--
Lead	1,162	31	0	1,111	39.4	1,097	1,126	-4.4	3.55	--
Manganese	638	31	0	501.9	56.77	481.1	522.7	-21.3	11.3	--
Zinc	350.4	31	0	304.7	22.6	296.4	313	-13.0	7.42	--
NCS DC 73308 standard										
Arsenic	25	39	1	21.04	3.86	19.79	22.29	-15.8	18.3	--
Barium	42	38	7	190	78.7	164.2	215.9	352.4	41.4	--
Cadmium	1.1	38	35	<11.6	1.88	<11.01	<12.3	--	--	--
Lead	27	39	3	23.3	5.31	21.53	24.97	-13.7	22.8	--
Manganese	1,010	39	0	722.2	74.07	698.2	746.2	-28.5	10.26	--
Zinc	46	39	0	39.05	7.04	36.77	41.33	-15.1	18.0	--
RCRA standard										
Arsenic	500	27	0	469	39.8	453.3	484.8	-6.2	8.49	--
Barium	--	27	0	826	75.3	796.2	855.8	--	9.12	--
Cadmium	500	26	0	541.6	25.4	531.3	551.8	8.3	4.69	--
Lead	500	27	0	485.5	26.5	474.9	495.9	-2.9	5.46	--
Manganese	--	26	0	590.2	41	573.6	606.8	--	6.95	--
Zinc	--	27	0	74.7	11.5	70.1	79.3	--	15.4	--

^aNumber of samples with result less than the XRF limit of detection (LOD).

^bAverage relative percent difference (RPD) of all four check standards where the RPD for each standard is the XRF standard deviation divided by the average value reported by the XRF.

30 percent of the MPV for all standards (table 6). The mean RSD for these four metals averaged over the several standards was <15 percent and within the DQO for precision of 20 percent; however, individual RSD values for arsenic in the NIST medium standard (23.0 percent), barium in the NCS DC 73308 standard (41.4 percent), cadmium in the NIST high standard (21.0 percent), and lead in the NCS DC 77308 standard (22.8 percent) were slightly larger than the DQO for precision (table 6). The XRF results for lead, manganese, and zinc tended to be biased slightly low compared to the standard MPVs (table 6). The bias generally increased with decreasing concentration in the standards (fig. 6; table 6). Results for lead concentrations were most accurate with the percent difference

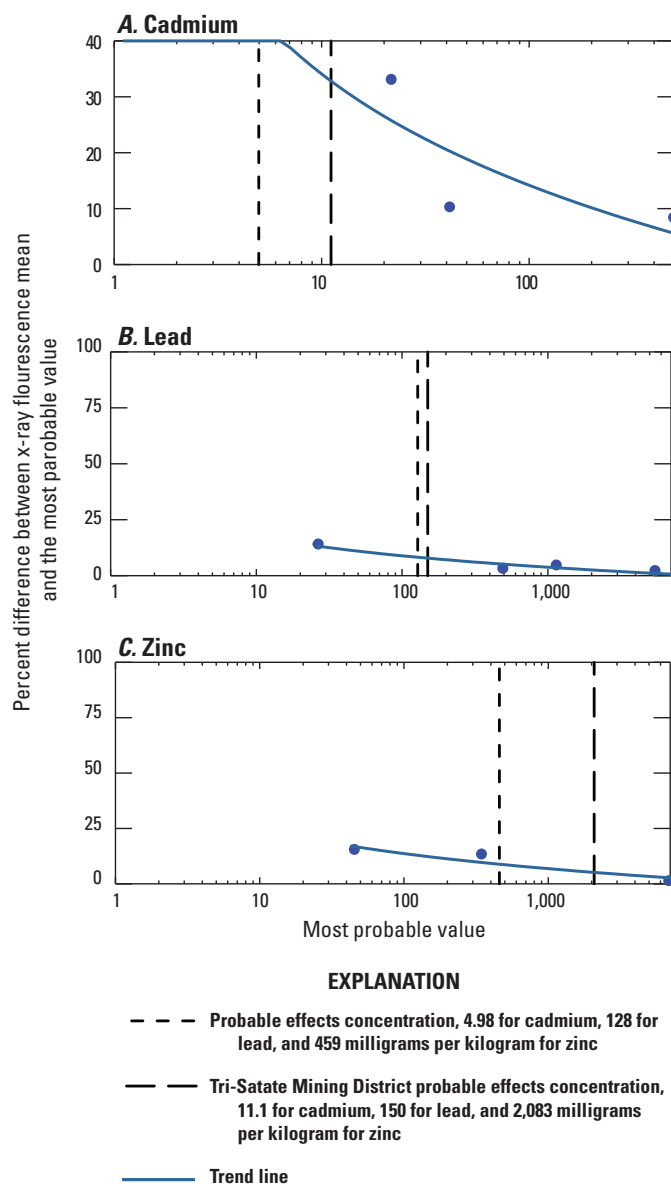


Figure 6. Relations of percent difference between mean concentration by x-ray fluorescence with the most-probable-value concentrations of A, cadmium; B, lead; and C, zinc in standard reference materials.

of the XRF mean from the MPV in the standards ranging from -13.7 to -1.8 percent, followed by zinc (-15.1 to -1.0 percent), and manganese (-28.5 to -2.1 percent). For arsenic, the pattern was somewhat different, as the bias of the XRF mean concentration was of similar magnitude for the two standards with minimum and maximum MPVs (associated biases of -15.8 to 15.3 percent, respectively), and a much smaller bias (-0.5 percent) for the NIST medium standard. The standard MPV in relation to the upper and lower 95th percentile is also an indicator of non-zero bias. MPVs that are higher than the upper 95th percentile indicate a positive bias (XRF results that are higher than the laboratory results), whereas MPVs that are lower than the lower 95th percentile indicate a negative bias (XRF results that are lower than the laboratory results). All standard MPVs fell below the upper 95th percentile with the exception of all cadmium MPVs and the arsenic MPV for the NIST high standard. All standard MPVs fell below the lower 95th percentile with the exception of all cadmium MPVs and the arsenic and zinc MPVs for the NIST high standard. No time trends were noted in XRF results of standards based on qualitative inspection of the data.

Based on analysis of the standards, concentrations of barium and cadmium reported by the XRF are less accurate than those reported for arsenic, lead, manganese, and zinc. The mean cadmium concentrations reported by the XRF in the NIST high standard exceeded the 30-percent accuracy goal for the project and the NCS DC 73308 standard was below the LOD for XRF; however, these were for the standards with the smallest MPV values (table 6). The mean cadmium concentration of 29 mg/kg reported by the XRF for the NIST high standard was about 33 percent larger than the MPV of 21.8 mg/kg. The mean measured cadmium concentrations in the NIST medium standard (MPV of 41.7 mg/kg) and RCRA standard (MPV of 500 mg/kg) were within 11 percent of the MPVs indicating the XRF can reliably determine cadmium concentrations in the 41.7 to 500 mg/kg range in environmental samples but the XRF could attain the reliability levels corresponding to the project DQOs in concentrations less than about 41 mg/kg. The mean barium concentration of 190 mg/kg reported by the XRF for the NCS DC 77308 standard was more than 350 percent larger than the MPV of 42 mg/kg, and the 41.4 percent RSD for barium in this standard was the poorest precision result for the XRF among the target elements (table 6). The mean barium concentrations reported by the XRF in the NIST medium and NIST high standards (MPVs of 726 and 707 mg/kg, respectively) were more reliable, within 18 percent of MPVs; moreover, the associated RSDs were <10 percent, whereas the mean barium concentrations reported by the XRF in the NCS DC 73308 standard (MPV of 42 mg/kg) were greater than 350 percent and did not attain the reliability levels corresponding to the project DQOs.

Environmental samples were not excluded based on the range of concentrations and the corresponding XRF reliability for reporting a specific constituent's concentration at those ranges. The statistics calculated on the standard reference material is important for stakeholders when interpreting the data.

Blanks

A total of 45 silica sand blanks were analyzed during XRF analysis of environmental samples for the project. The XRF did not report concentrations in these samples of arsenic, lead, or manganese above the XRF LOD for these metals of 11 mg/kg, 13 mg/kg, and 85 mg/kg, respectively. The XRF did report a zinc concentration (17.3 mg/kg) in one sample that was below its LOD of 25 mg/kg for zinc. The XRF reported cadmium concentrations (14.8 to 18.7 mg/kg) greater than its LOD of 12 mg/kg in 6 of 43 blank samples. This indicates that the XRF does tend to have a positive bias in the reported cadmium concentrations compared to the standard's MPV, which can also be seen in the analysis of the standards (table 6). The LOD for the non-target metals cobalt (260 mg/kg) and nickel (65 mg/kg) were relatively large compared to other metals reported by the XRF, and the XRF did not report concentrations of these constituents.

Replicate X-Ray Fluorescence Analyses

Because flood-plain core samples were analyzed intact and not disaggregated, examination of the precision of the XRF results on these samples was done using 24 sets of triplicate (19) or septuplet (5) analyses of flood-plain core samples. These were replicate analyses (3 or 7) at the same location of the core without moving the XRF instrument. Metal concentrations should be similar for each replicate analysis, limited by the precision of the XRF instrument, when analyzing the same location of the core. The mean, standard deviation, and RSD were calculated for each set of analyses. The project DQO for precision of the XRF used with flood-plain sediment was to attain an RSD of <30 percent of the calculated mean measured concentration for groups of triplicate and septuplet analyses.

Results of the triplicate and septuplet replicate analyses indicate that the XRF results for intact flood-plain core generally were less than or near the DQO of 30 percent for the RSD. Metals with mean RSDs <30 percent were arsenic (27), barium (6), lead (25), and zinc (16; table 7). Manganese generally exceeded the DQO for precision with a mean RSD of 34.3 percent. Fourteen out of 24 samples were not scanned with the required length of time for measuring the concentration of barium. Standard deviations and RSDs were not calculated for samples with no measured values for barium and for samples that were below the LOD. Another measure of precision is the standard deviation of the replicate analyses. The mean standard deviation for arsenic was 10 mg/kg, barium was 28 mg/kg, lead was 28 mg/kg, and zinc was 33 mg/kg (table 7), and all were relatively low compared to manganese (204 mg/kg). The trimmed mean standard deviation for lead the outlier of 495 mg/kg (table 7) was 7.1 mg/kg, which indicates very high precision for lead. There was very little data to examine the precision for cobalt, copper, and nickel because of their low concentrations in the samples.

Laboratory Confirmation Samples

The results of the XRF instrument's analysis of 85 split samples (76 stream channel samples and 9 flood-plain samples) collected during this study were compared to the CMERSC laboratory results as a quality check on the accuracy of the XRF results and to determine the comparability of XRF to laboratory results. The laboratory results are listed in the Laboratory confirmation data (Smith, 2016). The split samples were analyzed by the XRF before submission to the CMERSC laboratory to provide a direct comparison between the XRF values and the laboratory values of the same sample. This provided three datasets for comparison: the results of the XRF instrument's analysis of the original sample, the results of XRF instrument's analysis of the split sample for the laboratory, and the laboratory results of the split sample.

Overall, the XRF results from analysis of the original sample for the target elements lead and zinc compared favorably to laboratory results, with linear regression coefficient of determination 0.87 for lead and 0.78 for zinc (fig. 7D and 7G). The results for the target element cadmium were less favorable with a coefficient of determination of 0.15 (fig. 7A) and the residuals are strongly biased towards one side of the line and no inferences should be made using the cadmium regression model. The XRF results of the original sample compared more favorably to the XRF results of the subsample with linear regression correlation coefficients of 0.84 for lead, 0.80 for zinc, and 0.76 for cadmium (fig. 7F, 7I, and 7C), indicating that compositing 1 to 3 subsamples to prepare the split sample was adequate for representativeness of the laboratory split samples. Concentrations of arsenic, cobalt, copper, and nickel in the split samples were generally below the LOD of the XRF instrument.

To compare the results between analytical methods, the relative percent difference (RPD) was computed as the absolute value of the difference between the two values being compared divided by the mean of the two values being compared, expressed as a percentage. In the computation of the RPD values, the LOD level was substituted for samples where the value determined by the XRF was less than the LOD. Comparisons were made using (1) the RPD between the XRF result for the original sample and the laboratory result for the split sample (RPD-1), and (2) the RPD between the XRF result for the split sample and the laboratory result for the same split sample (RPD-2; table 8 at the back of this report). For the three metals of most concern for this study, the mean RPD values for lead (22–23 percent) was less than the project DQO for accuracy of 30 percent, and the mean RPD values for cadmium and zinc (58–67 percent and 38–39 percent, respectively) exceeded the project DQO (table 8).

Excluding samples where the cadmium concentration reported by the laboratory was less than the LOD of the XRF, there is a tendency for the RPD-1 and RPD-2 values for cadmium, lead, and zinc to increase with increasing concentration reported by the laboratory (fig. 8). The cause for this trend is not known but could be related to heterogeneity in the

Table 7. Statistical summary of triplicate and septuplet x-ray fluorescence scans of intact flood-plain cores in the Tri-State Lead and Zinc Mining District, 2011–12.

[ft, foot; <, less than; --, not calculated (samples were not scanned for sufficient time for the detection of constituent); cells with gray shading exceeded the project goal of 30 percent for relative standard deviation; all concentrations are in milligrams per kilogram; analysis was conducted using an x-ray fluorescence instrument owned and operated by the U.S. Fish and Wildlife Service personnel following the U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office]

Coring or sample identifier	Depth (ft)	Number of replicate measurements	Arithmetic mean					Standard deviation					Relative standard deviation				
			Arsenic	Barium	Lead	Manganese	Zinc	Arsenic	Barium	Lead	Manganese	Zinc	Arsenic	Barium	Lead	Manganese	Zinc
CTR-FB-2	9	3	14.8	504	21	307	154	4	49	4	114	18	24	10	20	37	12
CTR-FP-1	4	3	<11.0	--	590	85	1,520	--	--	495	--	116	--	--	84	--	8
CTR-FP-2	4	3	<11.0	--	16	306	307	--	--	4	111	15	--	--	23	36	5
CTR-FP-3	6	3	<11.0	--	19	497	55	--	--	1	162	2	--	--	6	33	4
CTR-FP-3	8.8	7	<11.0	--	25	2,798	74	--	--	6	185	8	--	--	23	7	11
CTR-FP-4	5	3	<11.0	--	15	85	50	--	--	4	--	22	--	--	26	--	44
CTR-FP-5	9	2	<11.0	--	16	85	56	--	--	6	--	12	--	--	37	--	22
TKC-FB-1	12	3	<11.0	--	62	618	615	--	--	8	155	148	--	--	13	25	24
TKC-FB-2	13	3	<11.0	--	51	364	133	--	--	9	111	11	--	--	17	31	8
TKC-FB-2	5	7	<11.0	--	21	97	70	--	--	5	21	13	--	--	21	22	19
TKC-FP-1	2	3	<11.0	606	20	456	860	--	6	7	89	174	--	1	37	20	20
TKC-FP-2	12	3	<11.0	518	102	612	356	--	71	7	870	51	--	14	6	142	14
TKC-FP-3	5	3	<11.0	565	46	349	133	--	17	8	177	14	--	3	16	51	10
SH-FB-2	1	7	<11.0	424	64	277	376	--	20	7	43	12	--	5	11	16	3
SH-FB-3	4	3	<11.0	380	43	256	117	--	14	9	79	7	--	4	20	31	6
SH-FP-1	3	3	<11.0	--	31	409	76	--	--	7	54	14	--	--	23	13	19
SH-FP-4	4	3	11.5	611	14	141	87	1	26	2	52	5	8	4	17	37	5
TAR-FB1	8	3	92.9	--	64	3,083	206	41	--	43	1,497	92	44	--	68	49	45
TAR-FB4	8	3	12.3	--	19	565	55	2	--	6	297	5	18	--	29	53	10
TAR-FP1-2	13	7	17.0	--	17	541	122	8	--	7	69	12	47	--	39	13	10
TAR-FP2-1	11	3	12.4	--	15	246	65	2	--	2	93	15	20	--	13	38	23
TAR-FP2-2	3	3	<11.0	--	13	116	37	--	--	--	35	11	--	--	--	30	28
TAR-FP2-3 ^a	11	7	<11.0	550	17	245	49	--	25	4	47	6	--	5	26	19	11
TAR-FP2-4	3	3	<11.0	--	14	97	57	--	--	1	20	9	--	--	8	21	15
Averages	--	--	--	--	--	--	--	10	28	28	204	33	27	6	25	34	16
Trimmed mean	--	--	--	--	--	--	--	--	--	7.1 ^b	--	--	--	--	--	--	--
Number of values summarized	--	--	--	--	--	--	--	6	8	23	21	24	6	8	23	21	24

^aMaterial identified as sough by the onsite hydrologist, indicating that the material likely fell from a shallower depth and is not representative of the soil at the 11-ft depth.

^bAverage standard deviation of lead excluding the value 495.3.

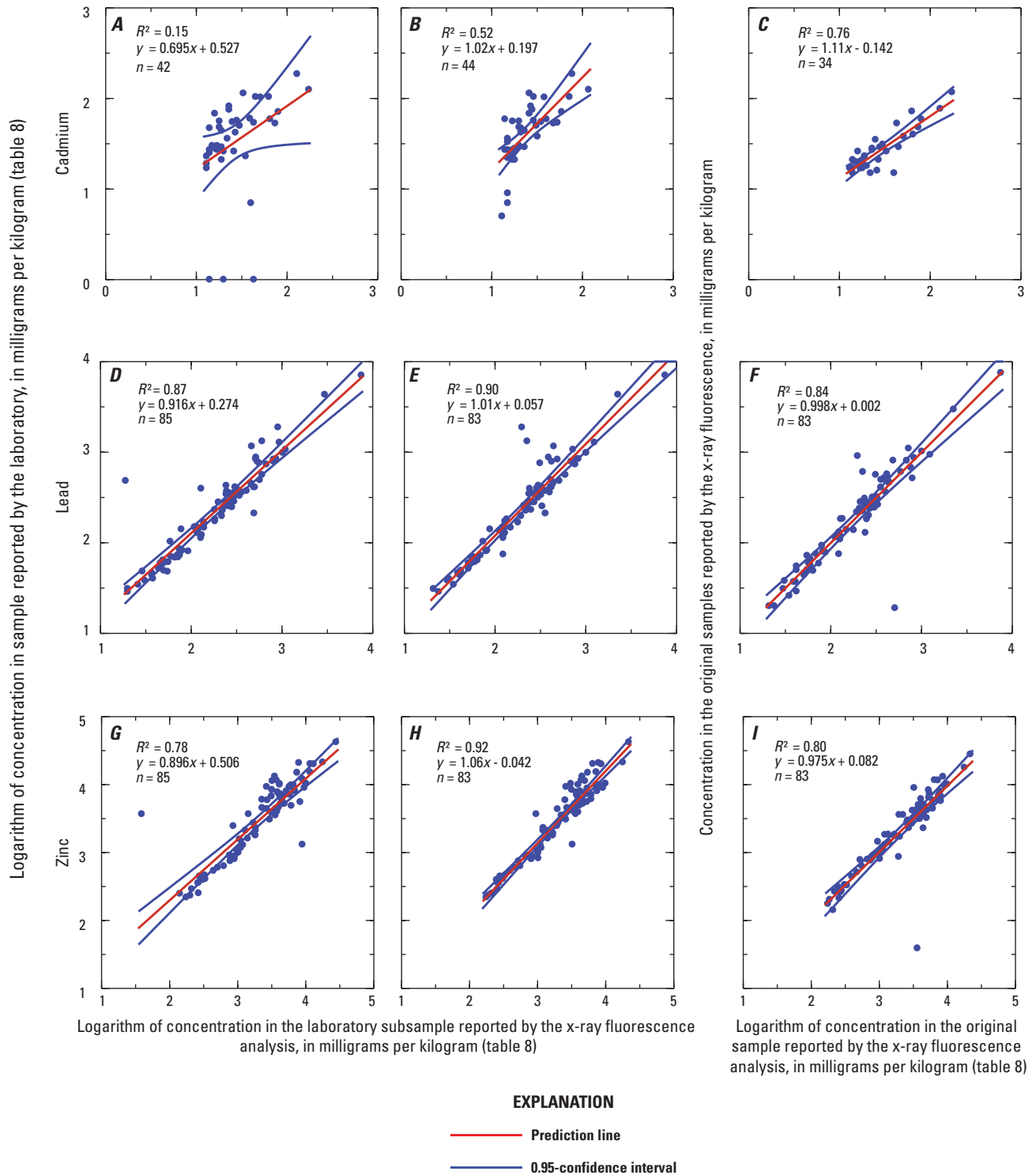


Figure 7. Relations between concentrations of A–C, cadmium; D–F, lead; G–I, zinc in laboratory subsamples determined by x-ray fluorescence and laboratory methods, and between concentrations determined by x-ray fluorescence in original and split subsamples.

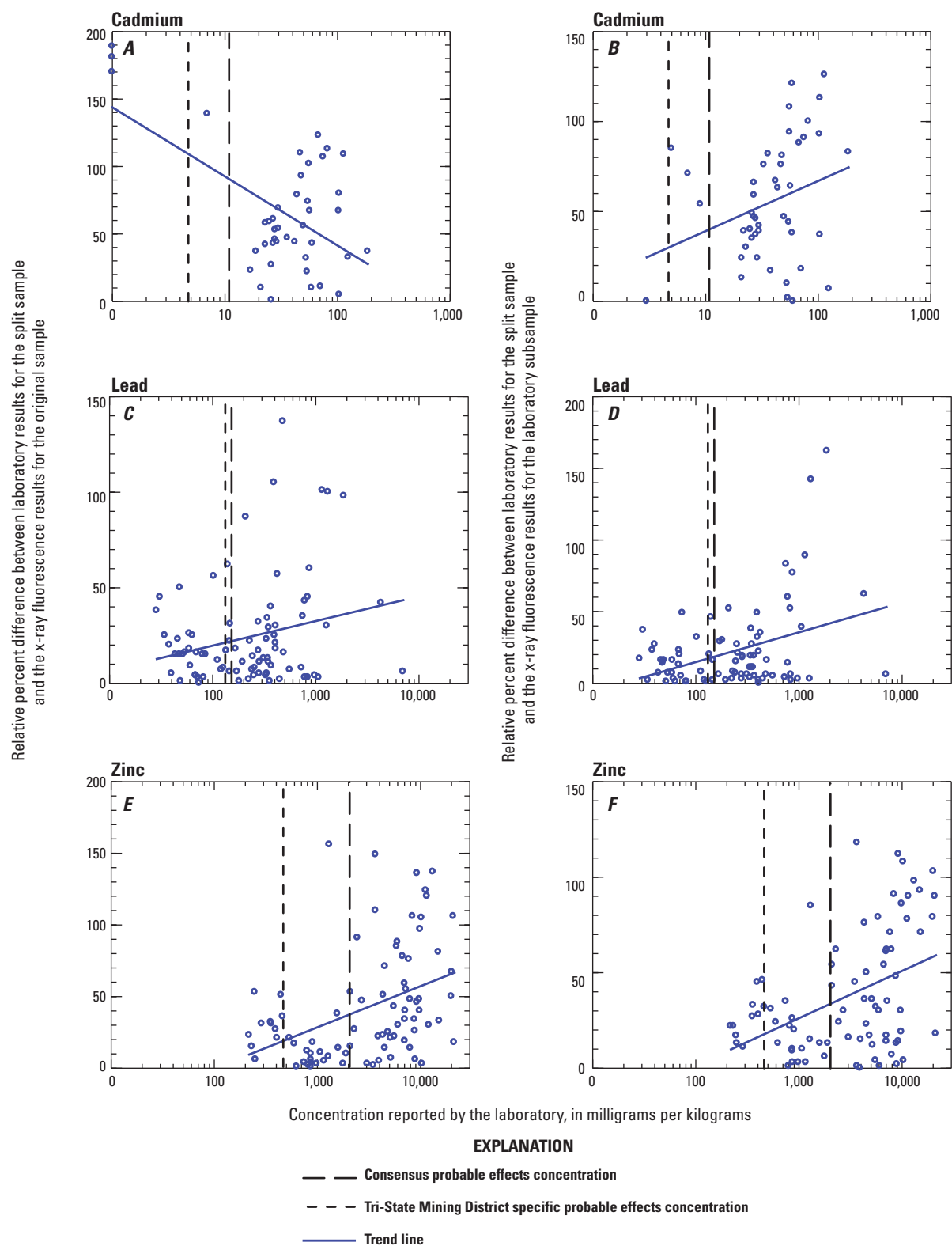


Figure 8. Comparison of relative percent difference between laboratory results for A–B, cadmium; C–D, lead; and E–F, zinc in the split samples, and the x-ray fluorescence results for either the original samples (A, C, and E) or the split sample before its submittal to the laboratory (B, D, and F) for stream channel sediment, Tri-State Mining District.

distribution of metals in the samples or in sample grain size. It is possible that larger concentrations of metals may reflect the effect of a proportionately smaller number of very metal-rich grains (perhaps grains consisting of mostly ore minerals) that are not evenly distributed throughout the sample; however, sample-preparation differences also could explain the observed upward trend in RPD between XRF and laboratory results as concentrations increase. The laboratory completely digested a thoroughly homogenized fraction of the split sample submitted to the laboratory, whereas the XRF method measured only three small locations within the entire subsample.

Occurrence, Distribution, and Volume of Metals-Contaminated Sediment

This section presents the data from the XRF analysis of the sediments collected in the Spring River and four tributaries draining mined areas in the TSMD. Data from the XRF field measurements were also used to estimate the total volume of sediment deposited in selected sampled reaches (fig. 1) of the stream channel with concentrations of lead or zinc greater than the CPEC and TPEC sediment-quality guidelines. The estimated volume of contaminated sediments is based on sediments in gravel bars because insufficient data was obtained to characterize sediment volumes beneath other channel features such as pools.

Center Creek

Center Creek has a drainage area of 300 mi² at its confluence with Spring River and is approximately 66.0 mi in length from the headwaters to the mouth. Approximately 18.6 mi of the lower part of the creek were studied and the lower 11.1 mi were used in the estimation of the volume of contaminated sediment (table 5).

Site Selection and Description

The Center Creek study reach consisted of an area of intensive study (gravel bar sites C1, C2, and nearby flood plain; fig. 9) and four upstream supplementary gravel bar sites (C3, C4, C5, C6; figs. 10 and 11). The intensive study on Center Creek was done over a 1-week period in November 2011. Samples also were collected on four supplemental gravel bars during 2 weeks of drilling in the summer of 2012. In total, samples were collected from 24 channel locations and 7 flood-plain locations in the Center Creek study reach.

The intensive study area was just west of Highway JJ, north of Joplin, Mo. (fig. 9). Gravel bar-sediment samples were centered on two gravel bars at sites C1 and C2 (fig. 9). Five cores (CTR-CH-5, CTR-CH-6, CTR-CH-7, CTR-WC-3, and CTR-WC-4) were on or near the gravel bar at site C2 near the flood-plain transect CTR–CTR'. The wetted channel (WC)

cores were located adjacent to the gravel bar. The cores (CTR-CH-1, CTR-CH-2, CTR-CH-3, CTR-CH-4, CTR-WC-1, and CTR-WC-2) were at site C1 on and near a gravel bar on the left bank about 1,500 ft downstream from the flood-plain transect CTR–CTR' at site C2. Core CTR-GB-1 was a hand scoop from a small gravel bar on the right bank of the stream. A transect (CTR–CTR') of five cores (CTR-FP-1, CTR-FP-2, CTR-FP-3, CTR-FP-4, and CTR-FP-5) were drilled across the flood plain with three on the north side of the creek and two on the south. Two flood-plain bias cores (CTR-FB-1 and CTR-FB-2), located on features of interest, were drilled off the flood-plain transect CTR–CTR' line. The flood-plain borehole CTR-FB-1 was 1,300 ft west of CTR-FP-4. The flood-plain borehole CTR-FB-2 was on the inside of a creek meander. The locations of CTR-FB-1 and CTR-FB-2 were selected because of an apparent lower elevation within the flood plain, which may be subject to greater frequency of flooding.

Four additional gravel bars farther upstream were selected for sampling. The gravel bar at site C3 with two core locations (CC-A-HD1 and CC-A-HD2) was located about 1,000 ft downstream from the Highway 171 bridge (fig. 10). The gravel bar at site C4 had three core locations (CC-D-HD1, CC-D-HD2, and CC-D-WC-1) and was located about 1.7 river mi upstream from site C3. Gravel bar at site C5 had three cores (CC-C-HD1, CC-C-HD2, and CC-C-WC1; fig. 11) and was located 700 ft downstream from the Highway O bridge (not shown). The gravel bar at site C6 had two core locations (CC-B-HD1 and CC-B-HD2) and two hand scoop sample locations (CC-B-HS1 and CC-B-HS2). It was the farthest upstream site on Center Creek and was located directly downstream from the Highway 175 bridge east of Joplin, Mo. (fig. 11).

Depth and Concentration of Metals in Channel Sediments

A total of 89 gravel bar-sediment samples from 24 locations were collected from gravel bar deposits along the lower 18.6 miles of Center Creek. The maximum sample depth was 9.5 ft below the gravel bar surface. Most of the gravel bar-sediment samples from Center Creek exceeded the CPEC and the TPEC for lead or zinc for sites C1, C2, C3, C4, and C5. About 45 percent of these had detections of cadmium greater than the LOD for the XRF. Because the CPEC (4.98 mg/kg) and TPEC (11.1 mg/kg) for cadmium is less than the LOD (12 mg/kg), the frequency of cadmium exceeding the PEC's is at least 45 percent. Site C6 is upstream from most of the historic mining activity in the Center Creek basin, and none of the samples from this site had concentrations of lead, or zinc that exceeded the CPEC or TPEC or concentrations of cadmium that exceeded the LOD. Overall, median concentrations of lead and zinc increased dramatically from upstream site C6 to site C5, peaked at sites C4 and C3, and decreased downstream through sites C2 and C1; however, lead and zinc median concentrations at site C1 remained enriched significantly above their

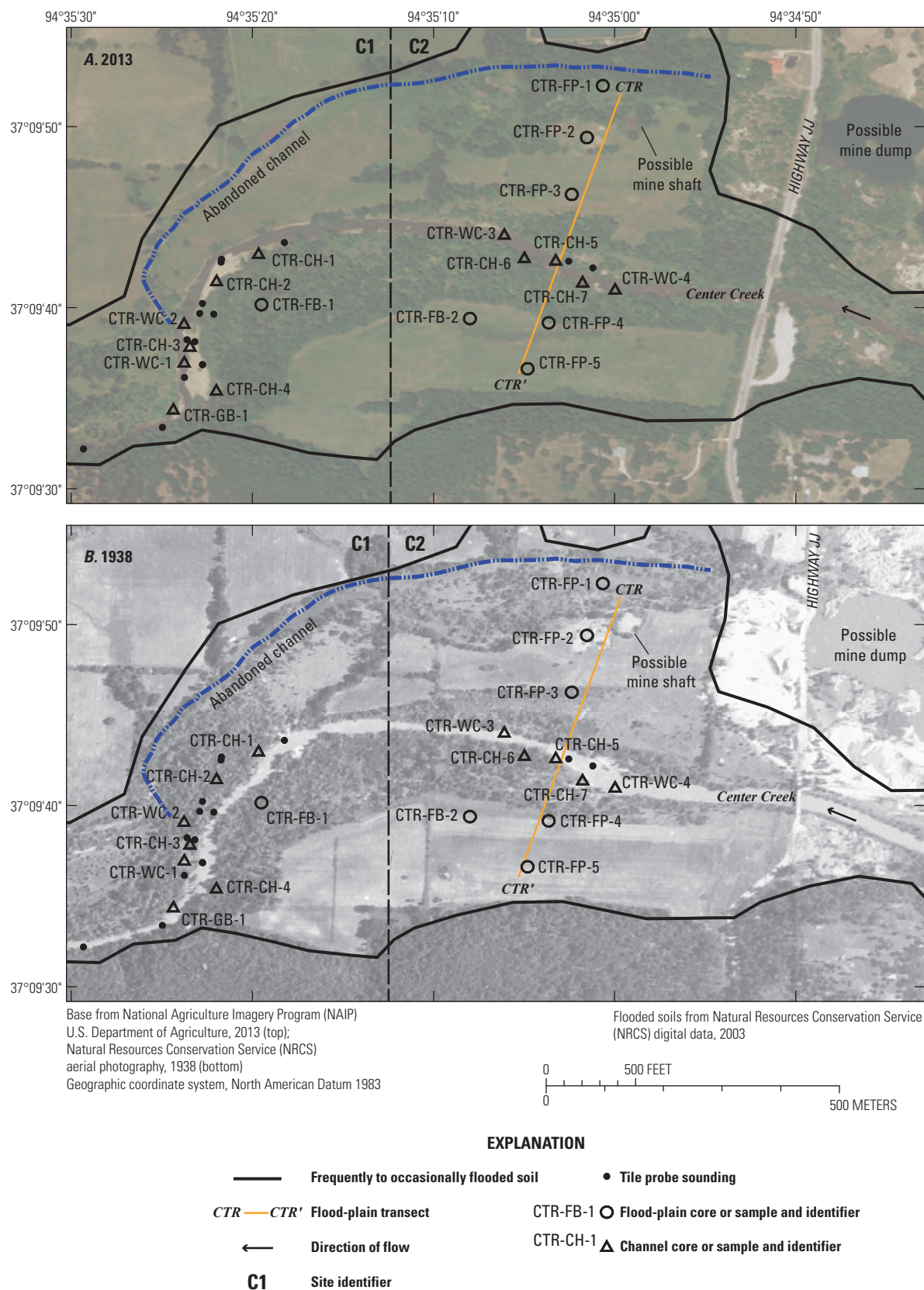


Figure 9. Aerial photographs from A, 2013 and B, 1938 showing location of cores, samples, and tile probe soundings for sites C1 and C2 of intensive study on Center Creek, Missouri, 2011–12.

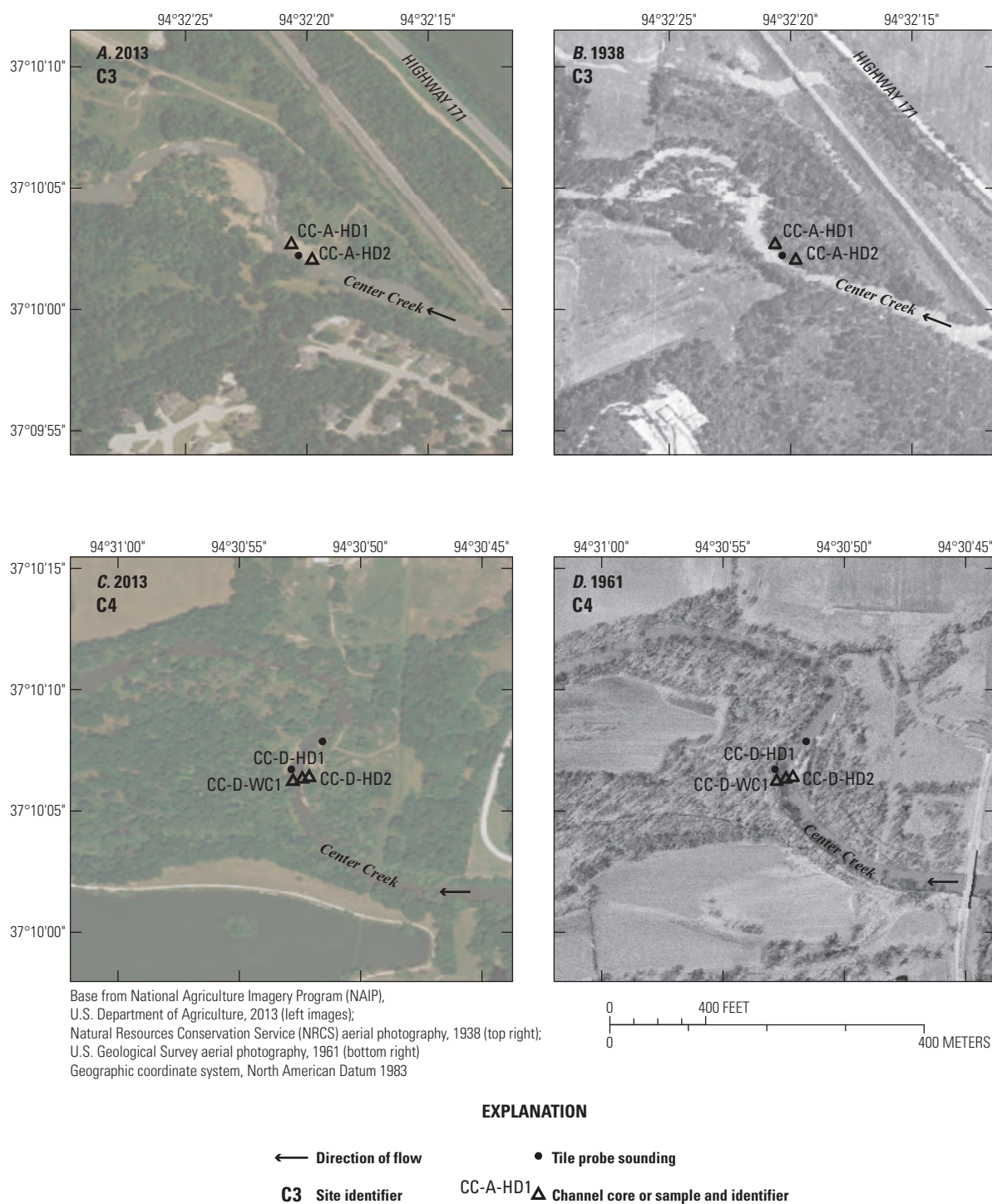


Figure 10. Aerial photographs from A, 2013 and B, 1938 for site C3 and from C, 2013 and D, 1961 for site C4 showing location of cores, samples, and tile probe soundings on Center Creek, Missouri, 2011–12.

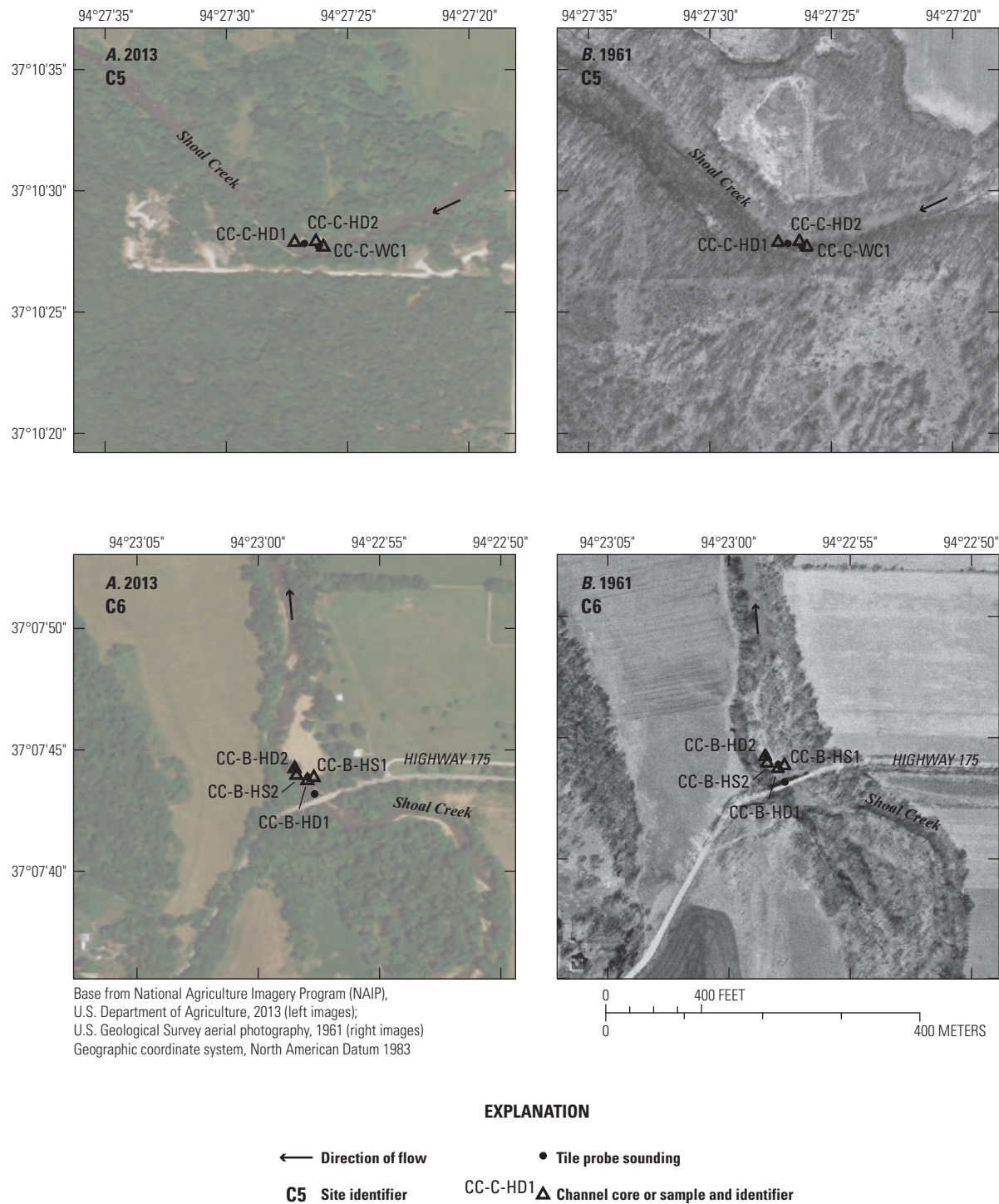


Figure 11. Aerial photographs from *A*, 2013 and *B*, 1961 showing location of cores, samples, and tile probe soundings for sites C5 and C6 on Center Creek, Missouri, 2011–12.

levels at upstream site C6 (fig. 12). Although no samples from site C6 had XRF-detectable cadmium concentrations, concentrations of cadmium followed a similar but more subdued pattern. Laboratory results from four samples from site C6 had detectable concentrations of lead, zinc, and cadmium all below the respective CPECs. Very few gravel bar-sediment samples from Center Creek exceeded the CPEC for other metals (one exceedance for arsenic and six exceedances for nickel), although exceedances for nickel may be underrepresented because the CPEC is less than the XRF LOD of 65 mg/kg.

Lead concentrations ranged from 14.0 mg/kg to 1,880 mg/kg (Smith, 2016; Stream channel sediment samples) in the <2-mm size fraction of the 89 channel-sediment samples from Center Creek and exceeded the CPEC in 60 samples (67 percent). The largest lead concentration was at site C1 in borehole CTR-CH-3 at a depth of 4 to 5 ft below surface. Hereinafter, all depths in the body of this report will be referenced to the local land surface. The deepest sample with a lead concentration (177 mg/kg) greater than the CPEC was at site C1 in borehole CTR-CH-2 at a depth of 6.5 to 7.5 ft (fig. 13). Of the 80 samples from sites C1–C5, 60 had lead concentrations greater than the CPEC and 57 were greater than the TPEC. Excluding upstream site C6, concentrations of lead in the upper 5 ft of most cores exceeded the CPEC or TPEC for one or more depth intervals (fig. 13), and in a few cases, concentrations tended to increase with depth. As examples of the latter, see results in figure 13 for CTR-CH-3, CC-A-HD2, and CC-C-HD1.

Zinc concentrations in the <2-mm size fraction in channel-sediment samples from Center Creek ranged from 201 mg/kg to 25,200 mg/kg exceeding the CPEC in 76 samples (85 percent). The largest zinc concentration was in borehole CC-A-HD1 at a depth of 3 to 4 ft (Smith, 2016; Stream channel sediment samples). The deepest sample with a zinc concentration (1,100 mg/kg) greater than the CPEC was at site C1 at a depth of 8.5 to 9.5 ft in borehole CTR-CH-2 (fig. 14), the same borehole that had the deepest lead concentration greater than the CPEC (fig. 13). The deepest sample with a zinc concentration (3,470 mg/kg) greater than the TPEC was at site C1 in borehole CTR-CH-1 at a depth of 6 to 7 ft. Because the zinc TPEC is more than 4 times larger than the CPEC, the frequency of samples from sites C1 to C5 with zinc exceeding the TPEC is smaller (53 of 80, or 66 percent) than the frequency of samples exceeding the CPEC (76 of 80, or 95 percent). Perhaps more importantly, the depth of contamination is greatly dependent on which PEC (CPEC or TPEC) value is used. Of the 56 samples from sites C1 to C5 collected from depths <4 ft, 55 samples (98 percent) exceeded the CPEC and 45 samples (80 percent) exceeded the TPEC; however, of the 24 samples collected from depths greater than 4 ft, 21 of 24 (88 percent) exceeded the CPEC, whereas only 8 (33 percent) exceeded the TPEC.

Cadmium concentrations in the <2-mm size fraction in stream channel sediments were detected above the 12 mg/kg LOD in 34 samples (38 percent) and the maximum concentration was 171 mg/kg (Smith, 2016; Stream channel sediment samples).

The median concentrations (fig. 12) tended to increase downstream from no detection at site C6 to a peak at site C3 and then decreased to site C1, which is nearest to the confluence with Spring River. Gravel bars at sites C3, C4, and C5 had detectable cadmium concentrations that exceeded the CPEC and TPEC in 24 out of 27 samples. The farthest downstream sites (C1 and C2) had fewer cadmium concentrations that exceeded the CPEC and LOD (10 out of 53 samples).

Estimated Volume of Channel Sediment Contaminated by Mine Waste

The total volume of sediment deposited in gravel bars along the lower 11.1 mi of Center Creek from site C1 to site C5 was estimated on the basis of the mean maximum sediment depths with concentrations of lead and zinc that exceeded the CPEC and the TPEC. Site C5 was chosen as the farthest upstream extent of known sediment contamination because no lead or zinc concentrations exceeding their respective CPEC or TPEC values were upstream from site C5. Site C6 was approximately 7.5 mi upstream from site C5. The mean thickness of sediment that would need excavation based on the CPEC for Center Creek was 4.0 ft, and the mean thickness of sediment that would need excavation based on the TPEC was 3.4 ft (table 5). The total area of studied gravel bars for Center Creek was 916,000 square feet (ft²; 21.0 acres; table 5). The estimated minimum volume of sediment in gravel bars that would need excavation based on the CPEC along Center Creek from the mouth to site C5 was 136,000 cubic yards (yd³), and the estimated minimum volume of gravel bar sediment exceeding the TPEC was 115,000 yd³ (table 5). These estimates are considered minimum volumes because they were only based on the visible gravel bars and do not include sediment beneath the wetted channel in other features such as pools, and presumably some of these deposits are negatively affected by mine-waste contaminated sediment but were not sufficiently characterized to be included in the volume estimate.

Depth and Concentration of Metals in Flood-Plain Sediments

A total of 84 samples were collected from 7 locations on the Center Creek flood plain at sites C1 and C2 within the intensive study. Four of the seven boreholes had at least one depth interval where lead or zinc exceeded the CPEC or TPEC. Intervals that exceeded the lead or zinc CPEC and TPEC were generally <3 ft deep with occasional detections greater than the CPEC at deeper intervals. Because of time limitations, concentrations of cadmium or barium were not analyzed in many core intervals. For the intervals that were analyzed, 15 out of 23 had concentrations of cadmium greater than the LOD, CPEC, and TPEC, 3 of which were greater than 2 times the LOD. Core samples from borehole CTR-FB-2 had cadmium concentrations analyzed at every sampled interval,

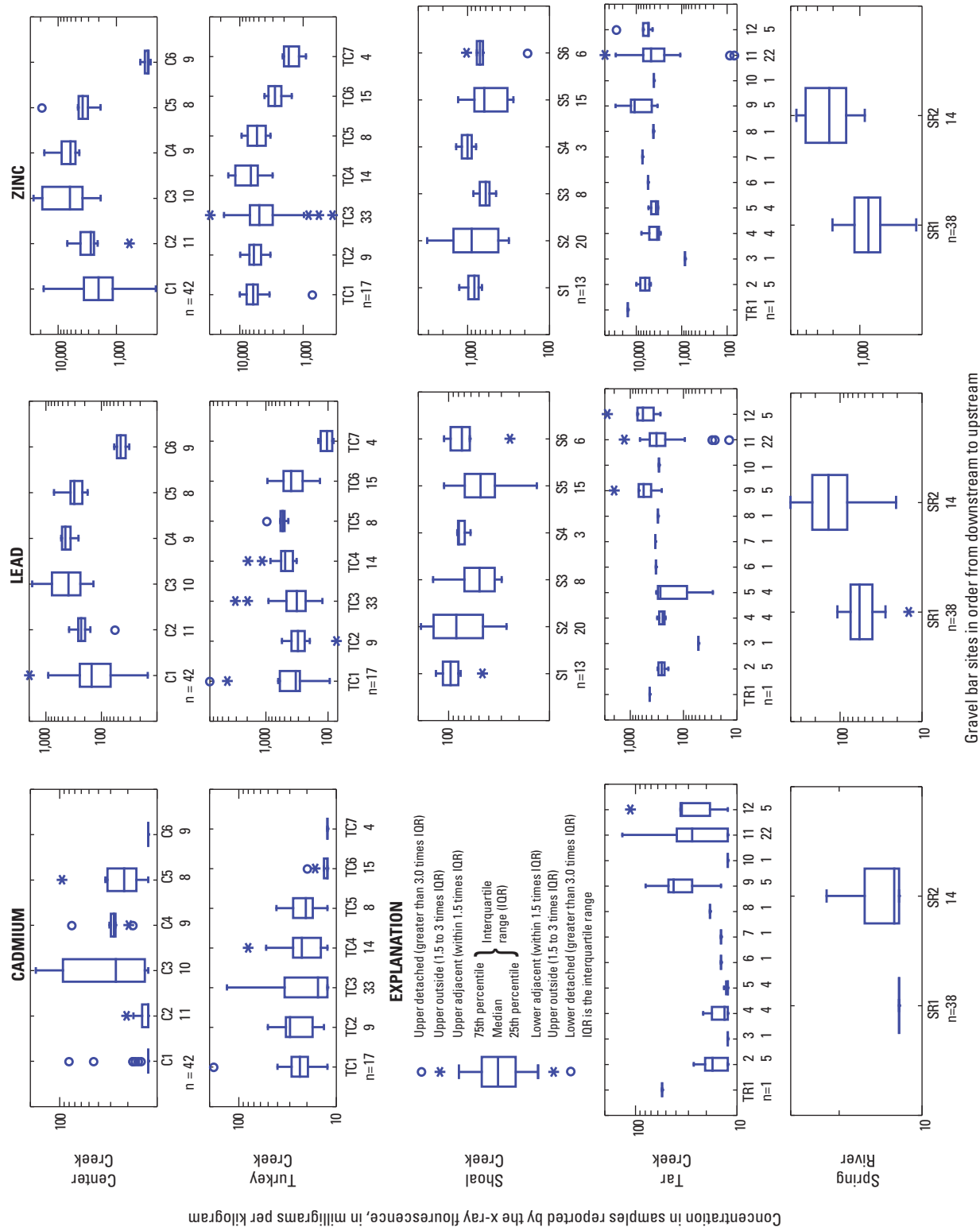


Figure 12. Frequency distributions of the concentrations of cadmium, lead, and zinc at specific sites in order from downstream to upstream.

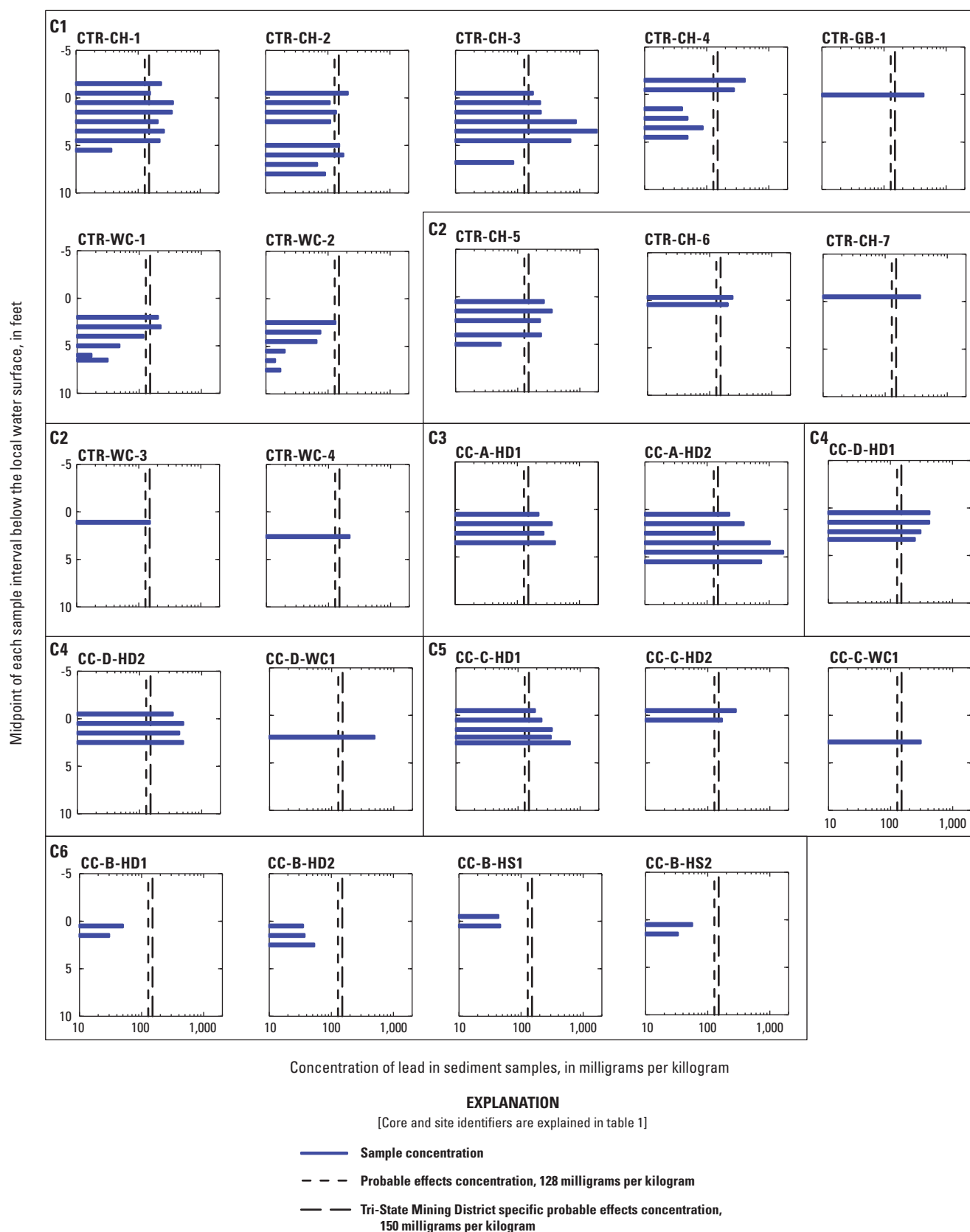


Figure 13. Vertical concentration profiles for lead in the less than 2-millimeter size fraction of gravel bar-sediment samples scanned by x-ray fluorescence, Center Creek, Missouri, 2011–12.

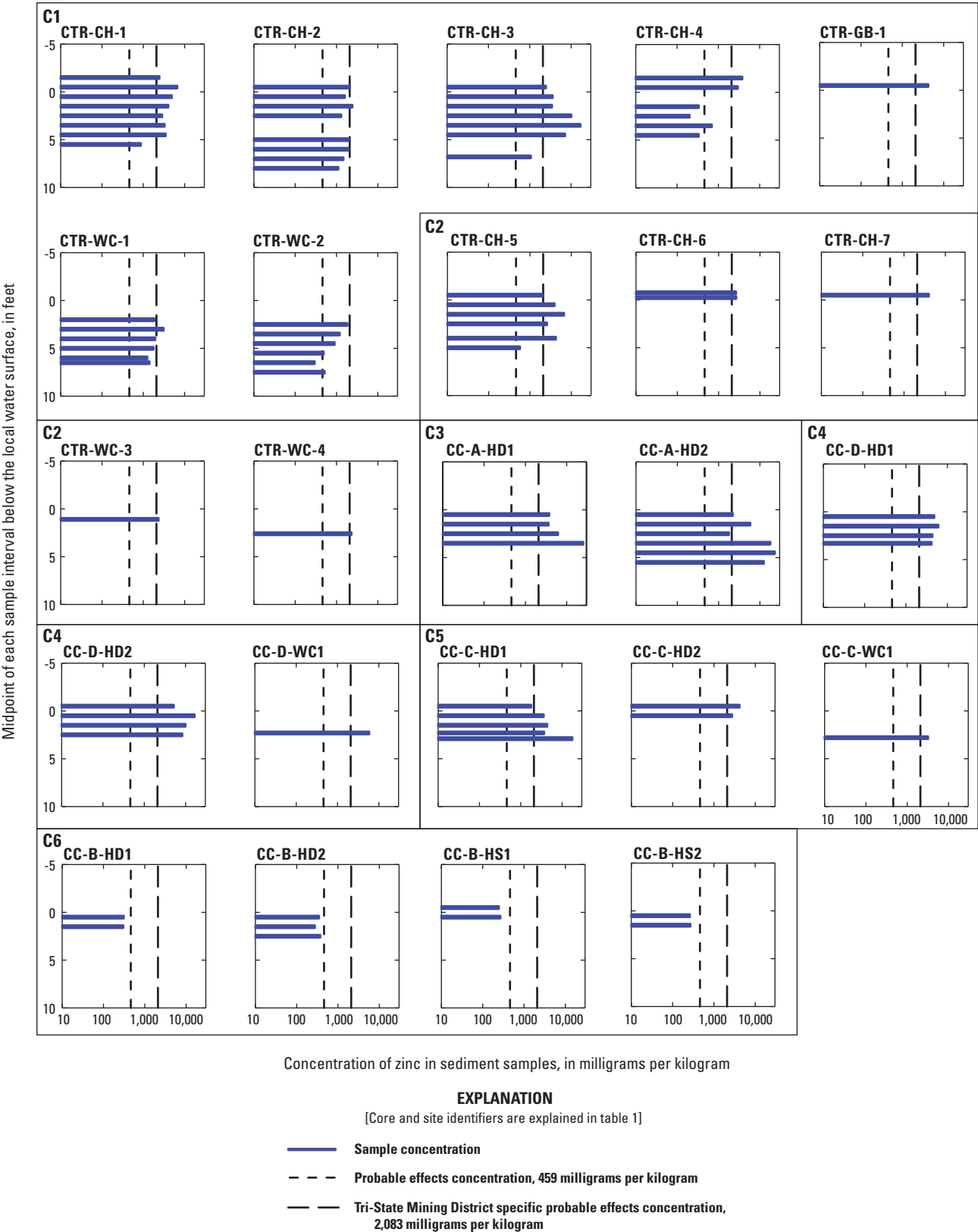


Figure 14. Vertical concentration profiles for zinc in the less than 2-millimeter size fraction of gravel bar-sediment samples scanned by x-ray fluorescence, Center Creek, Missouri, 2011–12.

and concentrations exceeded the CPEC and TPEC in every interval shallower than 7 ft and at the 8 to 9 ft interval (Smith, 2016; Flood-plain cores) but had no exceedances of the CPEC or TPEC for lead or zinc.

Of 84 samples on the Center Creek flood plain, 14 had concentrations of lead greater than the CPEC (13 greater than the TPEC) and 25 had concentrations of zinc greater than the CPEC (10 greater than the TPEC [Smith, 2016; Flood-plain cores]). Three of the seven boreholes (CTR-FB-2, CTR-FP-4, and CTR-FP-5) had no samples with lead or zinc concentrations greater than the CPEC, and borehole CTR-FP-3 had lead and zinc exceed their CPEC values in only the 0 to 1 ft interval (figs. 15 and 16). One borehole, CTR-FP-1, had lead concentrations generally exceeding the CPEC value in intervals <8 ft deep and zinc concentrations exceeding the CPEC in intervals <11 ft deep. From the 1938 aerial photograph (fig. 9B), borehole CTR-FP-1 was within or very near an old stream channel draining what appears to be a possible mine-waste dump and mine shaft. Borehole CTR-FP-2 was farther from the old stream channel, and lead and zinc contamination levels greater than the CPEC values were limited to intervals <3 ft deep (figs. 15 and 16). In deeper intervals of most flood-plain boreholes, lead concentrations generally were between 20 and 50 mg/kg, and zinc concentrations were more variable ranging from <25 mg/kg to about 175 mg/kg.

The concentrations of lead and zinc in deeper core intervals are similar to background concentrations estimated by Pope (2005) of 20 mg/kg for lead and 100 mg/kg for zinc except for an anomalous zinc concentration (33,700 mg/kg) at the bottom of borehole CTR-FP-2. This anomalous zinc sample also had the largest cadmium concentration (183 mg/kg) detected in any flood-plain sample or streambed-sediment sample from this study (Smith, 2016; Flood-plain cores), but visual inspection of the core indicated the presence of the zinc ore mineral, sphalerite, which is known to contain abundant quantities of cadmium (Jolly and Van Heyl, 1968). Changes in the geologic character of the core at depth, and the abrupt increases in concentrations at the bottom of the core, lead to the interpretation that the anomalous concentrations of zinc and cadmium in the sample from 15 to 16 ft depth are most likely derived from naturally occurring minerals in weathered bedrock and not the result of mine contamination.

Turkey Creek

Turkey Creek has a drainage area of 46 mi² at its confluence with Spring River and is approximately 20.8 mi in length from the headwaters to the mouth. Approximately 10.1 mi of the lower part of the creek was studied and used in the estimation of the volume of contaminated sediment (table 5).

Site Selection and Description

Turkey Creek gravel bar-sediment samples and flood-plain samples were collected during a period of 3 weeks in the

summer of 2012. The Turkey Creek study reach consisted of an area of intensive study (TC1, TC2, and TC3; fig. 17) and four upstream supplemental gravel bar sites (TC4, TC5, TC6, and TC7 [the farthest upstream]; figs. 18, 19). The intensive study area was west of Joplin (fig. 1). Twenty-three gravel bar locations and six flood-plain locations were cored along Turkey Creek. Transect TC–TC' with five cores spanning gravel bar sites TC2 and TC3 (TKC-FP-1, TKC-FP-2, TKC-FP-3, TKC-FB-1, and TKC-FP-4) were drilled across the flood plain with four on the north side of the creek and one on the south (fig. 17). There were three gravel bar coring locations along transect TC–TC' at gravel bar site TC3: two on the dry part of the gravel bar (TKC-CH-2 and TKC-CH-3) and one in the wetted channel (TKC-WC-1). One gravel bar borehole at gravel bar site TC3 (TKC-CH-1) was located a short distance out of the transect line but on the same gravel bar (fig. 17).

Additional cores were collected in the intensive study area downstream from transect TC–TC'. Another core at gravel bar site TC2 (TKC-CH-4) was located about 600 ft downstream from the transect line on the north side of the creek. Another flood-plain borehole at gravel bar site TC1 (TKC-FB-2) was drilled south of the creek and about 1,000 ft downstream from transect TC–TC'. Four additional gravel bar-sediment sample locations at site TC1 were on gravel bars <1,500 ft downstream from transect TC–TC', near an overflow channel that exists north of the main channel of Turkey Creek (fig. 17). The overflow channel branches off of the main channel and rejoins it less than half a mile downstream. At the time of sampling, the overflow channel contained only small pools of standing water and was choked with sand and gravel, especially at the upstream end. Flow through the overflow channel likely only occurs during periods of high flow in Turkey Creek, which makes it a likely depositional area for sediment transported during storm events. Four cores were drilled in and between the overflow and main channels. At site TC1, one core (TKC-CH-7) was drilled on a gravel bar and one core (TKC-WC-3) was drilled in the adjacent submerged part of the gravel bar in the overflow channel (fig. 17). At site TC1, hand sample TKC-CH-5P and core TKC-CH-5 were on opposite sides of the main channel. At site TC1, hand samples were collected from TKC-CH-5P from 0 to 2 ft on a gravel bar on the opposite side of the stream from coring location TKC-CH-5. At site TC1, core TKC-CH-6 was drilled between the main channel and overflow channel (fig. 17).

Thirteen locations were sampled at five supplemental gravel bars upstream from the intensive study site. Site TC4 had two cores (TC-D-HD1 and TC-D-HD2) and was located about 1,000 ft downstream from the bridge at North Black Cat Road (fig. 18). Site TC5 had three cores (TC-E-HD1, TC-E-HD2, and TC-E-WC1), and was located about 3,000 ft upstream from the bridge at site TC4. At site TC5, core TC-E-WC1 was in the wetted channel while the remaining cores were drilled on the gravel bar itself (fig. 18). Site TC6 had two adjacent gravel bars (fig. 19) and was located about 3 mi upstream from the site TC5. The upstream gravel bar at site TC6 had a single core (TC-B-HD1). Coring was attempted in

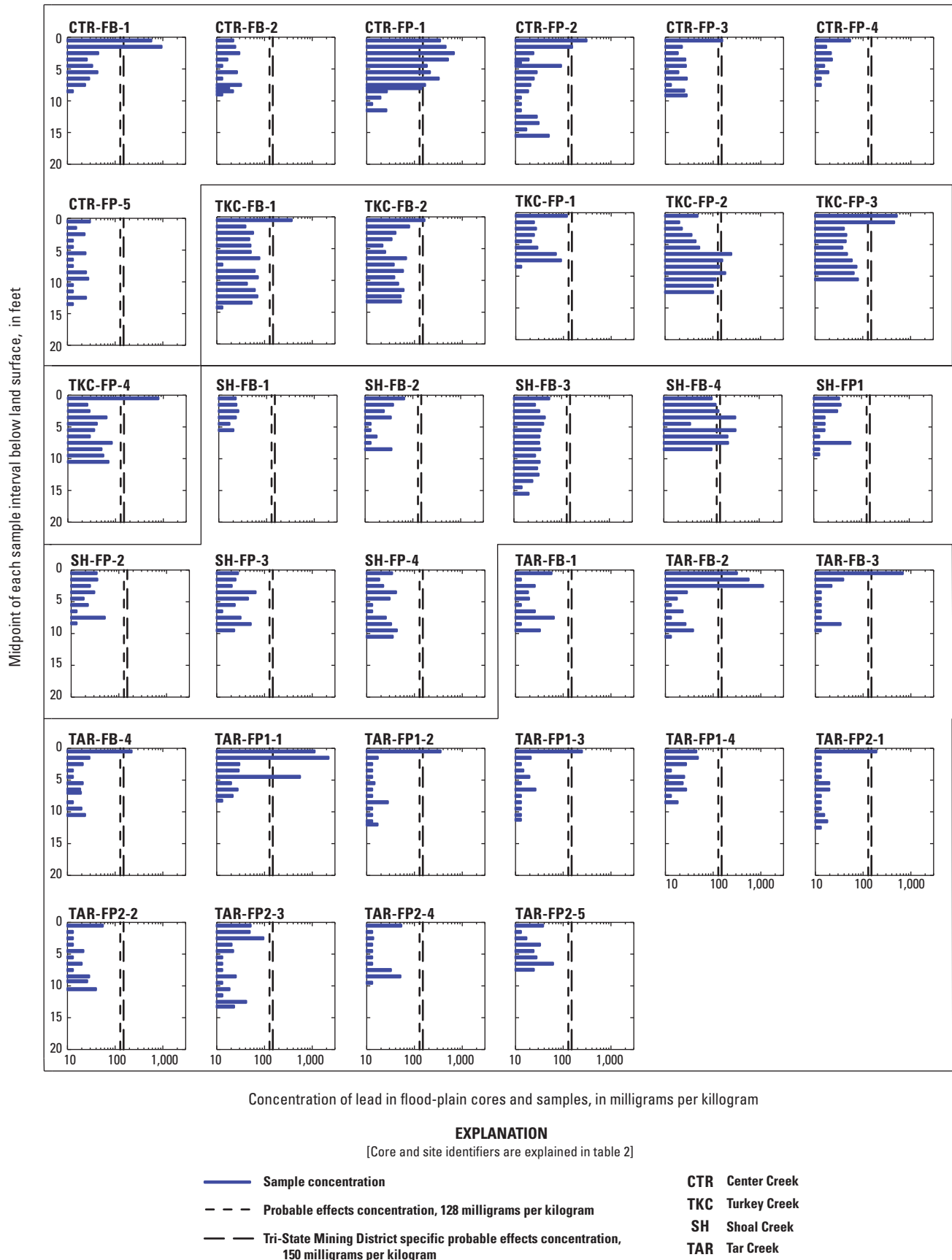


Figure 15. Vertical profiles by flood-plain core and sample location of lead concentrations analyzed by x-ray fluorescence in Center Creek, Turkey Creek, Shoal Creek, and Tar Creek, 2011–12.

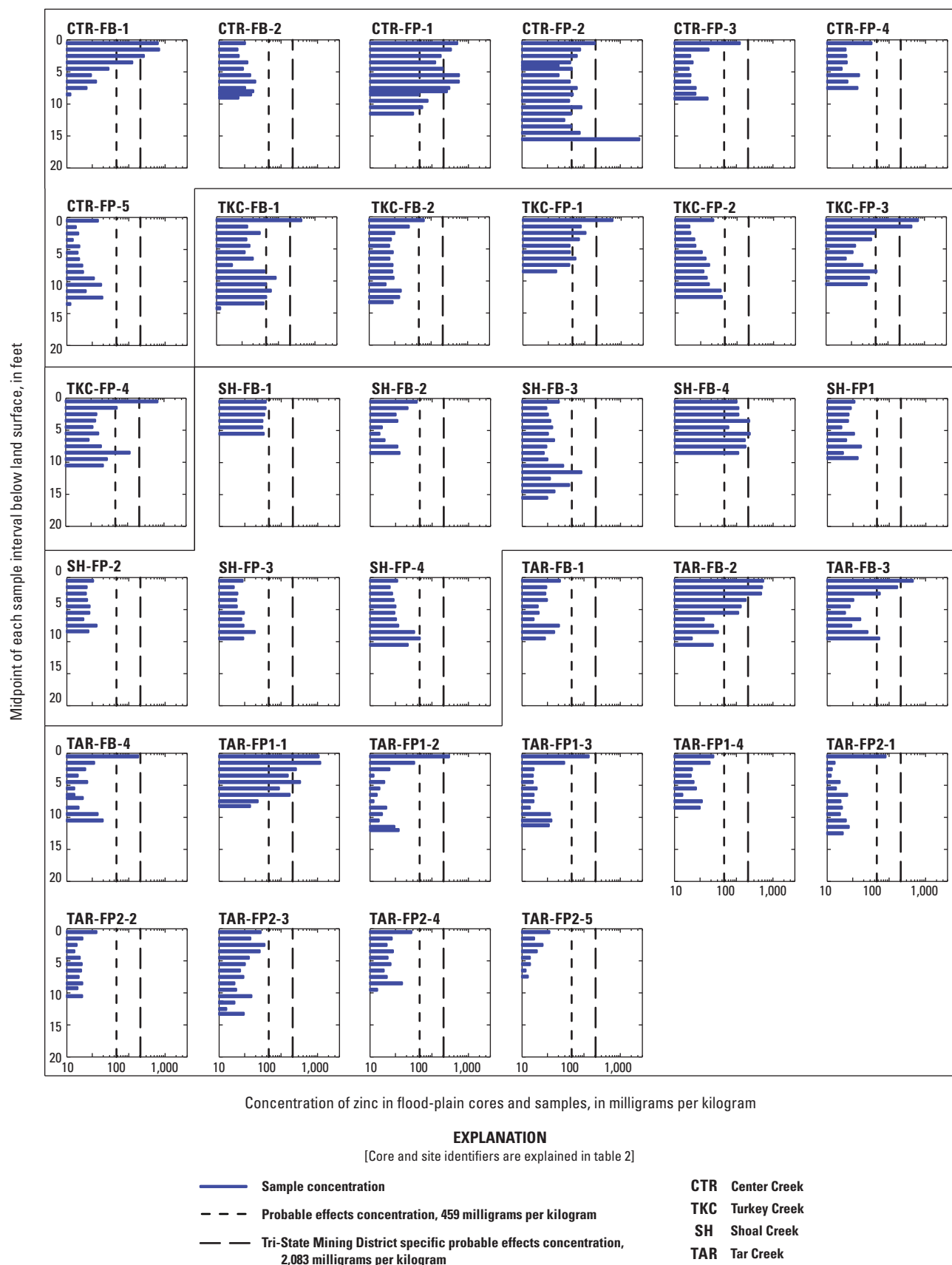


Figure 16. Vertical profiles by flood-plain core and sample location of zinc concentrations analyzed by x-ray fluorescence in Center Creek, Turkey Creek, Shoal Creek, and Tar Creek, 2011–12.

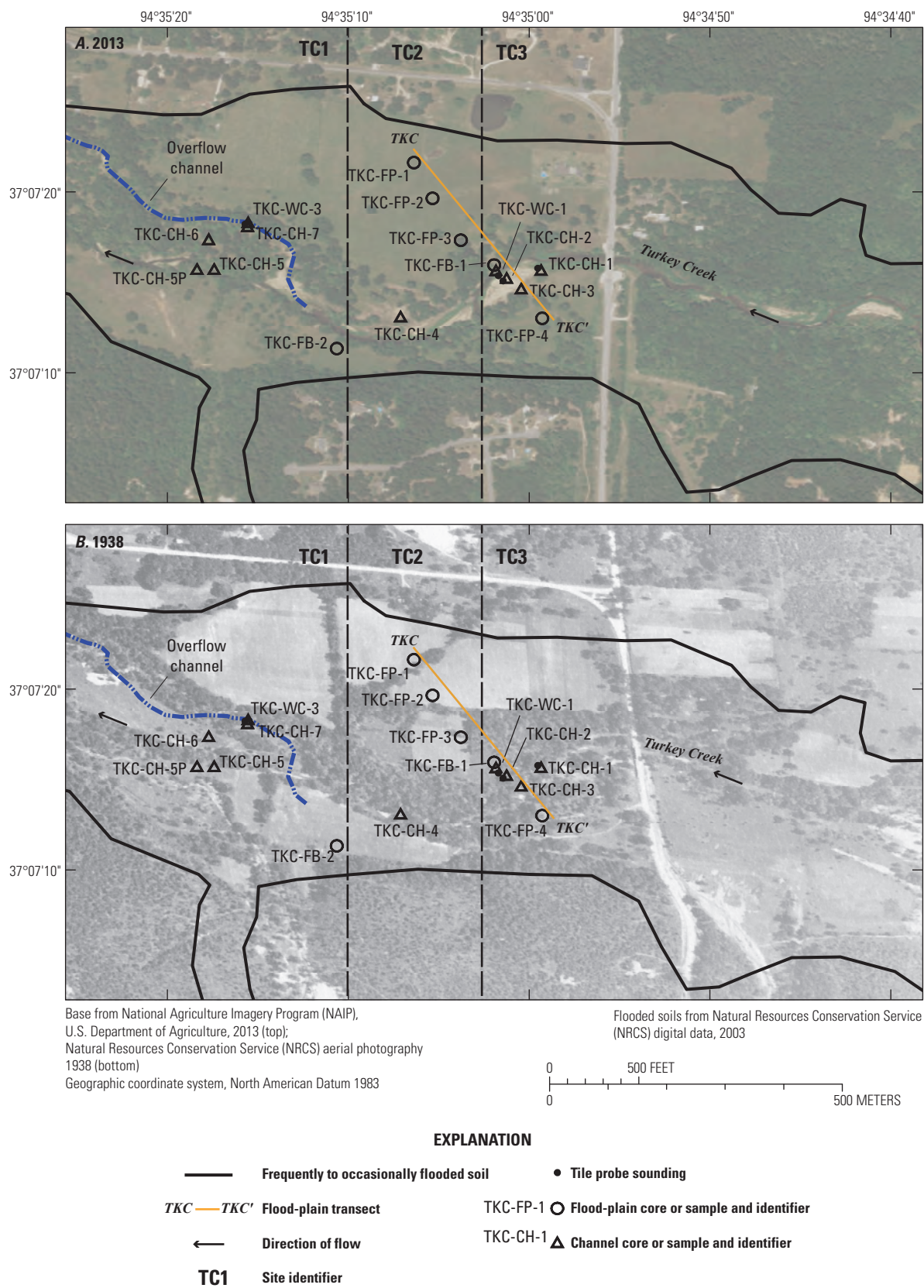


Figure 17. Aerial photographs from A, 2013 and B, 1938 showing location of bed-sediment cores, samples, and tile probe soundings for sites TC1, TC2, and TC3 in Turkey Creek, Missouri, 2012.

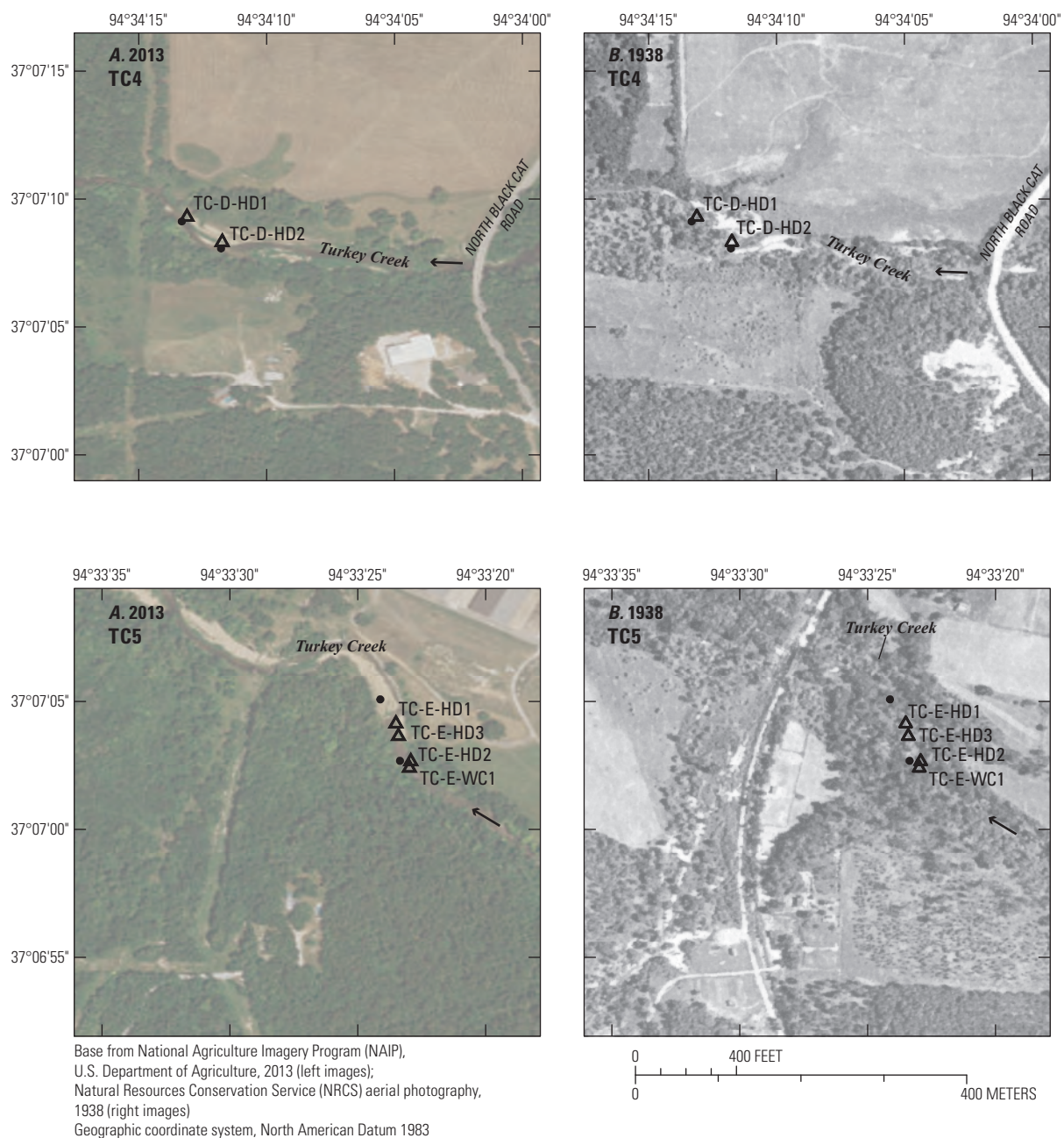


Figure 18. Aerial photographs from A, 2013 and B, 1938 showing location of bed-sediment cores, samples, and tile probe soundings for sites TC4 and TC5 in Turkey Creek, Missouri, 2012.

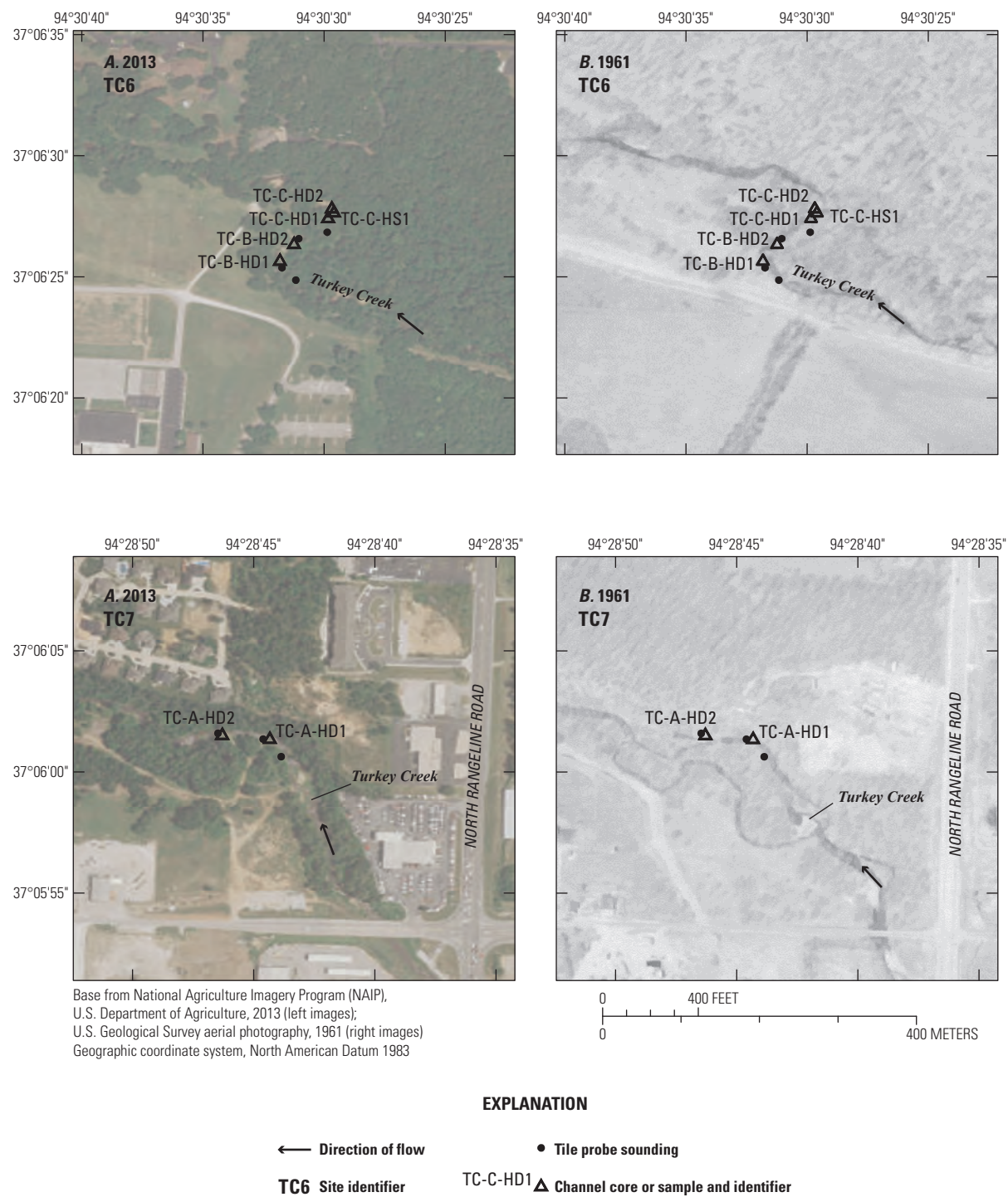


Figure 19. Aerial photographs from *A*, 2013 and *B*, 1961 showing location of bed-sediment cores, samples, and tile probe soundings for sites TC6 and TC7 in Turkey Creek, Missouri, 2012.

other parts of the gravel bar with no success. Coring at this location was extremely difficult because of large boulders and broken concrete rubble placed in the creek to control erosion. The downstream gravel bar at site TC6 had two cores (TC-C-HD1 and TC-C-HD2) and one hand sample location (TC-C-HS1; fig. 19). Site TC7, located near North Rangeline Road, had two cores (TC-A-HD1 and TC-A-HD2) and was the farthest upstream bar sampled on Turkey Creek (fig. 19).

Depth and Concentration of Metals in Channel Sediments

A total of 100 samples were collected from 23 locations on gravel bar deposits along Turkey Creek. The maximum sample depth was 13 ft, with the thickest channel deposits in the gravel bars at sites TC2 and TC3 (table 5) and thinnest deposits at upstream site TC7 (<2 ft thick). Excluding samples with concentrations below the LOD, median lead concentrations increased from the most upstream site TC7 to a peak at TC5 and decreased somewhat at the two downstream sites TC1 and TC2 (fig. 12). Median zinc concentrations increased from the most upstream site at TC7 to a peak at TC4 then remained relatively steady to the most downstream site at TC1 (fig. 12). Median cadmium concentrations increased from concentrations below the LOD at the upstream site TC7 to site TC3 and then remained relatively steady to the most downstream site at TC1 (fig. 12).

Lead and zinc concentrations in nearly all gravel bar-sediment samples from Turkey Creek exceeded the CPEC and TPEC often to the maximum depth of the boreholes. Lead concentrations exceeded the CPEC in all but 6 samples (94 percent) and exceeded the TPEC in all but 11 samples. Zinc concentrations exceeded the CPEC in all but 1 sample (99 percent) and exceeded the TPEC in all but 13 samples. Most samples also had exceedances of both PECs for cadmium (minimum of 70 percent; <12 to 175 mg/kg), although this number of exceedances may be greater because the XRF LOD is greater than the CPEC and TPEC for cadmium. Cadmium concentrations exceeding the CPEC and TPEC were present as deep as 11.5 ft. Few samples exceeded the CPECs for metals other than lead, zinc, and cadmium, although exceedances for nickel may be underrepresented because the CPEC for nickel (48.6 mg/kg) is less than the XRF LOD (65 mg/kg).

Lead concentrations in gravel bar-sediment samples from Turkey Creek ranged from 70 mg/kg to 7,520 mg/kg and zinc concentrations ranged from 329 mg/kg to 27,900 mg/kg (Smith, 2016; Stream channel sediment samples). The smallest lead and zinc concentrations generally were from upstream site TC7 where lead and zinc concentrations were less than the TPEC in all four samples from this site. At site TC7, the lead concentration exceeded the CPEC in one sample, and the zinc concentration exceeded the CPEC in all four samples (figs. 20 and 21). All samples collected from sites downstream from TC7 contained lead concentrations greater than the CPEC with the exception of three samples

with concentrations <120 mg/kg (at boreholes TKC-CH-4 [0 to 2 ft], TKC-CH-6 [8 ft], and TKC-WC-1 [3.6 to 4.6 ft]). Samples that exceeded the CPEC in Turkey Creek generally exceeded the larger TPEC with the exception of 5 samples: TC-C-HS1 from 0 to 1 ft (129 mg/kg), TC-A-HD2 from 0 to 1 ft (137 mg/kg), TKC-CH-2 from 7.2 to 8.2 ft (140 mg/kg), TKC-CH-3 from 8 to 9 ft (128 mg/kg), and TKC-CH-3 from 9 to 10 ft (138 mg/kg) (Smith, 2016; Stream channel sediment samples; fig. 20).

Estimated Volume of Channel Sediment Contaminated by Mine Waste

Sediment deposited in gravel bars along the entire 10.1-mi study reach of Turkey Creek had concentrations of lead and zinc that exceeded the CPEC and the TPEC, from the gravel bar at site TC7 to the creek's mouth at the Spring River. The gravel bar at site TC7 was chosen as the farthest upstream extent for the estimated volume of sediment because no data were collected farther upstream from this site. The mean thickness of sediment that would need excavation based on the CPEC for Turkey Creek was 4.9 ft and the mean thickness of sediment that would need excavation based on the TPEC was 4.6 ft (table 5). The total area of studied gravel bars for Turkey Creek was 632,000 ft² (14.5 acres; table 5). The estimated minimum volume of sediment in gravel bars exceeding the CPEC for the chosen reach of Turkey Creek was 115,000 yd³ and 108,000 yd³ of sediment in gravel bars exceeding the TPEC (table 5). These estimates are considered minimum volumes because they were only based on the visible gravel bars and do not include sediment beneath the wetted channel in other features such as pools, and presumably some of these deposits are negatively affected by mine-waste contaminated sediment but were not sufficiently characterized to be included in the volume estimate.

Depth and Concentration of Metals in Flood-Plain Sediments

A total of 73 samples were collected from six locations on the Turkey Creek flood plain (Smith, 2016; Flood-plain cores). Of these, cadmium concentrations were analyzed in 51 samples (Smith, 2016; Flood-plain cores). Nine of the 73 samples had concentrations of lead greater than the CPEC and 15 had concentrations of zinc greater than the CPEC. Lead concentrations in eight samples and zinc concentrations in five samples exceeded their respective TPECs. The exceedances of the TPEC for lead or zinc were limited to the upper 1 or 2 feet of the cores except for core TKC-FP-2 where concentrations of lead and zinc were less than the CPEC and TPEC in the upper few feet. Concentrations for lead and zinc for core TKC-FP-2 gradually increased with depth and lead exceeded the CPEC between 6 and 10 ft (fig. 15). The largest concentrations of lead (789 mg/kg from core TKC-FP-4) and zinc (6,620 mg/kg from core TKC-FP-3) were in the 0 to 1 ft intervals

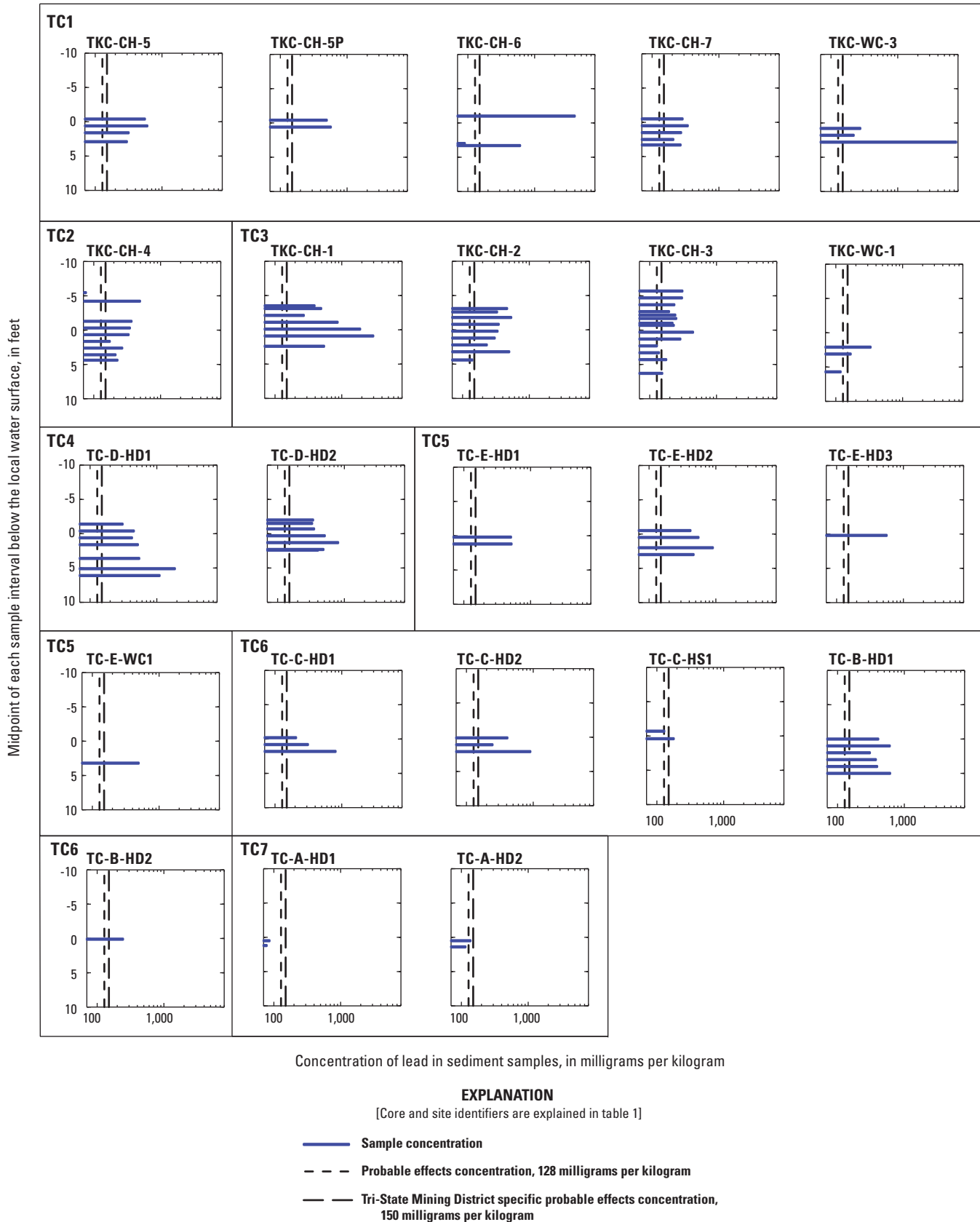


Figure 20. Vertical profiles by core and sample location of lead concentrations in the less than 2-millimeter size fraction of gravel bar-sediment samples analyzed by x-ray fluorescence in Turkey Creek, Missouri, 2012.

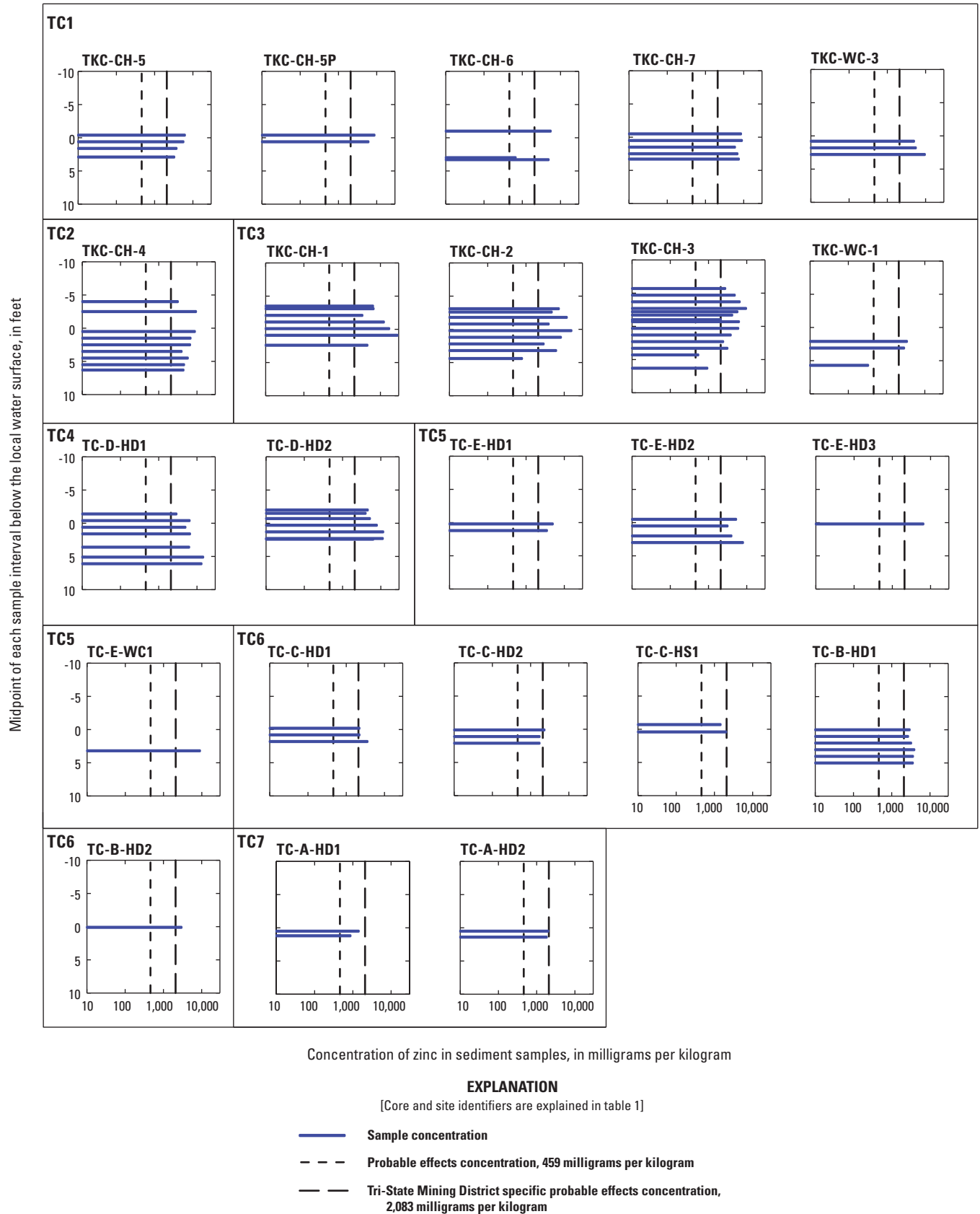


Figure 21. Vertical profiles by core and sample location of zinc concentrations in the less than 2-millimeter size fraction of gravel bar-sediment samples analyzed by x-ray fluorescence in Turkey Creek, Missouri, 2012.

(figs. 15, 16). Borehole TKC-FP-1 was farthest from the creek and lead concentrations in all samples from this core were less than the CPEC, however, zinc concentrations were greater than the CPEC in most samples <7 ft deep. Three cores (TKC-FB-1, TKC-FB-2, and TKC-FP-4) had lead concentrations exceed both PECs in the top 1 ft of depth only (fig. 15). Those lead concentrations were 371 mg/kg (TKC-FB-1), 162 mg/kg (TKC-FB-2), and 789 mg/kg (TKC-FP-4).

Cadmium concentrations exceeded the CPEC at most depths in flood-plain cores on Turkey Creek. Out of 51 samples from the flood plain that were analyzed for cadmium concentrations, a minimum 44 concentrations exceeded both PECs for cadmium (Smith, 2016; Flood-plain cores). The number of cadmium concentration exceedances may be greater because the LOD (12 mg/kg) is larger than the CPEC (4.98 mg/kg) and TPEC (11.1 mg/kg).

Shoal Creek

Shoal Creek has a drainage area of 251 mi² at its confluence with Spring River and is approximately 80.2 mi in length from the headwaters to the mouth. Approximately 19 mi of the lower part of the creek was studied and the lower 9 mi was used in the estimation of the volume of contaminated sediment (table 5).

Site Selection and Description

Shoal Creek gravel bar-sediment samples and flood-plain samples were collected from eight sites during a period of 3 weeks during the summer of 2012. Because of difficulties with permission to access the flood plain in the vicinity of sampled gravel bars, an intensive study area with a number of co-located flood-plain borehole and channel core samples was not possible. Flood-plain boreholes were drilled at two sites (SFP1 and SFP2) with no corresponding gravel bar-sediment samples, and hand samples of flood-plain deposits were obtained from a cut bank and the side wall of an excavation at site S4. The flood-plain transect SH-SH' along Shoal Creek was at the downstream most site (SFP1) about 2.0 mi south of Galena, Kansas (fig. 1). Four boreholes were drilled on the north side of the stream at distances of about 450 ft (SH-FP-1), 900 ft (SH-FP-2), 1,400 ft (SH-FP-3), and 1,900 ft (SH-FP-4) from the stream (fig. 22). Two additional flood-plain boreholes (SH-FB-2 and SH-FB-3) were drilled on the south side of Shoal Creek at site SFP2 (fig. 23) about 5.5 mi upstream from site SFP1. Access to the channel at these two sites was limited to a reach that contained few channel deposits at either site; therefore, no gravel bar-sediment samples were collected at the sites with the flood-plain samples.

Gravel bar-sediment samples from Shoal Creek were collected from 12 locations at 5 sites along the lower 19 mi of Shoal Creek (S1, S2, S3, S4, and S5; fig. 1). Sites S1, S2, S3, and S4 were along about a 6-mi reach of Shoal Creek ranging from about 2.5 mi to about 10.5 mi upstream from Empire

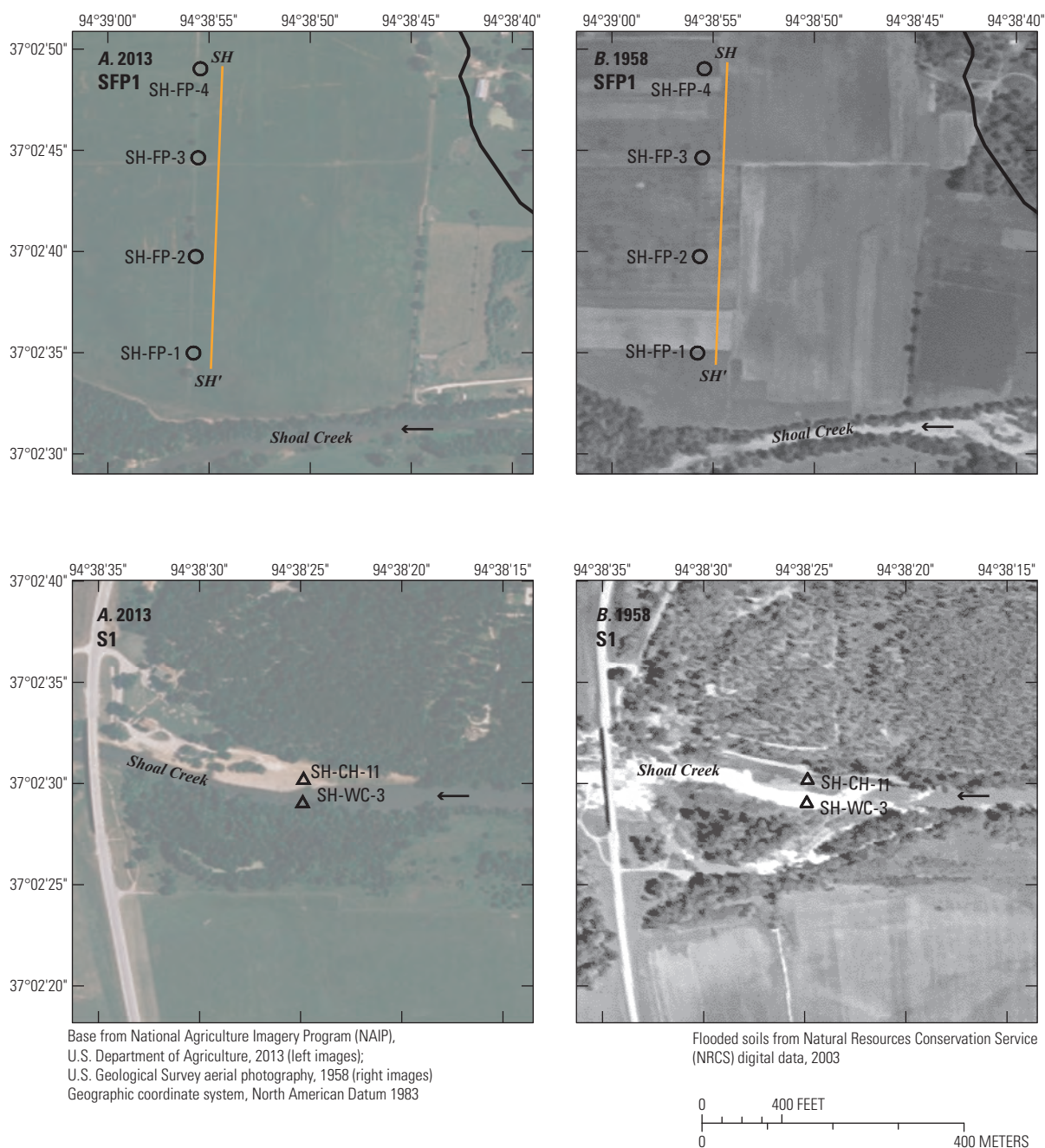
Lake. The upstream most site (S5) was about 10 mi upstream from site S4. Site S4 was about 1,000 ft upstream from the Schifferdecker Road Bridge (fig. 24). This site included three channel sediment cores (SH-CH-1, SH-CH-2, and SH-WC-1) and two nearby flood-plain sample locations (SH-FB-1 and SH-FB-4). Flood-plain locations SH-FB-1 and SH-FB-4 were samples of soil from the side wall of an excavation made by a gravel mining operation (SH-FB-1) and the side of an inactive cut bank on the north side of the creek (SH-FB-4; fig. 24). Three channel sediment cores were collected about 0.1 mi downstream at site S3 (fig. 24). Core SH-CH-5 was on a gravel bar 400 ft upstream from the Schifferdecker Road Bridge on the north side of the channel. Core SH-WC-2 was also upstream from the bridge but inside the wetted channel. Downstream from the bridge, core SH-CH-7 was collected on the south side of the creek (fig. 24). Site S2 was centered on a gravel bar near the City of Joplin's Shoal Creek Wastewater Plant and had two cores (SH-CH-8 and SH-CH-9; fig. 23). Site S1 was on the south side of Galena, Kans., and included the gravel bar cores SH-CH-11 and SH-WC-3 (fig. 22). Two boreholes (SC-A-HD1 and SC-A-HD2) were drilled on a gravel bar about 10 mi upstream from site S4 at site S5 (fig. 24).

Depth and Concentration of Metals in Channel Sediments

A total of 65 samples were collected from 12 locations on gravel-bar deposits along Shoal Creek. The maximum sample depth was 11.9 ft. The maximum depth of sediments that had concentrations of lead and zinc that exceeded the respective CPEC for those metals was 7 ft for lead and 9 ft for zinc. Overall, cores from Shoal Creek generally had concentrations of zinc that exceeded the CPEC at many depths, including the upstream site S5 about 19 mi upstream from Empire Lake. Few samples had exceedances of the TPEC for any MVT-related metals in channel sediments from Shoal Creek.

In the <2-mm size fraction of gravel bar-sediment samples from Shoal Creek, lead concentrations ranged from <13 mg/kg to 183 mg/kg (Smith, 2016; Stream channel sediment samples). Of the 65 samples, 8 samples (12 percent) had lead concentrations greater than the CPEC and only 4 samples (about 6 percent) had concentrations greater than the TPEC. Five of the eight gravel bar-sediment samples greater than the CPEC for lead and three greater than the TPEC for lead were from site S2 at borehole SH-CH-9 (2 to 7 ft). The other samples were from site S3 from borehole SH-CH-7 from 2 to 3 ft (139 mg/kg), site S2 from borehole SH-CH-8 from 0 to 1 ft (181 mg/kg), and site S1 from borehole SH-CH-11 from 1 to 2 ft (130 mg/kg) (Smith, 2016; Stream channel sediment samples; fig. 25).

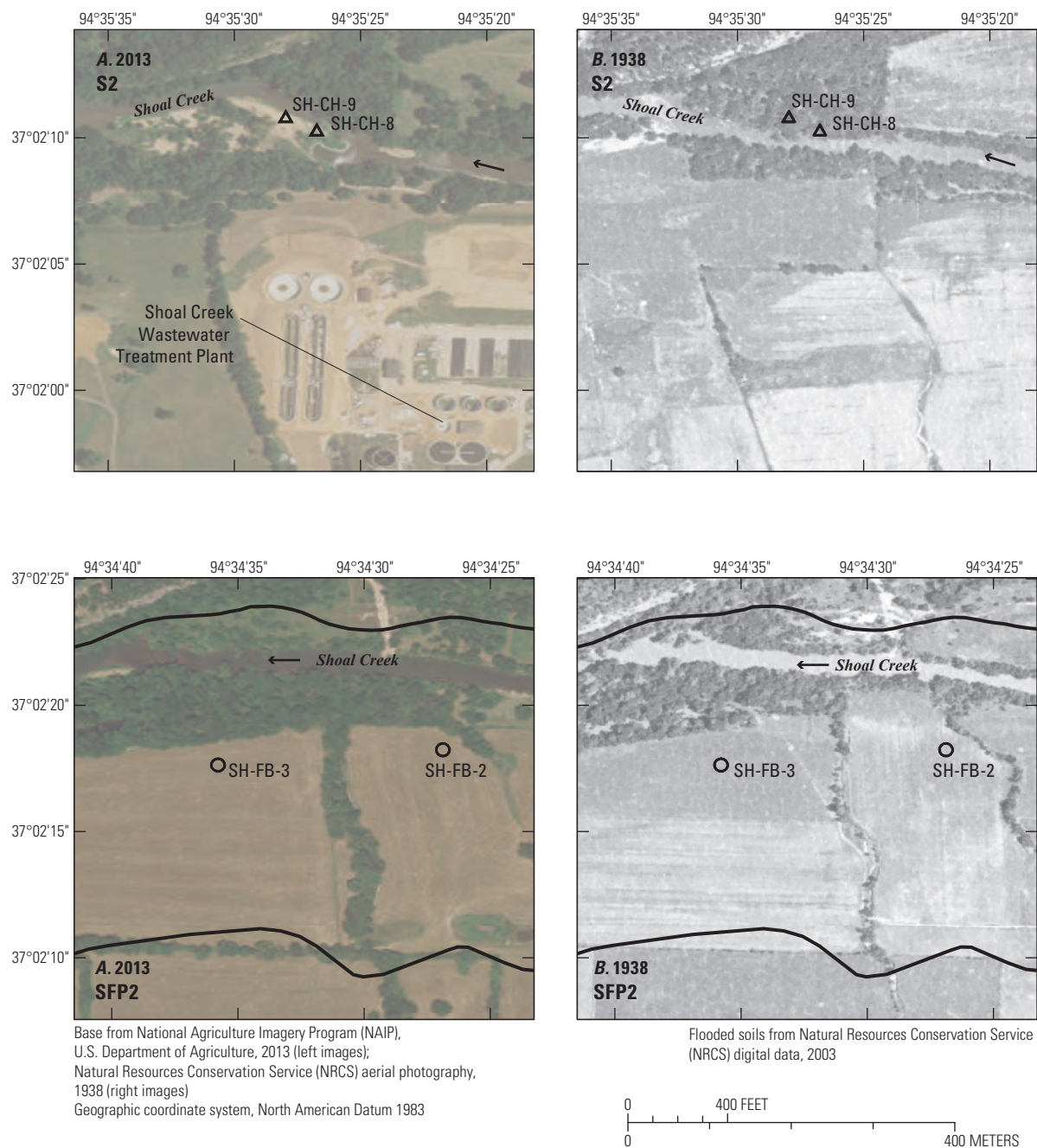
Zinc concentrations in the <2-mm size fraction in samples ranged from 176 mg/kg to 3,010 mg/kg and cadmium concentrations were <12 mg/kg in all samples (Smith, 2016; Stream channel sediment samples). Almost 74 percent of the samples (48 of 65) had zinc concentrations greater than



EXPLANATION

- | | | | |
|---------|---|---------|---|
| | Frequently to occasionally flooded soil | SH-FP-1 | Flood-plain core or sample and identifier |
| SH SH' | Flood-plain transect | SH-CH-1 | Channel core or sample and identifier |
| | Direction of flow | | |
| S1 | Site identifier | | |

Figure 22. Aerial photographs from A, 2013 and B, 1958 showing location of bed-sediment cores and sample locations for sites SFP1 and S1 in Shoal Creek, Missouri, 2012.



EXPLANATION

- Frequently to occasionally flooded soil
← Direction of flow
S2 Site identifier
SH-FB-2 ○ Flood-plain core or sample and identifier
SH-CH-9 ▲ Channel core or sample and identifier

Figure 23. Aerial photographs from A, 2013 and B, 1938 showing location of bed-sediment cores and sample locations for sites S2 and SFP2 in Shoal Creek, Missouri, 2012.

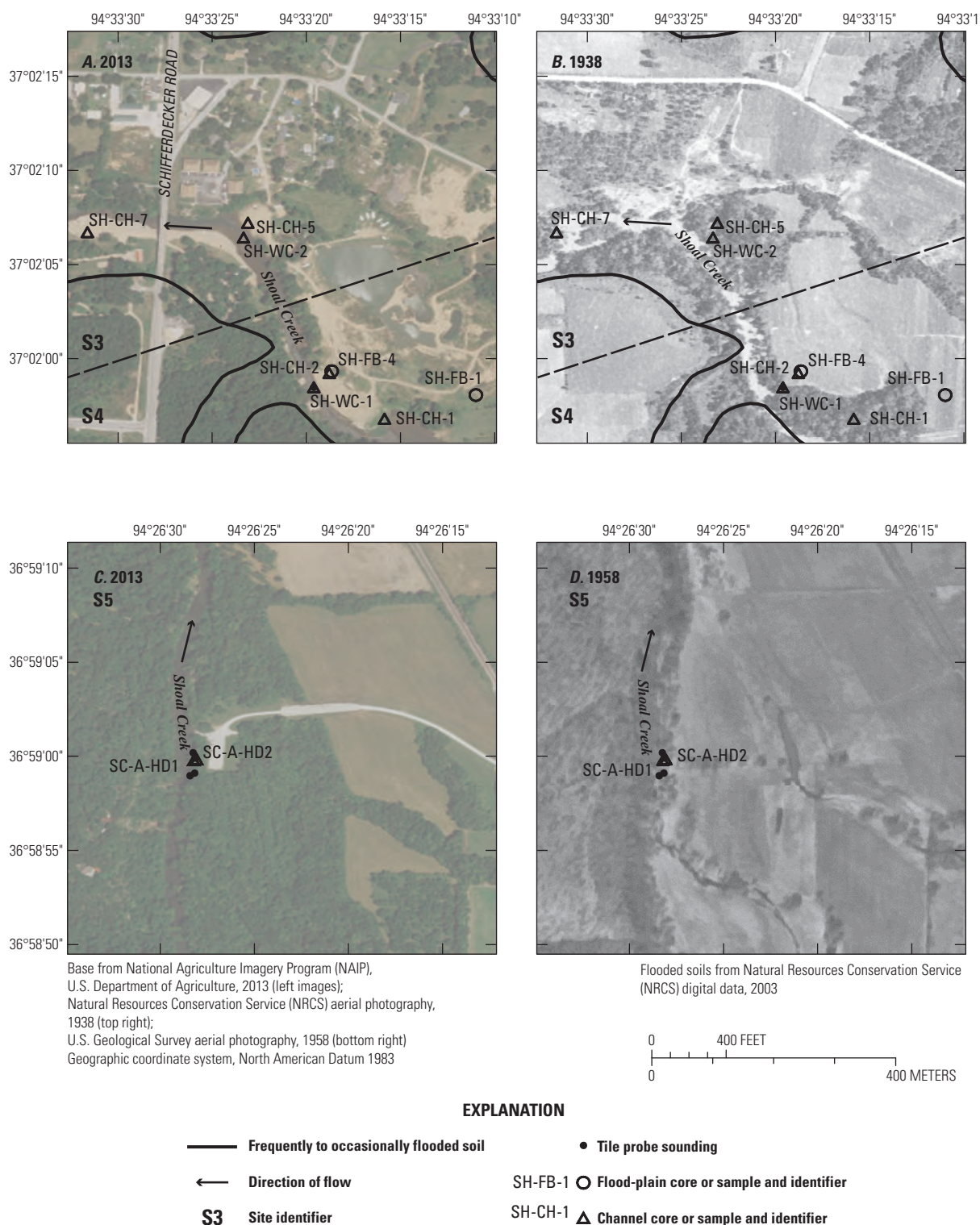


Figure 24. Aerial photographs from A, 2013 and B, 1938 for sites S3 and S4, and from C, 2013 and D, 1958 for site S5 showing location of cores, samples, and tile probes in Shoal Creek, Missouri, 2012.

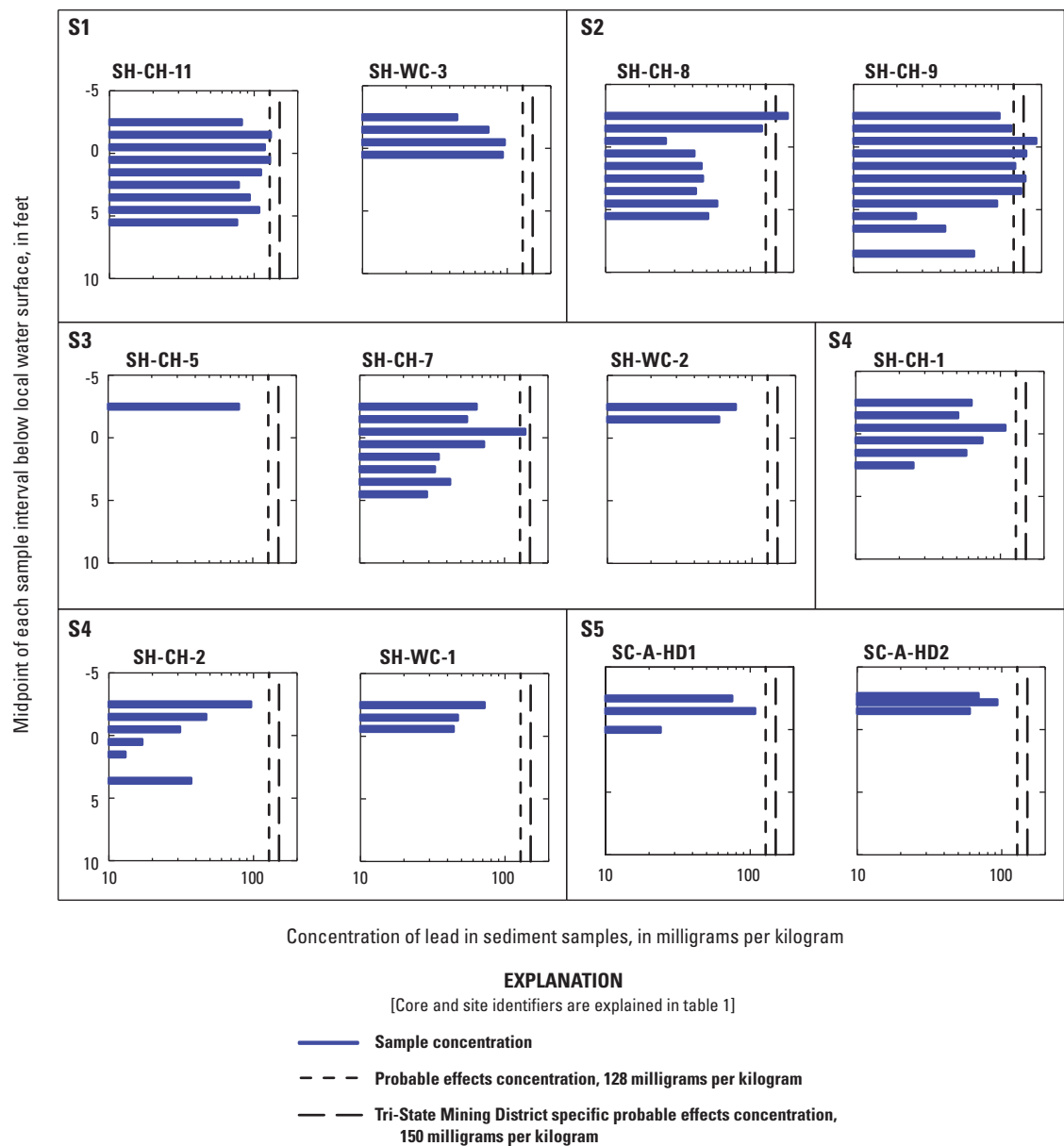


Figure 25. Vertical profiles by core and sample location of lead concentrations in the less than 2-millimeter size fraction of stream channel samples analyzed by x-ray fluorescence in Shoal Creek, Missouri, 2012.

the CPEC, but only one sample had a concentration greater than the TPEC (borehole SH-CH-8 at depth interval 0 to 1 ft (Smith, 2016; Stream channel sediment samples). This sample was collected at the same site (S2) where all four samples exceeding the lead TPEC were found. The wastewater plant outfall has created a large pool (fig. 23), which may act as a trap and allow fine material to collect at this site. Concentrations of zinc that exceeded the CPEC generally extended several feet to as much as 9 ft below the surface of the channel sediment (Smith, 2016; Stream channel sediment samples; fig. 26). Concentrations of zinc in 9 of the 15 samples from site S5 were greater than the CPEC with the maximum of 996 mg/kg in samples from <1 ft deep (Smith, 2016; Stream channel sediment samples). None of the stream channel sediments contained detectable concentrations of cadmium, and only four samples contained concentrations of nickel greater than the LOD of 65 mg/kg.

Estimated Volume of Channel Sediment Contaminated by Mine Waste

The volume of contaminated sediment within sampled gravel bars was estimated for the 9-mi reach of Shoal Creek from site S4 to the upper end of the south arm of Empire Lake (fig. 1). Although channel sediments at site S5 contained zinc concentrations greater than the CPEC, the absence of data along the nearly 10-mi reach between this site and the next downstream site (S4) precluded the estimation of contaminated sediment volume along this reach. The mean thickness of sediment along the lower, 9-mi reach of Shoal Creek that would need excavation based on the CPEC was 4.5 ft, and the mean thickness of sediment that would need excavation based on the TPEC was 0.8 ft (table 5). The total area of studied gravel bars for Shoal Creek was 146,000 ft² (3.4 acres; table 5). Using the mean thickness of contaminated sediment and a total area of sampled gravel bars along this reach of 146,000 ft², the estimated minimum volume of contaminated sediment in gravel bars exceeding the CPEC is about 24,000 yd³ (table 5). The estimated minimum volume of sediment in gravel bars exceeding the TPEC is smaller at about 4,000 yd³ (table 5). These estimates are considered minimum volumes because they were only based on the visible gravel bars and do not include sediment beneath the wetted channel in other features such as pools, and presumably some of these deposits are negatively affected by mine-waste contaminated sediment but were not sufficiently characterized to be included in the volume estimate.

Depth and Concentration of Metals in Flood-Plain Sediments

A total of 80 flood-plain samples were collected from 8 locations along the Shoal Creek flood plain (Smith, 2016; Flood-plain cores). Lead concentrations greater than the CPEC were present in 5 of the 80 (about 6 percent) flood-plain

samples from Shoal Creek. Zinc concentrations exceeded the CPEC in 11 samples (about 14 percent). Flood-plain cores sampled along Shoal Creek tended to have concentrations of lead and zinc below the CPEC and TPEC, even in the upper 2 ft of depth; however, the samples from borehole SH-FB-4 had lead or zinc concentrations that exceeded the CPEC and TPEC to depths greater than 8 ft (Smith, 2016; Flood-plain cores; figs. 15, 16). All 5 of the CPEC exceedances by lead concentration and 9 of the 11 CPEC exceedances by zinc were from this single location. Samples at this location were collected from a cut bank on the north side of Shoal Creek at site S4 (fig. 24). It is possible that the stream channel at this location has migrated southward leaving a thick metal-rich deposit of recently (post mining) deposited sediment but comparison of the 1938 and 2013 imagery the migration of what would be defined as the thalweg is not definitive (fig. 24). The area also has active gravel mining and other disturbances such as maintenance of the nearby gravel road for access to the gravel bar or erosion control may have occurred since 1938, and this material may have been reworked at some point as well. This would mean that nearby metal-rich surficial material could have been filled and graded in this area, which could create an anthropogenic sediment profile that is not representative of the natural deposition of sediment from the nearby stream.

Tar Creek

Tar Creek has a drainage area of 53 mi² at its confluence with the Neosho River and is approximately 19.3 mi in length from the headwaters to the mouth. Approximately 7.4 mi of the creek was studied and was used in the estimation of the volume of contaminated sediment (table 5).

Site Selection and Description

Tar Creek gravel bar-sediment samples and flood-plain samples were collected during a period of 3 weeks in the summer of 2012. The Tar Creek study reach consisted of multiple sites including 22 stream channel cores and 13 flood-plain cores collected in gravel bars, wetted channels, and the adjacent flood plain. One of the more intensively studied sites (TR4) was located just east of Miami, Oklahoma. Transect TR2–TR2' with five cores at site TRFP2 (TAR-FP2-1, TAR-FP2-2, TAR-FP2-3, TAR-FP2-4, and TAR-FP2-5) were drilled across the flood plain (figs. 1 and 27). Three additional flood-plain cores (TAR-FB-1, TAR-FB-2, and TAR-FB-3) were located off transect TR2–TR2'. Cores TAR-FB-2 and TAR-FB-3 were in what may have been an older channel of the creek. Core TAR-FB-1 was in an area to contrast the locations of cores TAR-FB-2 and TAR-FB-3 and was located slightly upstream from the other cores and farther away from the stream (1,500 ft). Near flood-plain transect TR2–TR2' were six stream channel cores (site TR4); two cores (TAR-TR-4 and TAR-4-HC1) were on a gravel bar downstream from the flood-plain transect TR2–TR2' and four cores (TAR-BAR-1,

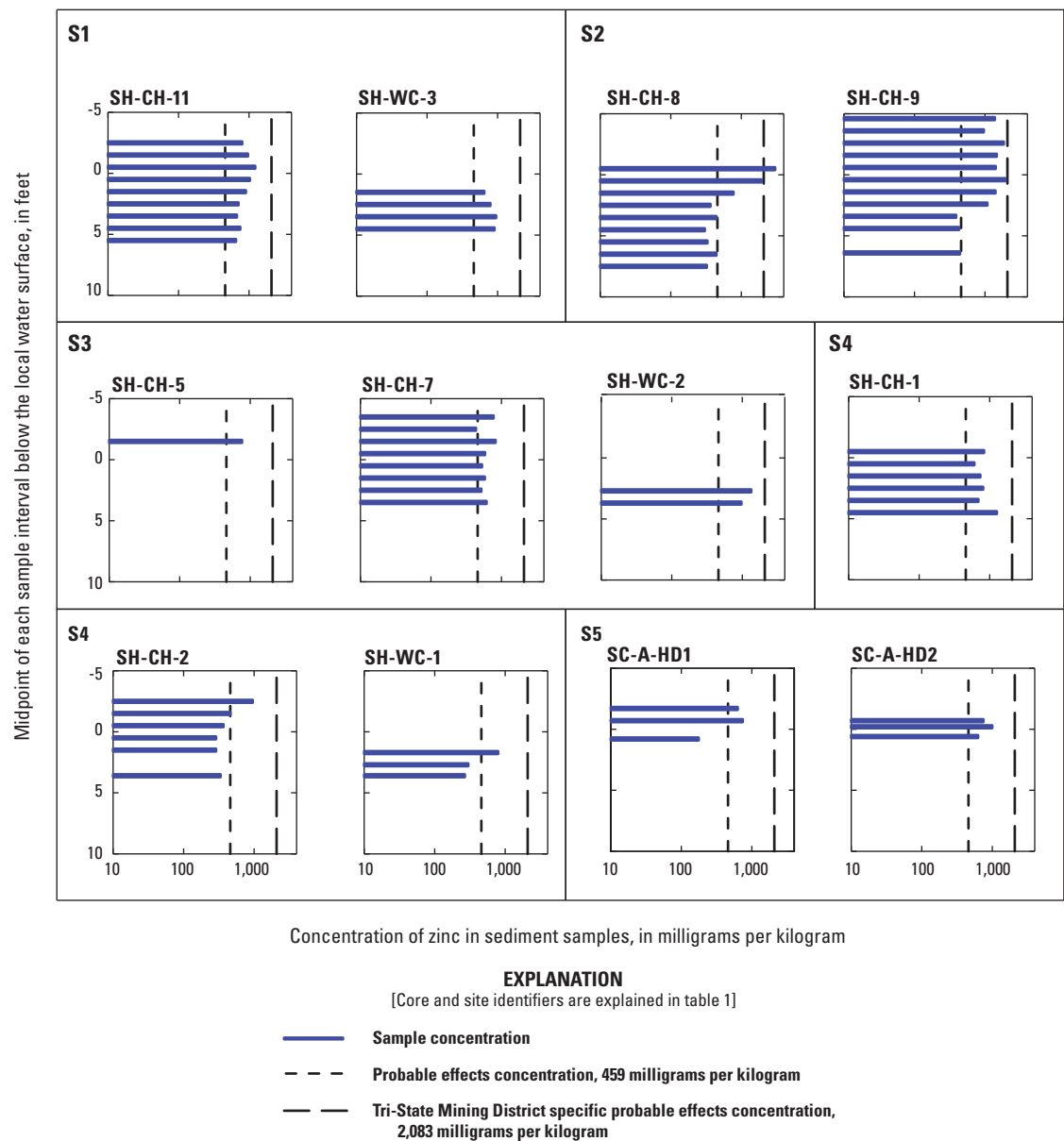


Figure 26. Vertical profiles by core and sample location of zinc concentrations in the less than 2-millimeter size fraction of stream channel samples analyzed by x-ray fluorescence in Shoal Creek, Missouri, 2012.

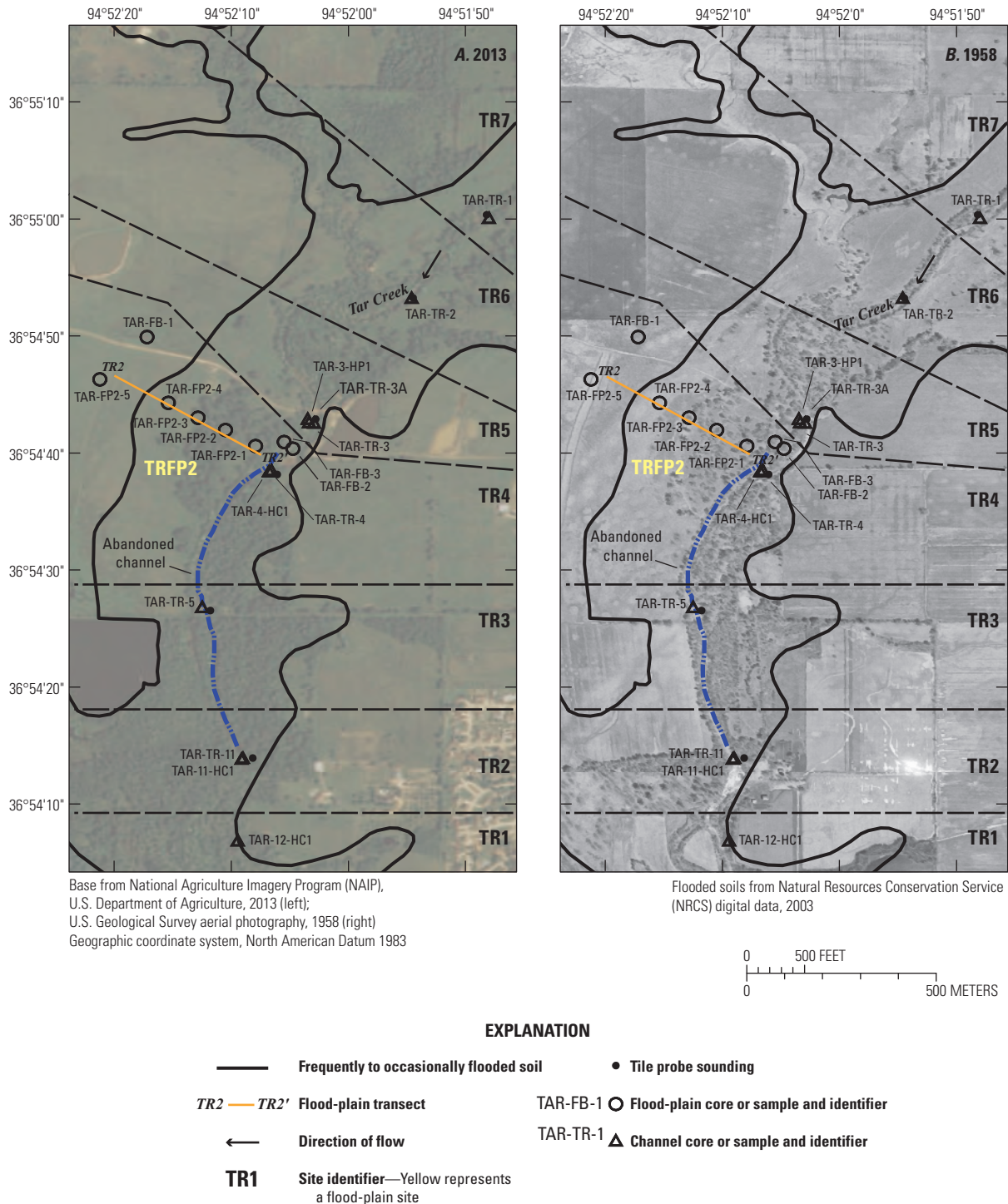


Figure 27. Aerial photographs from A, 2013 and B, 1958 showing location of sediment cores, samples, and tile probe soundings for sites TR7, TR6, TR5, TRFP2, TR4, TR3, TR2, and TR1 on Tar Creek, Oklahoma, 2011.

TAR-3-HP1, TAR-TR-3, and TAR-TR-3A were on a gravel bar upstream from the flood-plain transect TR2–TR2'. Within about 0.5 mi of site TR4 were six additional core and sample locations at five different sites. Sites TR7 (TAR-TR-1) and TR6 (TAR-TR-2) are upstream and sites TR3 (TAR-TR-5), TR2 (TAR-11-HC1 and TAR-TR-11), and TR1 (TAR-12-HC1) are downstream sites (fig. 27).

Another area, east of Commerce, Okla., and about 2 mi upstream from the flood-plain transect TR1–TR1' at site TRFP1, had 6 sites with 11 gravel bar-sediment samples and sample locations and 5 flood-plain cores. Those sites (fig. 28), in order from upstream to downstream, are TR12 (TAR-8-VC1 and TAR-TR-8), TR11 (TAR-FB-4, TAR-9-PT1, TAR-9-VC1, TAR-9-VC1A, and TAR-TR-9), TRFP1 (TAR-FP1-1, TAR-FP1-2, TAR-FP1-3, and TAR-FP1-4), TR10 (TAR-TR-7), TR9 (TAR-TR-6 and TAR-6-VC1), and TR8 (TAR-TR-10).

Depth and Concentration of Metals in Channel Sediments

A total of 51 samples were collected on gravel bar deposits along Tar Creek. The maximum sample depth was 6.6 ft. Overall, concentrations of lead and zinc generally exceeded the CPEC in cores from the surface to the top of bedrock that was generally <5 ft deep and in some cases <1 ft deep. Lead and zinc concentrations generally also exceeded the TPEC from the surface to the maximum depth. Lead concentrations, in the <2-mm size fraction in these samples, ranged from a single non-detection (<13 mg/kg) to 2,540 mg/kg (Smith, 2016; Stream channel sediment samples). Out of the 51 gravel bar-sediment samples, all but 6 (88 percent) had lead concentrations greater than the CPEC and the TPEC. All samples collected in Tar Creek that exceeded the CPEC for lead also exceeded the TPEC (Smith, 2016; Stream channel sediment samples; fig. 29). Zinc concentrations, in the <2-mm size fraction in these samples, ranged from 63.0 mg/kg to 46,600 mg/kg (Smith, 2016; Stream channel sediment samples). Out of the 51 stream channel samples, all but 2 (96 percent) had zinc concentrations that exceeded the CPEC, and all but 5 had concentrations that exceeded the TPEC (Smith, 2016; Stream channel sediment samples; fig. 30).

Cadmium concentrations, in the <2-mm size fraction in these cores, ranged from non-detection (<12 mg/kg) to 131 mg/kg (Smith, 2016; Stream channel sediment samples). Of 51 stream channel samples, 35 had detectable cadmium (69 percent) and exceeded the CPEC and TPEC. Cadmium concentrations exceeded the CPEC and TPEC in samples from multiple depths. The number of cadmium concentration exceedances may be greater because the LOD (12 mg/kg) is larger than the CPEC (4.98 mg/kg) and TPEC (11.1 mg/kg).

Of the 51 samples, 31 (61 percent) had concentrations of nickel that exceeded the CPEC (48.6 mg/kg). There is no TPEC for nickel. Exceedances of the CPEC for nickel generally extended several feet below the surface and were present as deep as 6.6 ft (sample TAR-9-VC1A). Nickel CPEC

exceedance frequencies may be underreported because the LOD (65 mg/kg) is larger than the CPEC (48.6 mg/kg).

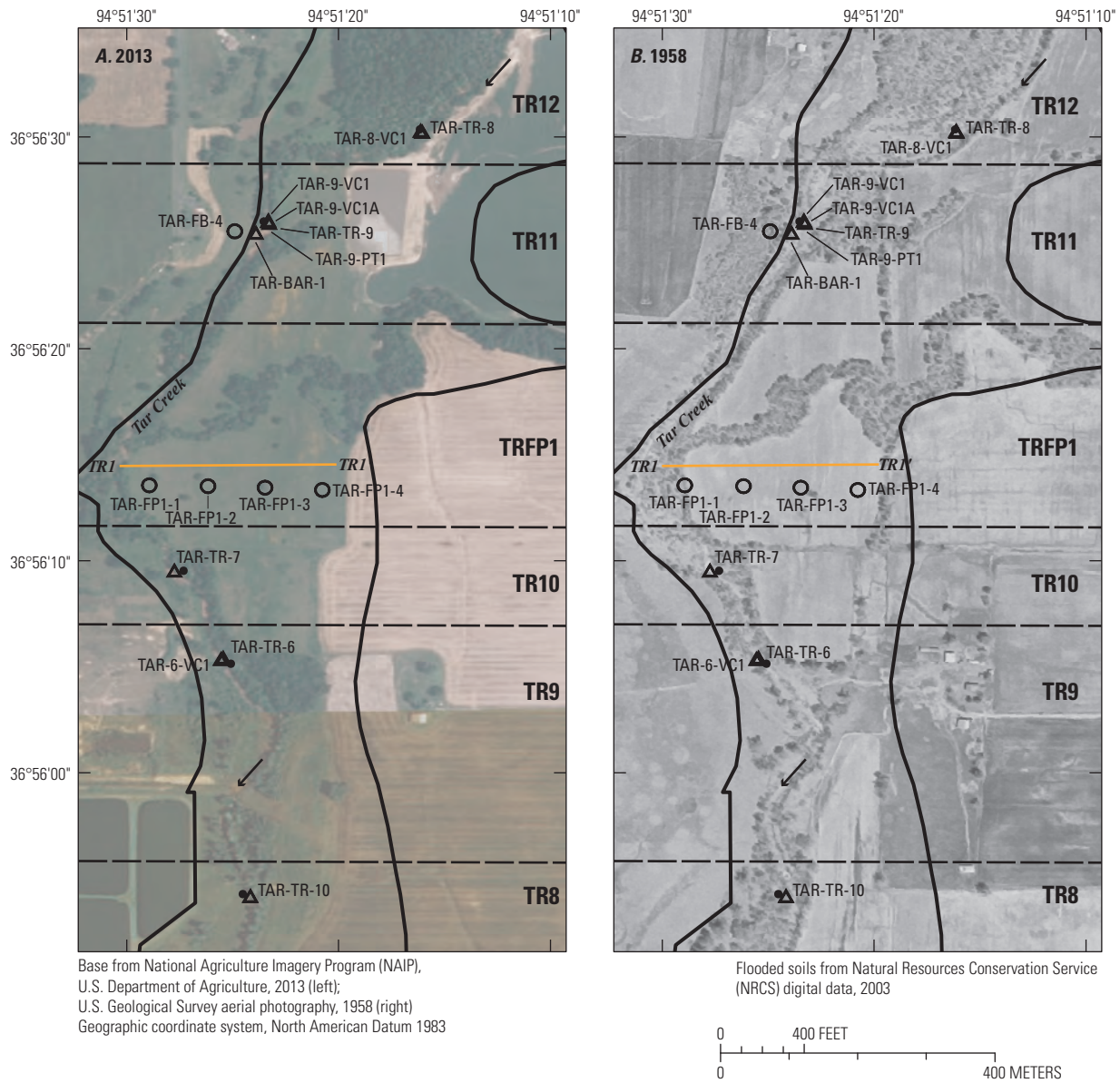
Estimated Volume of Channel Sediment Contaminated by Mine Waste

The total volume of sediment in Tar Creek gravel bar deposits that had concentrations of lead and zinc that exceeded the CPEC and the TPEC was estimated using data collected in this study. The estimated volume was computed for the 7.4-mi Tar Creek reach from about 800 ft upstream from site TR12 to the creek's confluence at the Neosho River. Although large mine-waste piles and past mining areas are upstream from the site chosen as the farthest upstream extent of the contaminated sediment-volume analysis, no data were collected upstream from the TR12 location. The mean thickness of sediment that exceeded the CPEC and the TPEC for Tar Creek was 1.1 ft (table 5). The total area of studied gravel bars for Tar Creek was 230,000 ft² (5.3 acres; table 5). The estimated minimum volume of sediment in sampled gravel bars exceeding the CPEC and TPEC for the chosen reach of Tar Creek was 9,000 yd³ (table 5). These estimates are considered minimum volumes because they were only based on the visible gravel bars and do not include sediment beneath the wetted channel in other features such as pools, and presumably some of these deposits are negatively affected by mine-waste contaminated sediment but were not sufficiently characterized to be included in the volume estimate.

Depth and Concentration of Metals in Flood-Plain Sediments

A total of 142 samples were collected from 13 locations along the Tar Creek flood plain (Smith, 2016; Flood-plain cores). Concentrations of lead and zinc in flood-plain samples from Tar Creek generally exceeded the CPEC and the TPEC in the upper 1 or 2 ft of soil, and the concentrations were generally greater than concentrations in samples deeper than 2 or 3 ft by an order of magnitude or more. Lead and zinc concentrations in flood-plain samples seemed to decrease with distance from the creek. The 7 cores located within 450 ft of the creek had lead and zinc concentrations that exceeded the CPEC and the TPEC, whereas the 6 cores at distances greater than 450 ft from the creek had no exceedances. Lead concentrations in 11 of 142 analyzed flood-plain core sections from Tar Creek exceeded the CPEC and the TPEC. Concentrations of zinc exceeded the CPEC in 21 flood-plain core sections and exceeded the TPEC in 9 flood-plain core sections. Cadmium concentrations exceeded the CPEC and the TPEC in 25 of 33 flood-plain core sections where cadmium was analyzed.

Site TRFP1 (figs. 1, 28) was east of Commerce, Okla. This site had four cores (in order from nearest to the creek to the farthest): TAR-FP1-1, TAR-FP1-2, TAR-FP1-3, and TAR-FP1-4 (fig. 28). The lead concentration in samples from TAR-FP1-1 exceeded the CPEC and TPEC at depths <2 ft



EXPLANATION

- | | | | |
|--|---|--|--|
| | Frequently to occasionally flooded soil | | Tile probe sounding |
| | Flood-plain transect | | TAR-FB-4 Flood-plain core or sample and identifier |
| | Direction of flow | | TAR-TR-8 Channel core or sample and identifier |
| | Site identifier | | |

Figure 28. Aerial photographs from *A*, 2013 and *B*, 1958 showing location of sediment cores, samples, and tile probe soundings for sites TR12, TR11, TRFP1, TR10, TR9, and TR8 on Tar Creek, Oklahoma, 2011.

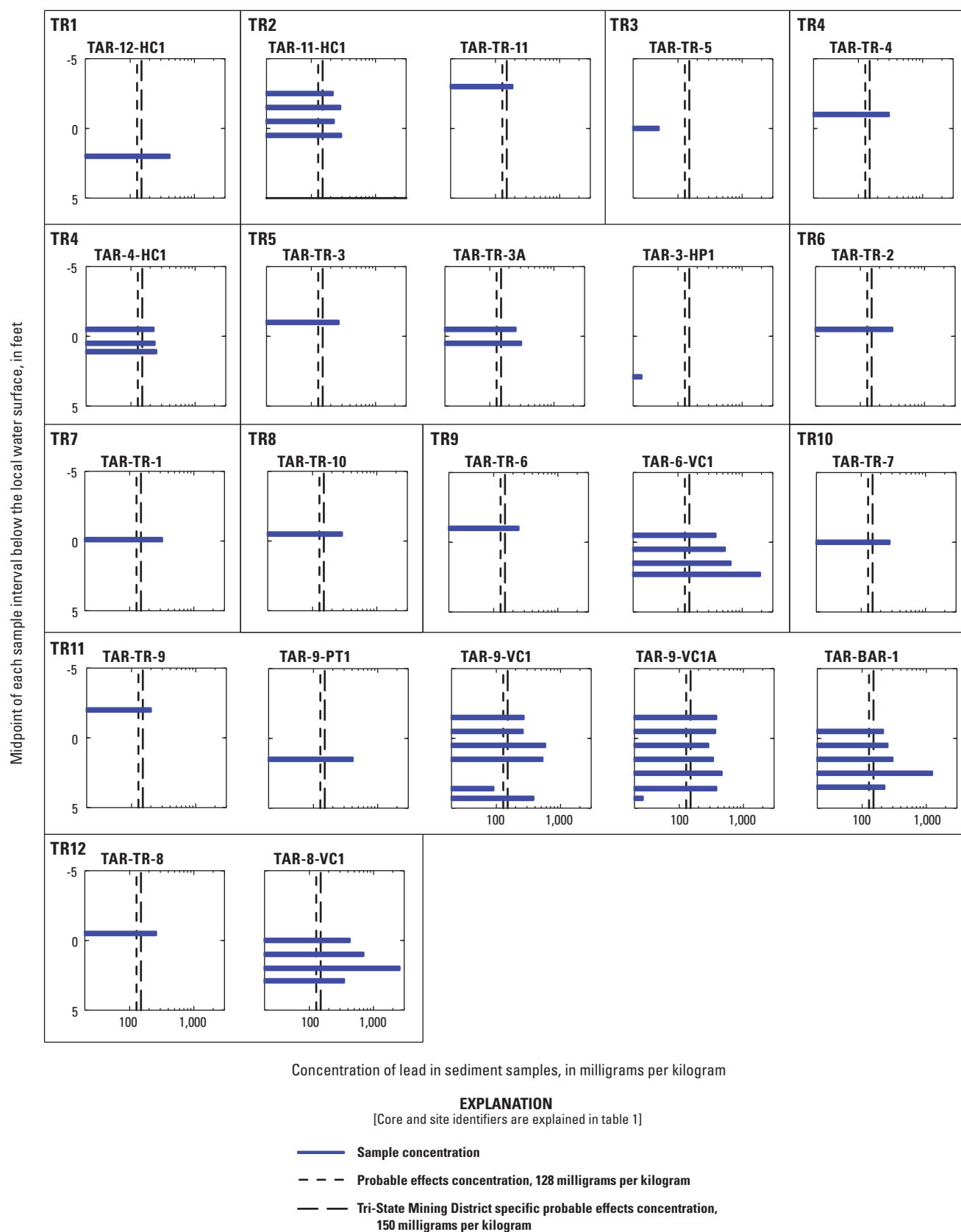


Figure 29. Vertical profiles by core and sample location of lead concentrations in the less than 2-millimeter size fraction of stream channel samples analyzed by x-ray fluorescence in Tar Creek, Oklahoma, 2011.

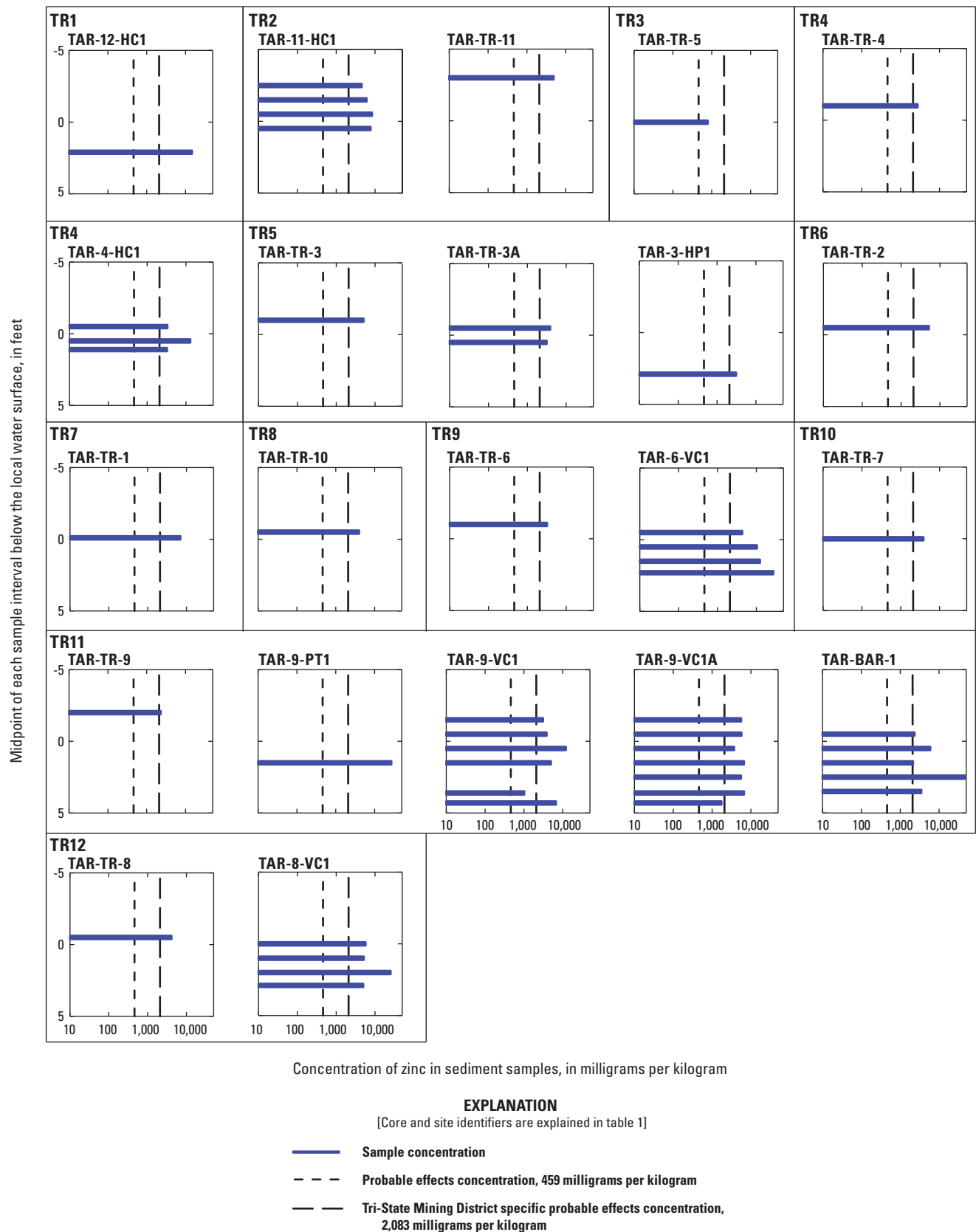


Figure 30. Vertical profiles by core and sample location of zinc concentrations in the less than 2-millimeter size fraction of stream channel samples analyzed by x-ray fluorescence in Tar Creek, Oklahoma, 2011.

and depths between 4 and 5 ft with the greatest concentrations in the top 2 ft (1,120 mg/kg in the interval 0 to 1 ft and 2,190 mg/kg in the interval 1 to 2 ft). The largest zinc concentrations were also in the top 2 ft (10,700 mg/kg in the interval 0 to 1 ft and 11,900 mg/kg in the interval 1 to 2 ft). Zinc concentration in core TAR-FP1-1 exceeded the CPEC for all samples from depths <7 ft but only exceeded the TPEC for depths <3 ft and the depth interval between 4 and 5 ft. Lead and zinc concentrations in samples from depths <1 ft in cores TAR-FP1-2 and TAR-FP1-3 exceeded the CPEC and TPEC, except for zinc concentrations in TAR-FP1-3, which only exceeded the CPEC. The lead and zinc concentrations generally decreased with depth in core TAR-FP1-4, as they did generally for all flood-plain cores, but concentrations in core TAR-FP1-4 did not exceed the PECs. Site TR11 was about 1,300 ft upstream from site TRFP1 and had a single flood-plain core (TAR-FB-4). Core TAR-FB-4 was within 100 ft of the creek, and lead concentrations exceeded the CPEC and the TPEC only in the sample from 0 to 1 ft (220 mg/kg), whereas the zinc concentration in that sample exceeded only the CPEC (1,810 mg/kg) (Smith, 2016; Flood-plain cores; fig. 16).

Site TRFP2 (fig. 27) is the downstream flood-plain site. A total of eight flood-plain cores were drilled at this location. Cores TAR-FB-1, TAR-FP2-2, TAR-FP2-3, TAR-FP2-4, and TAR-FP2-5 were located more than 450 ft from the creek and none of the 54 samples from these cores had concentrations of lead or zinc that exceeded the respective CPEC or TPEC (Smith, 2016; Flood-plain cores; figs. 15, 16). TAR-FP2-1 was <300 ft from the creek, and the lead concentration at 0–1 ft below soil surface (190 mg/kg) exceeded the CPEC and TPEC, whereas the zinc concentration in that depth interval (795 mg/kg) exceeded the CPEC only. Cores TAR-FB-2 and TAR-FB-3 were the nearest to the creek (<300 ft) and had concentrations at various depths that exceeded the CPEC or both PECs for lead and zinc. Concentrations of lead and zinc in core TAR-FB-2 exceeded the CPEC and TPEC for all samples from depths <3 ft, whereas for zinc concentrations also exceeded the CPEC for all samples from depths 3–6 ft. Lead concentrations from samples <3 ft deep from TAR-FB-2 were 1 to 2 orders of magnitude greater than concentrations from samples deeper than 3 ft, and zinc concentrations from samples <6 ft deep averaged more than 1 order of magnitude greater than concentrations from samples deeper than 6 ft. Concentrations in samples from core TAR-FB-3 exceeded the CPEC for lead at depths <1 ft and for zinc at depths <3 ft and in the 9 to 10 ft depth interval. The lead and zinc concentrations in core TAR-FB-3 exceeded the TPEC only for the sample from depth 0–1 ft. Like core TAR-FB-2, concentrations of lead and zinc less than the CPEC were generally more than 1 order of magnitude less than the concentrations that exceeded the CPEC (Smith, 2016; Flood-plain cores; figs. 15, 16).

Spring River

The Spring River has a drainage area of 2,590 mi² where it enters the Grand Lake O' the Cherokees and is approximately 133.6 mi in length. The Spring River was heavily affected by lead and zinc mining in the TSMD because the Spring River and many of its tributary streams received sediment loads including waste material derived from mining activities.

Site Selection and Description

Spring River gravel bar-sediment samples were collected during a 1-week period in the summer of 2012. Juracek (2013) completed a study on the flood plain located adjacent to the downstream gravel bar site sampled in this study so the Spring River flood plain was not sampled during this study. Estimates of the volume of contaminated sediment along the Spring River were also not made because of the small number of locations sampled. The Spring River study reach consisted of two sites (SR1 and SR2; fig. 31) where five gravel bar cores were collected. Three cores (SR-CH-1, SR-CH-2, and SR-CH-3) were drilled at site SR1 just north of Baxter Springs, Kans. (figs. 1, 31). Two cores (SR-CH-4 and SR-CH-5) were drilled at site SR2 near the mouth of Turkey Creek, north of Galena, Kans. (figs. 2, 31).

Depth and Concentration of Metals in Channel Sediments

A total of 52 samples were collected from 5 locations on gravel bar deposits along the Spring River (Smith, 2016; Stream channel sediment samples). The maximum depth sampled was 19.1 ft. Lead concentrations ranged from 14 to 390 mg/kg and exceeded the CPEC in 7 samples (14 percent). Zinc concentrations ranged from 225 to 5,020 mg/kg exceeding the CPEC in 46 (89 percent) of the samples. Lead concentrations in gravel bar-sediment samples at the site downstream from Empire Lake (SR1) were generally less than concentrations in samples collected at the upstream site (SR2). Lead concentrations in the <2-mm size fraction from all 38 samples from the downstream site (SR1) were <105 mg/kg, which was less than the CPEC; however, zinc concentrations exceeded the CPEC in 32 of these samples. Lead concentrations at the upstream site (SR2) were larger, exceeding the CPEC and TPEC in 7 of the 14 samples with the largest concentration of 390 mg/kg detected in a sample from 1 to 2 ft deep (Smith, 2016; Stream channel sediment samples). Zinc exceeded the CPEC in all 14 samples from the upstream site and exceeded the TPEC in 7 samples from site SR2. Lead and zinc concentrations in core SR-CH-4 from upstream site SR2 exceeded the respective CPEC and TPEC in all samples from depths up to 5 ft (Smith, 2016;

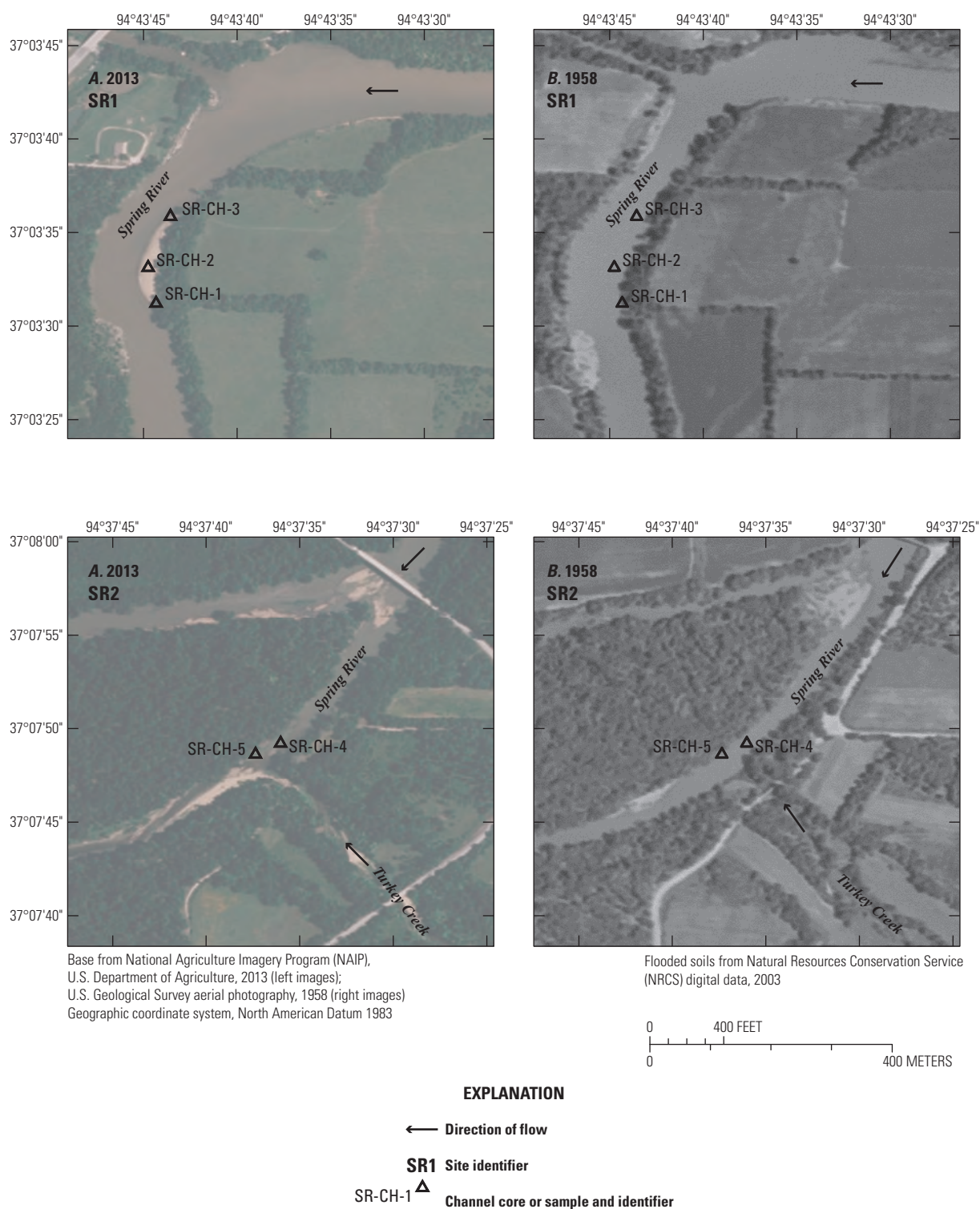


Figure 31. Aerial photographs from A, 2013 and B, 1958 showing location of sediment cores and samples for sites SR1 and SR2 on Spring River, Kansas, 2012.

Stream channel sediment samples; fig. 32). Lead and zinc concentrations in core SR-CH-5 from site SR2 exceeded the respective CPEC and TPEC in both samples from depths <2 ft.

Cadmium was detected in 7 of the 52 (14 percent) samples at a maximum concentration of 22 mg/kg. The detected cadmium concentrations in samples exceeded the CPEC and TPEC at site SR2 near the mouth of Turkey Creek. Cadmium concentrations in samples from core SR-CH-4 exceeded both PECs at depths <5 ft, and cadmium concentrations in samples from core SR-CH-5 exceeded both PECs for depths <2 ft. The number of cadmium concentration exceedances may be greater because the LOD (12 mg/kg) is larger than the CPEC (4.98 mg/kg) and TPEC (11.1 mg/kg).

Nickel concentrations in samples from Spring River also had several exceedances of the CPEC at one or more depths in each of four cores. The CPEC for nickel is less than the LOD (65 mg/kg) for nickel, so the frequency of nickel concentration exceedances of PECs may be underreported. Ten of the 52 samples (19 percent) had measured exceedances of the CPEC.

Summary and Conclusions

The Tri-State Mining District (TSMD) covers about 2,500 square miles (mi²) in southwest Missouri, northeast Oklahoma, and southeast Kansas and has a rich history of lead and zinc mining beginning in the early 1800s and continued through the mid-1900s. Most of the ore deposits were in Jasper and Newton Counties in Missouri, Ottawa County in Oklahoma, and Cherokee County in Kansas. More than 100 years of mining in the area has left a legacy of metal-contaminated mine-waste areas, contaminated soils and stream sediment, and contaminated groundwater in the region.

Although previous work has been done to characterize the spatial extent of surficial streambed sediments contaminated by mine waste in the TSMD, little information is available on the depth or thickness of contaminated sediments in the streams. Based on surficial streambed-sediment samples compiled from various sources, it is estimated that approximately 49 miles of Center Creek, Turkey Creek, Shoal Creek,

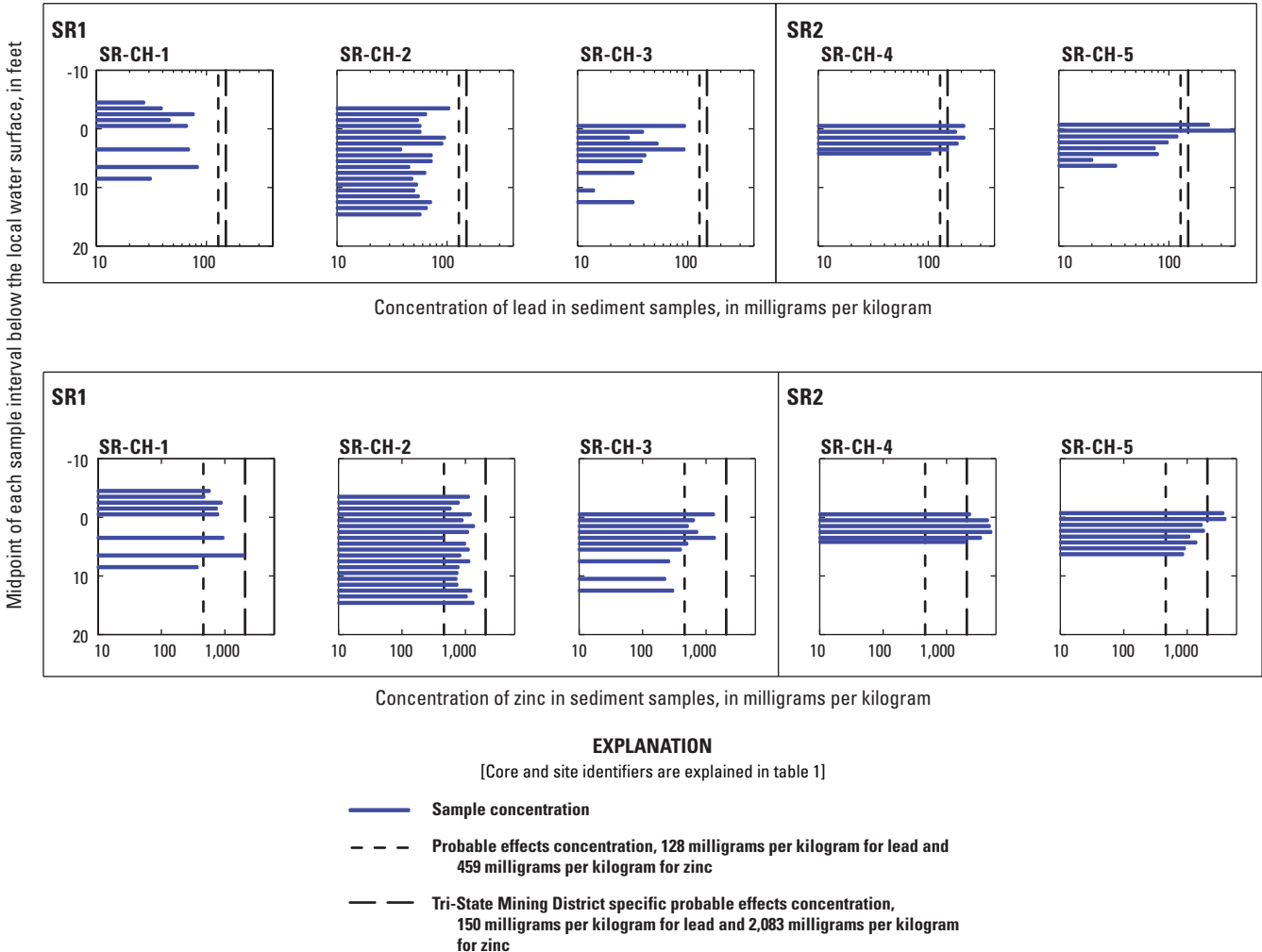


Figure 32. Vertical profiles by core and sample location of lead and zinc concentrations in the less than 2-millimeter size fraction of gravel bar-sediment samples analyzed by x-ray fluorescence, Spring River, Kansas, 2012.

and Tar Creek have streambed sediments that have a moderate to high risk for toxicity to benthic invertebrates, as do sediments in the entire reach of the Spring River downstream from the mouth of Center Creek. Information on the depth of contamination is important to the U.S. Fish and Wildlife Service (USFWS) and other natural resource agencies entrusted with assessing damage to the ecosystem and evaluating restoration alternatives in the TSMD. Determining the depth of metal contamination is difficult in saturated streambed sediment because of the wide range of grain size of the sediments (silt and sand interspersed with coarse gravels and large cobbles) that are difficult to sample with traditional methods that are generally used to collect sands, silts, and clays. The USFWS requested assistance from the U.S. Geological Survey to provide information on the depth of mine-waste contaminated sediments in selected streams in the TSMD. The U.S. Geological Survey set the goals of (1) determination of the relation between concentration and depth for lead, zinc, and cadmium in channel sediments and flood-plain sediments, and (2) determination of the volume of channel sediment from the surface to the maximum depth with concentrations of lead, zinc, and cadmium that exceeded sediment-quality guidelines.

The large area of the TSMD required an array of methods for collecting samples from the stream channels along selected stream reaches and adjacent flood plains. The initial approach was to identify a representative reach along each stream that would be studied and this selected reach would include several geomorphic channel units, such as riffle, run, and pool. Several possible study sites along each stream were identified, but during an initial field reconnaissance of the area, landowner permission to access was not granted at most proposed study sites. Alternative study sites were selected that often were shorter in length and contained fewer geomorphic channel features. In an effort to provide more spatial data on depth of mine-waste contaminated sediments along each stream, additional study locations focusing on gravel bars were added along each stream. Collection of channel sediments focused primarily on gravel bars, and the thickness of sediments was determined using various coring techniques and a tile probe.

Five streams in the TSMD were selected for study: Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and the Spring River. These streams were selected because they drain mined areas, are spatially distributed across the TSMD, and have a range of drainage areas—Turkey Creek (46 mi²), Tar Creek (53 mi²), Shoal Creek (251 mi²), and Center Creek (300 mi²). The Spring River has a drainage area of about 2,422 mi² from the downstream-most sampling site near Baxter Springs, Kansas, but the overall drainage area from its mouth at the Grand Lake O' the Cherokees is 2,590 mi².

Volume of gravel-bar sediment is considered to be distributed in two forms, gravel bars and the wetted channel, and this study focused on gravel bars. Most of the readily available sediment is found in gravel bars for large to moderate streams and characterization of gravel-bar sediments in this study focused on gravel bars with some additional samples collected in adjacent areas. Estimates of the volume of contaminated

gravel bar deposits were computed relative to two benchmarks of contamination—that is, for both probable effects concentration (PEC) values (consensus PEC [CPEC] and Tri-State Mining District specific PEC [TPEC])—because of the importance of such information to the USFWS and other natural resource agencies of the TSMD for assessing damage to the ecosystem and evaluating restoration alternatives. The maximum depth of contamination was determined as the maximum depth where either the lead or zinc concentration exceeded the respective PEC values. Cadmium concentrations were not used to determine contaminated sediment depths because the limit of detection (LOD) for cadmium from the x-ray fluorescence (XRF) analysis (12 milligrams per kilogram [mg/kg]) was larger than the cadmium PECs: CPEC (4.98 mg/kg) and TPEC (11.1 mg/kg). Thus, no sample analyzed by XRF could be determined with certainty from any depth to have a cadmium concentration below either PEC value.

To efficiently analyze the large number of samples collected (357 stream channel samples and 379 flood-plain samples) in this study, all samples were analyzed using the XRF. Several quality control and quality assurance procedures were implemented to ensure the quality of the data acquired using the XRF. A series of standards and blanks were analyzed at the beginning, end, and several times throughout the day when environmental samples were analyzed. In addition to standards, triplicate and septuplet analyses of the selected flood-plain cores were done during the analysis.

During the study, more than 700 sediment samples were collected from borings at multiple sites along Center Creek, Turkey Creek, Shoal Creek, Tar Creek, and Spring River in order to characterize the vertical extent of mine waste in select streams in the TSMD. The largest concentrations of lead, zinc, and cadmium in gravel bar-sediment samples generally were detected in Turkey Creek and Tar Creek and the smallest concentrations were detected in Shoal Creek followed by the Spring River. Gravel bar-sediment samples from Turkey Creek exceeded the CPEC for cadmium (minimum of 70 percent of samples), lead (94 percent), and zinc (99 percent) at a slightly higher frequency than similar samples from Tar Creek (69 percent, 88 percent, and 96 percent, respectively). Gravel bar-sediment samples from Turkey Creek also contained the largest concentrations of cadmium (174 milligrams per kilogram [mg/kg]) and lead (7,520 mg/kg) detected; however, the largest zinc concentration (46,600 mg/kg) was detected in a gravel bar-sediment sample from Tar Creek. In contrast, none of the 65 streambed-sediment samples from Shoal Creek contained cadmium above the x-ray fluorescence reporting level of 12 mg/kg, and lead and zinc exceeded the CPEC in only 12 percent and 74 percent of samples, respectively. In most cases, concentrations of lead and zinc above the CPEC or TPEC were present at the maximum depth of boring, which indicated that nearly the entire thickness of sediment in the stream has been contaminated by mine wastes. Approximately 284,000 cubic yards of channel sediment from land surface to the maximum depth that exceeded the CPEC and approximately 236,000 cubic yards of channel sediment from land

surface to the maximum depth that exceeded the TPEC were estimated along 37.6 of the 55.1 miles of Center Creek, Turkey Creek, Shoal Creek, and Tar Creek examined in this study. Mine-waste contamination reported along additional reaches of these streams is beyond the scope of this study. Flood-plain cores collected in the TSMD generally only had exceedances of the CPEC and TPEC for lead and zinc in the top 1 or 2 feet of soil with a few exceptions, such as cores in low areas near the stream or cores in areas disturbed by past mining.

A total of 89 gravel bar-sediment samples from 24 locations were collected from gravel bar deposits along the lower 18.6 miles of Center Creek. The maximum sample depth was 9.5 ft below the gravel bar surface. Most of the gravel bar-sediment samples from Center Creek exceeded the CPEC and the TPEC for lead or zinc at five (C1, C2, C3, C4, and C5) of the six sites along this stream. Site C6 is upstream from most of the historic mining activity in the Center Creek basin, and none of the samples from this site had concentrations of lead, or zinc that exceeded the CPEC or TPEC or concentrations of cadmium that exceeded the LOD. Overall, median concentrations of lead and zinc increased dramatically from upstream site C6 to site C5, peaked at sites C4 and C3, and decreased downstream through sites C2 and C1; however, lead and zinc median concentrations at site C1 remained enriched significantly above levels at upstream site C6. Lead concentrations ranged from 14.0 mg/kg to 1,880 mg/kg in the <2-millimeter (mm) size fraction of the 89 channel-sediment samples from Center Creek and exceeded the CPEC in 60 samples (67 percent). Zinc concentrations in the <2-mm size fraction in channel-sediment samples from Center Creek ranged from 201 mg/kg to 25,200 mg/kg exceeding the CPEC in 76 samples (85 percent). Cadmium concentrations in the <2-mm size fraction in stream channel sediments were detected above the 12 mg/kg LOD in 34 samples (38 percent) and the maximum concentration was 171 mg/kg. Very few gravel bar-sediment samples from Center Creek exceeded the CPEC for other metals.

The total area of studied gravel bars for Center Creek was 916,000 square feet (ft²; 21.0 acres). The estimated minimum volume of sediment in gravel bars that would need excavation based on the CPEC along Center Creek from the mouth to site C5 was 136,000 cubic yards (yd³), and the estimated minimum volume of gravel bar sediment exceeding the TPEC was 115,000 yd³. These estimates are considered minimum volumes because they were only based on the visible gravel bars and do not include sediment beneath the wetted channel in other features such as pools, and presumably some of these deposits are negatively affected by mine-waste contaminated sediment but were not sufficiently characterized to be included in the volume estimate.

A total of 84 samples were collected from 7 locations on the Center Creek flood plain at sites C1 and C2 within the intensive study area. Four of the seven boreholes had at least one depth interval where lead or zinc exceeded the CPEC or TPEC. Intervals that exceeded the lead or zinc CPEC and TPEC were generally <3 ft deep with occasional detections

greater than the CPEC at deeper intervals. Because of time limitations, concentrations of cadmium or barium were not analyzed in many core intervals. For the intervals that were analyzed, 15 out of 23 had concentrations of cadmium greater than the LOD, CPEC, and TPEC. Core samples from borehole CTR-FB-2 had cadmium concentrations analyzed at every sampled interval, and concentrations exceeded the CPEC and TPEC in every interval shallower than 7 ft and at the 8 to 9 ft interval but had no exceedances of the CPEC or TPEC for lead or zinc.

A total of 100 samples were collected from 23 locations on gravel bar deposits along Turkey Creek. The maximum sample depth was 13 ft, with the thickest channel deposits in the gravel bars at sites TC2 and TC3 and thinnest deposits at upstream site TC7 (<2 ft thick). Excluding samples with concentrations below the LOD, median lead concentrations increased from the most upstream site TC7 to a peak at site TC5 and decreased somewhat at the two downstream sites TC1 and TC2. Median zinc concentrations increased from the most upstream site at TC7 to a peak at TC4 then remained relatively steady to the most downstream site at TC1. Median cadmium concentrations increased from concentrations below the LOD at the upstream site TC7 to site TC3 and then remained relatively steady to the most downstream site at TC1.

Lead and zinc concentrations in nearly all gravel bar-sediment samples from Turkey Creek exceeded the CPEC and TPEC often to the maximum depth of the boreholes. Lead concentrations exceeded the CPEC in all but 6 samples and exceeded the TPEC in all but 11 samples. Zinc concentrations exceeded the CPEC in all but 1 sample and exceeded the TPEC in all but 13 samples. Most samples also had exceedances of both PECs for cadmium (minimum of 70 percent; <12 to 174 mg/kg), although this number of exceedances may be greater because the XRF LOD is greater than the CPEC and TPEC for cadmium. Lead concentrations in gravel bar-sediment samples from Turkey Creek ranged from 70.0 mg/kg to 7,520 mg/kg and zinc concentrations ranged from 329 mg/kg to 27,900 mg/kg. The total area of studied gravel bars for Turkey Creek was 632,000 ft². The estimated minimum volume of sediment in gravel bars exceeding the CPEC for the chosen reach of Turkey Creek was 115,000 yd³ and 108,000 yd³ of sediment in gravel bars exceeding the TPEC.

A total of 73 samples were collected from six locations on the Turkey Creek flood plain. Of these, cadmium concentrations were analyzed in 51 samples. Nine of the 73 samples had concentrations of lead greater than the CPEC and 15 had concentrations of zinc greater than the CPEC. Lead concentrations in eight samples and zinc concentrations in five samples exceeded their respective TPECs. The exceedances of the TPEC for lead or zinc were limited to the upper 1 or 2 feet of the cores except for core TKC-FP-2 where concentrations of lead and zinc were less than the CPEC and TPEC in the upper few feet. Concentrations for lead and zinc for core TKC-FP-2 gradually increased with depth and lead exceeded the CPEC between 6 and 10 ft.

A total of 65 samples were collected from 12 locations on gravel bar deposits along Shoal Creek. The maximum sample depth was 11.9 ft. The maximum depth of sediments that had concentrations of lead and zinc that exceeded the respective CPEC for those metals was 7 ft for lead and 9 ft for zinc. Overall, cores from Shoal Creek generally had concentrations of zinc that exceeded the CPEC at many depths, including the upstream site S5 about 19 miles upstream from Empire Lake. In channel sediments from Shoal Creek, few samples had exceedances of the TPEC for any Mississippi Valley-Type related metals. In the <2-mm size fraction of gravel bar-sediment samples from Shoal Creek, lead concentrations ranged from <13 mg/kg to 183 mg/kg. Out of the 65 samples, 8 samples (12 percent) had lead concentrations greater than the CPEC and only 4 samples (about 6 percent) had concentrations greater than the TPEC. Zinc concentrations in the <2-mm size fraction in samples ranged from 176 mg/kg to 3,010 mg/kg and cadmium concentrations were <12 mg/kg in all samples. Almost 74 percent of the samples (48 of 65) had zinc concentrations greater than the CPEC, but only one sample had a concentration greater than the TPEC (borehole SH-CH-8 at depth interval 0 to 1 ft). The total area of studied gravel bars for Shoal Creek was 146,000 ft² (3.4 acres). Using the mean thickness of contaminated sediment and a total area of sampled gravel bars along this reach of 146,000 ft², the estimated minimum volume of contaminated sediment in gravel bars exceeding the CPEC is about 24,000 yd³. The estimated minimum volume of sediment in gravel bars exceeding the TPEC is smaller at about 4,000 yd³.

A total of 80 flood-plain samples were collected from 8 locations along the Shoal Creek flood plain. Lead concentrations greater than the CPEC were present in 5 of the 80 (about 6 percent) flood-plain samples from Shoal Creek. Zinc concentrations exceeded the CPEC in 11 samples (about 14 percent). Flood-plain cores sampled along Shoal Creek tended to have concentrations of lead and zinc below the CPEC and TPEC, even in the upper 2 ft of depth.

A total of 51 samples were collected on gravel bar deposits along Tar Creek. The maximum sample depth was 6.6 ft. Overall, concentrations of lead and zinc generally exceeded the CPEC in cores from the surface to the top of bedrock that was generally <5 ft deep and in some cases <1 ft deep. Lead and zinc concentrations generally also exceeded the TPEC from the surface to the maximum depth. Lead concentrations, in the <2-mm size fraction in these samples, ranged from a single non-detection (<13 mg/kg) to 2,540 mg/kg. Out of the 51 gravel bar-sediment samples, all but 6 had lead concentrations greater than the CPEC and the TPEC. All samples collected in Tar Creek that exceeded the CPEC for lead also exceeded the TPEC. Zinc concentrations, in the <2-mm size fraction in these samples, ranged from 63.0 mg/kg to 46,600 mg/kg. Out of the 51 stream channel samples, all but 2 had zinc concentrations that exceeded the CPEC, and all but 5 had concentrations that exceeded the TPEC. Cadmium concentrations, in the <2-mm size fraction in these cores, ranged from non-detection to 131 mg/kg. Out of 51 stream

channel samples, 35 had detectable cadmium (69 percent) and exceeded the CPEC and TPEC. Out of the 51 samples, 31 (61 percent) had concentrations of nickel that exceeded the CPEC (48.6 mg/kg). There is no TPEC for nickel. Exceedances of the CPEC for nickel generally extended several feet below the surface and were present as deep as 6.6 ft. The total area of studied gravel bars for Tar Creek was 230,000 ft² (5.3 acres). The estimated minimum volume of sediment in sampled gravel bars exceeding the CPEC and TPEC for the chosen reach of Tar Creek was 9,000 yd³. These estimates are considered minimum volumes because they were only based on the visible gravel bars.

A total of 142 samples were collected from 13 locations along the Tar Creek flood plain. Concentrations of lead and zinc in flood-plain samples from Tar Creek generally exceeded the CPEC and the TPEC in the upper 1 or 2 ft of soil, and the concentrations were generally greater than concentrations in samples deeper than 2 or 3 ft by an order of magnitude or more. Lead and zinc concentrations in flood-plain samples seemed to decrease with distance from the creek. The 7 cores located within 450 ft of the creek had lead and zinc concentrations that exceeded the CPEC and the TPEC, whereas the 6 cores located at distances greater than 450 ft from the creek had no exceedances. Lead concentrations in 11 of 142 analyzed flood-plain core sections from Tar Creek exceeded the CPEC and the TPEC. Concentrations of zinc exceeded the CPEC in 21 flood-plain core sections and exceeded the TPEC in 9 flood-plain core sections. Cadmium concentrations exceeded the CPEC and the TPEC in 25 of 33 flood-plain core sections where cadmium was analyzed.

A total of 52 samples were collected from 5 locations on gravel bar deposits along the Spring River. The maximum depth sampled was 19.1 ft. Lead concentrations ranged from 14.0 to 390 mg/kg and exceeded the CPEC in 7 samples (14 percent). Zinc concentrations ranged from 225 to 5,020 mg/kg exceeding the CPEC in 46 (89 percent) of the samples. Lead concentrations in gravel bar-sediment samples at the site downstream from Empire Lake (SR1) were generally less than concentrations in samples collected at the upstream site (SR2). Lead concentrations in the <2-mm size fraction from all 38 samples from the downstream site (SR1) were <105 mg/kg, which was less than the CPEC; however, zinc concentrations exceeded the CPEC in 32 of these samples. Cadmium was detected in 7 of the 52 (14 percent) samples at a maximum concentration of 22 mg/kg. The detected cadmium concentrations in samples exceeded the CPEC and TPEC at site SR2 near the mouth of Turkey Creek.

References Cited

- Andrews, W.J., Becker, M.F., Mashburn, S.L., and Smith, S.J., 2009, Selected metals in sediments and streams in the Oklahoma part of the Tri-State mining district, 2000–2006: U.S. Geological Survey Scientific Investigations Report 2009–5032, 36 p.
- Angelo, R.T., Cringan, M.S., Chamberlain, D.L., Stahl, A.J., Haslouer, S.G., and Goodrich, C.A., 2007, Residual effects of lead and zinc mining on freshwater mussels in the Spring River Basin (Kansas, Missouri, and Oklahoma, USA): Science of the Total Environment, v. 384, p. 467–496.
- Bailey, E.H.S., 1911, Preliminary report on stream pollution by mine waters in southeastern Kansas, in Parker, H.N., Quality of the water supplies of Kansas: U.S. Geological Survey Water-Supply Paper 273, p. 349–361.
- Barks, J.H., 1977, Effects of abandoned lead and zinc mines and mine-waste piles on water quality in the Joplin area, Missouri: U.S. Geological Survey Water-Resources Investigations 77–75, 49 p.
- Bastin, E.S., 1939, Theories of formation of ore deposits: Scientific American, v. 49, no. 6, p. 538–547.
- Beasley, D.E., Koltz, A.M., Lambert, J.E., Fierer, N., and Dunn, R.R., 2015, The evolution of stomach acidity and its relevance to the human microbiome: PLoS ONE, v. 10, no. 7, 12 p.
- Christenson, S., 1995, Contamination of wells completed in the Roubidoux aquifer by abandoned zinc and lead mines, Ottawa County, Oklahoma: U.S. Geological Survey Water-Resources Investigation Report 95–4150, 65 p.
- Coduto, D.P., 1999, Geotechnical engineering—Principles and practices: Upper Saddle River, New Jersey, Prentice Hall, 759 p.
- Feder, G.L., Skelton, J., Jeffery, H.G., and Harvey, E.J., 1969, Water resources of the Joplin area, Missouri: Missouri Division of Geology and Land Survey Water Resources Report 24, 97 p. [Also available at <http://www.dnr.mo.gov/pubs/WR24.pdf>.]
- Gibson, A.M., 1972, Wilderness bonanza—The Tri-State District of Missouri, Kansas, and Oklahoma: Norman, Oklahoma, University of Oklahoma Press, 362 p.
- Google Earth™, 2011, Aerial imagery, Aerial imagery of Jasper and Newton Counties, Missouri, Cherokee County, Kansas, and Ottawa County, Oklahoma.
- Ingersoll, C.G., Ivey, C.D., Brumbaugh, W.G., Besser, J.M., and Kemble, N.E., 2009, Toxicity assessment of sediments from the Grand Lake O' the Cherokees with the amphipod *Hyalella azteca*: U.S. Geological Survey Administrative Report CERC-8335-FY09-20-01, 97 p., accessed December 2009 at <http://www.fws.gov/southwest/es/oklahoma/documents/contaminants/ingersoll%20et%20al.%20grand%20lake%20sediment%20toxicity%20report%20text%20final%20august%2027%202009.pdf>.
- Jolly, J.L., and Van Heyl, A., 1968, Mercury and other trace elements in sphalerite and wallrocks from central Kentucky, Tennessee, and Appalachian Zinc Districts: U.S. Geological Survey Bulletin 1252–F, 40 p.
- Juracek, K.E., 2006, Sedimentation and occurrence and trends of selected chemical constituents in bottom sediment, Empire Lake, Cherokee County, Kansas, 1905–2005: U.S. Geological Survey Scientific Investigations Report 2006–5307, 79 p.
- Juracek, K.E., 2013, Occurrence and variability of mining-related lead and zinc in the Spring River flood plain and tributary flood plains, Cherokee County, Kansas, 2009–11: U.S. Geological Survey Scientific Investigations Report 2013–5028, 70 p.
- Juracek, K.E., and Becker, M.F., 2009, Occurrence and trends of selected chemical constituents in bottom sediment, Grand Lake O' the Cherokees, northeast Oklahoma, 1940–2008: U.S. Geological Survey Scientific Investigations Report 2009–5258, 28 p.
- Lanesky, D.E., Logan, B.W., Brown, R.G., and Hine, A.C., 1979, A new approach to portable vibracoring underwater and on land: Journal of Sedimentary Petrology, v. 49, p. 654–657.
- Leach, D.L., Taylor, R.D., Fey, D.L., Diehl, S.F., and Saltus, R.W., 2010, A deposit model for Mississippi Valley-Type lead-zinc ores, chap. A of Mineral deposit models for resource assessment: U.S. Geological Survey Scientific Investigations Report 2010–5070–A, 52 p.
- Lisle, T.E., and Eads, R.E., 1991, Methods to measure sedimentation of spawning gravels: U.S. Department of Agriculture, Forest Service, Pacific Southwest Research Station Research Note PSW–411, 7 p.
- Luoma, S.N., 1983, Bioavailability of trace metals to aquatic organisms—A review: The Science of the Total Environment, v. 28, p. 1–22.
- Luoma, S. N., 1989, Can we determine the biological availability of sediment-bound trace elements?: Hydrobiologia, v. 176, no. 1, p. 379–396.

- MacDonald, D.D., Ingersoll, C.G., and Berger, T.A., 2000, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems: *Archives of Environmental Contamination and Toxicology*, v. 39, p. 20–31.
- MacDonald, D.D., Ingersoll, C.G., Crawford, Meara, Prencipe, Heather, Besser, J.M., Brumbaugh, W.G., Kemble, Nile, May, T.W., Ivey, C.D., Meneghetti, Melissa, Sinclair, Jesse, and O'Hare, Margaret, 2010, Advanced Screening-Level Ecological Risk Assessment (SLERA) for aquatic habitats within the Tri-State Mining District, Oklahoma, Kansas, and Missouri: Nanaimo, British Columbia, MacDonald Environmental Sciences Ltd., [variously paged].
- Merwe, D. van der, Carpenter, J.W., Nietfeld, J.C., and Miesner, J.F., 2011, Adverse health effects in Canada geese (*Branta Canadensis*) associated with waste from zinc and lead mines in the Tri-State Mining District (Kansas, Oklahoma, and Missouri, USA): *Journal of Wildlife Diseases*, v. 47, no. 3, p. 650–660.
- Murphy, F., and Herkelrath, W.N., 1996, A sample-freezing drive shoe for a wire-line piston core sampler: *Groundwater Monitoring and Remediation*, v. 16, no. 3, p. 86–90.
- Natural Resources Conservation Service, 2003, Soil survey of Jasper and Newton Counties, Missouri, Cherokee County, Kansas, and Ottawa County, Oklahoma: accessed November 2015 at <http://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx>.
- Natural Resources Conservation Service, 1938, Aerial imagery of Jasper and Newton Counties, Missouri.
- Pope, L.M., 2005, Assessment of contaminated streambed sediment in the Kansas part of the historic Tri-State Lead and Zinc Mining District, Cherokee County, 2004: U.S. Geological Survey Scientific Investigations Report 2005–5251, 61 p.
- Schmidt, A., and Leonhard, A., 1874, The lead and zinc regions of south-west Missouri, in Broadhead, G.C., ed., Report of the Geological Survey of the State of Missouri including field work of 1873–1874: Jefferson City, Missouri, Bureau of Geology and Mines, p. 381–502, accessed June 7, 2005, at <https://archive.org/details/aet7172.0001.001.umich.edu>.
- Schmitt, C.J., Whyte, J.J., Brumbaugh, W.G., and Tillitt, D.E., 2005, Biochemical effects of lead, zinc, and cadmium from mining on fish in the Tri-States District of northeastern Oklahoma, USA: *Environmental Toxicology and Chemistry*, v. 24, no. 6, p. 1483–1495.
- Smith, D., 2013, A modification of freeze-core technology for collecting granular fluvial sediment sample: Rolla, Mo., Missouri University of Science and Technology, Master's thesis, 60 p.
- Smith, D., and Elmore, A.C., 2013, A modification of freeze-core technology for collecting granular fluvial sediment samples: *Environmental Earth Sciences*, v. 71, no. 9, p. 4149–4156.
- Smith, D.C., 2016, Metals and other constituent concentrations in metals-contaminated sediment of selected streams draining the Tri-State Mining District, Missouri, Oklahoma, and Kansas, 2011–12: U.S. Geological Survey data release, accessed November 2016, at <https://dx.doi.org/10.5066/F7CZ359X>.
- Sullivan, K., Lisle, T.E., Dolloff, C.A., Grant, G.E. and Reid, L.M., 1987, Stream channels—The link between forests and fishes, in Salo, E.O. and Cundy, T.W., eds., *Streamside management—Forestry and fishery interactions*: Seattle, Washington, University of Washington, Institute of Forest Resources, no. 57, p. 39–97.
- Taggart, J.E., 2002, Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey: U.S. Geological Survey Open-File Report 02–223
- U.S. Department of Agriculture, 2010, Aerial imagery of Jasper and Newton Counties, Missouri, Cherokee County, Kansas, and Ottawa County, Oklahoma.
- U.S. Environmental Protection Agency, 2007, Method 6200, Field portable x-ray fluorescence spectrometry for the determination of elemental concentrations in soil and sediment: Washington, D.C., U.S. Environmental Protection Agency, 32 p. <https://www.epa.gov/sites/production/files/2015-12/documents/6200.pdf>.
- U.S. Geological Survey, 2011, National hydrography dataset: U.S. Geological Survey, accessed November 15, 2014, at <http://nhd.usgs.gov/>.
- Wang, F., Goulet, R.R., and Chapman, P.M., 2004, Testing sediment biological effects with the freshwater amphipod *Hyalella azteca*—The gap between laboratory and nature: *Chemosphere*, v. 57, no. 11, p. 1713–1724.
- Zapico, M.M., Vales, S., and Cherry, J.A., 1987, A wireline piston core barrel for sampling cohesionless sand and gravel below the water table: *Ground Water Monitoring Review*, v. 7, no. 3, p. 74–82.

Table 8

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.

[XRF, analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Arsenic				Barium				Cadmium					
		Original sample		Split sample		Original sample		Split sample		Original sample		Split sample			
		RPD-1 ^a		RPD-2 ^b		RPD-1 ^a		RPD-2 ^b		RPD-1 ^a		RPD-2 ^b			
		XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB		
Center Creek															
CC-A-HD1	2-3	30	<11	10	99	--	111	<100	158	35	34.8	<12	22.8	42	--
CC-A-HD2	3-4	25	<11	10	86	--	124	195	232	61	63.0	71.6	104.0	49	37
CC-B-HD1	0-1	<11	13	11	--	15	104	142	189	58	<12	<12	1.8	--	--
CC-B-HD2	1-2	14	<11	11	21	--	<100	135	152	--	<12	<12	1.8	--	--
CC-B-HS1	1-2	<11	14	8	--	53	109	165	594	138	113	<12	1.9	--	--
CC-B-HS2	0-1	<11	<11	8	--	--	144	223	269	61	19	<12	2.1	--	--
CC-C-HD1	1-2	19	<11	11	52	--	123	218	166	30	27	25.1	34.9	54.6	74
CC-C-HD2	0-1	<11	19	11	--	53	133	184	191	36	4	18.2	16.8	56.3	102
CC-C-WC1	0-0.5	<11	<11	9	--	--	106	143	236	76	49	17.6	20.4	47.9	93
CC-D-HD1	3-3.5	<11	<11	10	--	--	116	134	172	39	25	28.5	29.4	57.3	67
CC-D-HD2	3-4	21	<11	5	124	--	131	<100	91	36	--	25.7	15.5	25.6	1
CC-D-WC1	0.2-0.5	<11	<11	7	--	--	<100	<100	229	--	--	27.0	21.0	42.2	44
CTR-CH-1	7-8	<11	<11	5	--	--	119	183	252	72	31	<12	<12	3.8	--
CTR-CH-2	3-4	22	<11	12	57	--	148	251	146	2	53	<12	14.9	8.5	--
CTR-CH-3	3-4	<11	<11	11	--	--	179	254	292	48	14	42.7	52.7	53.5	22
CTR-CH-4	6-7	22	16	18	20	14	243	306	416	52	30	<12	<12	7.7	--
CTR-CH-4	0-1	<11	<11	8	--	--	<100	105	251	--	82	17.3	16.6	26.7	43
CTR-CH-5	4.5-5.5	18	<11	11	47	--	<100	109	261	--	82	<12	14.7	32.7	--
CTR-CH-6	0.5-1	<11	<11	10	--	--	125	155	148	17	4	<12	16.8	21.3	--
CTR-CH-7	0-1	<11	<11	6	--	--	<100	110	202	--	59	16.4	19.3	28.1	53
CTR-FB-1	1-2	<11	<11	8	--	--	520	274	376	32	31	73.6	47.9	53.1	32
CTR-FB-2	5-6	<11	<11	13	--	--	464	223	221	71	1	43.1	<12	1.2	189
CTR-GB-1	0-0.2	<11	<11	7	--	--	115	114	221	63	64	14.6	19.6	30.0	69
CTR-WC-1	5.5-6.5	<11	14	9	--	40	<100	182	145	--	23	<12	<12	3.3	--
CTR-WC-2	1-2	<11	<11	8	--	--	<100	125	278	--	76	<12	<12	6.6	--
CTR-WC-2	2-3	13	<11	7	62	--	<100	118	260	--	75	<12	<12	4.6	--
CTR-WC-4	0-0.2	19	<11	12	46	--	128	195	152	17	25	<12	<12	27.5	--

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.—Continued

[XRF; analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Colbalt			Copper			Lead								
		Original sample	Split sample		RPD-1 ^a	RPD-2 ^b	Original sample	Split sample								
			XRF	LAB				XRF	LAB	XRF	LAB					
Center Creek—Continued																
CC-A-HD1	2–3	<260	<260	11.7	--	--	<35	<35	12.6	--	263	331	253	4	27	
CC-A-HD2	3–4	<260	<260	13.1	--	--	<35	52.0	31.7	--	1,020	1,010	983	4	3	
CC-B-HD1	0–1	312	280	15.2	147	179	<35	<35	6.5	--	49.8	42.2	49.3	1	16	
CC-B-HD2	1–2	270	<260	14.0	180	--	<35	<35	6.9	--	37.5	40.9	43.8	15	7	
CC-B-HS1	1–2	<260	<260	13.4	--	--	<35	<35	9.9	--	46	51.1	59.7	26	16	
CC-B-HS2	0–1	<260	<260	12.8	--	--	<35	<35	8.8	--	56	59.6	61.2	9	3	
CC-C-HD1	1–2	<260	<260	12.9	--	--	<35	36.9	12.1	--	238	208	257	8	21	
CC-C-HD2	0–1	268	<260	12.4	182	--	<35	<35	552	--	282	213	247	13	15	
CC-C-WC1	0–0.5	<260	<260	12.4	--	--	<35	<35	15.4	--	305	329	411	30	22	
CC-D-HD1	3–3.5	<260	<260	7.7	--	--	37.3	<35	19.8	61	247	307	370	40	19	
CC-D-HD2	3–4	<260	<260	4.9	--	--	<35	<35	10.2	--	503	419	410	20	2	
CC-D-WC1	0.2–0.5	<260	<260	12.1	--	--	<35	<35	19.9	--	488	409	411	17	0	
CTR-CH-1	7–8	<260	<260	28.0	--	--	<35	<35	32.3	--	36.8	39.4	46.4	23	16	
CTR-CH-2	3–4	275	<260	15.1	179	--	<35	<35	8.4	--	109	127	149	31	16	
CTR-CH-3	3–4	<260	<260	13.9	--	--	53.1	40.1	1,180	266	187	866	828	843	3	
CTR-CH-4	6–7	<260	<260	20.0	--	--	42.8	49.2	24.6	47	67	49.1	64.4	64	26	
CTR-CH-4	0–1	<260	<260	14.0	--	--	<35	<35	14.0	--	409	357	374	9	5	
CTR-CH-5	4.5–5.5	<260	<260	15.5	--	--	<35	<35	37.0	--	237	271	280	17	3	
CTR-CH-6	0.5–1	<260	<260	11.9	--	--	<35	<35	98.7	--	182	250	231	24	8	
CTR-CH-7	0–1	<260	<260	11.1	--	--	<35	<35	16.0	--	364	401	360	1	11	
CTR-FB-1	1–2	<260	<260	13.3	--	--	38.2	45.8	31.9	16	36	938	1,240	1,280	31	
CTR-FB-2	5–6	430	<260	15.8	186	--	<35	<35	11.6	--	26.5	35	34.5	26	1	
CTR-GB-1	0–0.2	<260	<260	11.8	--	--	<35	<35	15.4	--	459	438	451	2	3	
CTR-WC-1	5.5–6.5	<260	<260	14.4	--	--	<35	<35	6.9	--	31.5	30.4	38.2	19	23	
CTR-WC-2	1–2	<260	<260	14.5	--	--	<35	<35	17.2	--	131	124	122	7	2	
CTR-WC-2	2–3	<260	279	11.3	--	184	<35	<35	9.7	--	74.5	68.8	72.4	3	5	
CTR-WC-4	0–0.2	<260	<260	13.6	--	--	<35	<35	9.8	--	218	194	197	10	2	

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.—Continued

[XRF, analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Manganese				Nickel				Zinc				
		Original sample		Split sample		RPD-1 ^a	RPD-2 ^b	Original sample		Split sample		RPD-1 ^a	RPD-2 ^b	
		XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB	
Center Creek—Continued														
CC-A-HD1	2–3	763	675	533	36	24	<65	<65	26.1	6,160	4,100	4,880	23	17
CC-A-HD2	3–4	416	260	315	28	19	<65	<65	31.4	17,800	17,900	21,300	18	17
CC-B-HD1	0–1	808	865	820	1	5	<65	<65	29.9	310	250	397	25	45
CC-B-HD2	1–2	997	802	761	27	5	<65	<65	28.0	275	281	447	48	46
CC-B-HS1	1–2	793	697	985	22	34	<65	<65	25.1	268	258	360	29	33
CC-B-HS2	0–1	747	1,150	832	11	32	<65	<65	25.3	262	272	356	30	27
CC-C-HD1	1–2	645	808	578	11	33	<65	<65	30.2	3,590	1,970	4,360	19	76
CC-C-HD2	0–1	859	825	556	43	39	<65	<65	26.3	4,140	3,090	10,300	85	108
CC-C-WC1	0–0.5	693	742	725	5	2	<65	<65	23.6	3,190	3,170	8,410	90	91
CC-D-HD1	3–3.5	535	496	476	12	4	<65	<65	18.3	4,140	3,960	9,980	83	86
CC-D-HD2	3–4	572	385	295	64	27	<65	<65	11.9	8,320	5,320	5,550	40	4
CC-D-WC1	0.2–0.5	1,110	1,070	951	15	12	<65	<65	21.6	5,860	6,160	7,090	19	14
CTR-CH-1	7–8	7,460	6,950	9,340	22	29	<65	105.7	61.0	873	793	868	1	9
CTR-CH-2	3–4	948	1,103	864	9	24	<65	<65	31.7	1,300	1,210	2,110	48	54
CTR-CH-3	3–4	848	734	759	11	3	73.2	<65	40.4	10,100	9,950	10,400	3	4
CTR-CH-4	6–7	3,670	4,380	3,130	16	33	<65	<65	78.6	335	310	409	20	28
CTR-CH-4	0–1	699	1,000	908	26	10	<65	<65	24.1	3,800	3,430	4,000	5	15
CTR-CH-5	4.5–5.5	994	1,260	1,230	21	2	66.3	<65	57.8	4,230	5,090	7,270	53	35
CTR-CH-6	0.5–1	749	637	564	28	12	<65	<65	26.4	2,670	3,040	4,380	49	36
CTR-CH-7	0–1	787	646	639	21	1	<65	<65	19.7	3,980	3,590	4,540	13	23
CTR-FB-1	1–2	437	481	547	22	13	<65	<65	23.5	6,830	7,770	8,870	26	13
CTR-FB-2	5–6	304	983	525	53	61	<65	<65	33.8	142	210	248	54	17
CTR-GB-1	0–0.2	526	594	624	17	5	<65	<65	21.9	4,260	3,560	5,150	19	37
CTR-WC-1	5.5–6.5	175	230	217	21	6	<65	<65	33.1	1,410	1,410	1,610	13	13
CTR-WC-2	1–2	988	1,040	869	13	18	<65	<65	27.1	1,830	1,680	1,790	2	6
CTR-WC-2	2–3	422	458	490	15	7	<65	<65	36.1	1,200	1,110	1,290	7	15
CTR-WC-4	0–0.2	982	909	726	30	22	<65	<65	31.6	2,300	2,720	4,550	66	50

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.—Continued

[XRF, analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Arsenic				Barium				Cadmium					
		Original sample		Split sample		Original sample		Split sample		Original sample		Split sample			
		XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB		
		Turkey Creek													
TC-A-HD1	1-1.3	<11	11	<11	--	--	137	233	190	33	21	<12	9.5	--	--
TC-A-HD2	1-1.8	<11	11	<11	--	--	109	<100	259	82	--	<12	9.4	--	--
TC-B-HD1	1-2	<11	11	<11	--	--	104	121	242	80	67	<12	14.5	59.3	121
TC-B-HD2	0-1	<11	8	<11	--	--	<100	<100	294	--	--	13.3	<12	19.2	37
TC-C-HD1	2-3	27	14	<11	64	--	106	<100	181	52	--	18.9	<12	20.8	10
TC-C-HD2	2-3	<11	11	<11	--	--	103	<100	168	48	--	13.2	<12	16.6	23
TC-C-HS1	0-1	23	11	<11	70	--	121	<100	104	15	--	<12	<12	17.7	--
TC-D-HD1	7.5-8.5	51	10	40	134	121	<100	113	106	--	6	51.3	37.6	103.0	67
TC-D-HD2	3-4	<11	10	<11	--	--	<100	142	153	--	8	22.8	27.2	81.8	113
TC-E-HD1	1-2	28	9	<11	103	--	<100	136	102	--	29	16.2	26.5	67.9	123
TC-E-HD2	3.5-4.5	<11	10	<11	--	--	104	112	107	3	5	33.3	26.0	114.0	109
TC-E-HD3	0-1	<11	7	<11	--	--	<100	125	110	--	13	19.0	23.0	44.0	79
TC-E-WC1	0-0.7	<11	8	<11	--	--	279	108	193	36	57	40.2	15.3	7.3	139
TKC-CH-1	4-5	46	8	<11	141	--	179	<100	180	1	--	128.5	77.3	186.0	37
TKC-CH-2	1-2	<11	8	26	--	105	141	170	116	19	38	44.7	28.9	104.0	80
TKC-CH-3	9-10	<11	9	<11	--	--	<100	136	192	--	34	<12	<12	13.6	--
TKC-CH-4	10-11	19	10	18	62	59	159	217	190	18	13	17.1	20.2	29.9	54
TKC-CH-5	2-3	<11	11	<11	--	--	<100	136	161	--	17	<12	20.1	55.8	--
TKC-CH-5P	1-2	<11	8	<11	--	--	110	204	143	26	35	30.0	30.9	49.8	50
TKC-CH-6	8-8.5	<11	9	<11	--	--	111	125	178	46	35	18.5	22.6	28.8	44
TKC-CH-7	1-2	17	7	<11	82	100	106	--	81	27	--	38.9	--	60.2	43
TKC-CH-7	4-4.5	<11	8	<11	--	--	106	164	80	28	69	22.7	28.2	75.1	107
TKC-FP-1	0-1	<11	6	<11	--	--	419	250	328	24	27	79.9	59.5	71.4	11
TKC-FP-3	0-1	<11	8	<11	--	--	455	243	438	4	57	65.2	40.1	59.1	10
TKC-WC-1	3.6-4.6	16	20	<11	22	--	161	149	335	70	77	<12	<12	2.4	--
TKC-WC-3	2-3	<11	14	77	--	139	632	261	321	65	21	173.6	116.6	125.0	33
															7

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.—Continued

[XRF, analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Colbalt			Copper			Lead						
		Original sample	Split sample		RPD-1 ^a	RPD-2 ^b	Original sample	Split sample		RPD-1 ^a	RPD-2 ^b			
			XRF	LAB				XRF	LAB			XRF	LAB	
Turkey Creek—Continued														
TC-A-HD1	1–1.3	<260	<260	12.0	--	--	--	<35	<35	10.2	88.1	141	58	46
TC-A-HD2	1–1.8	<260	<260	12.8	--	--	--	<35	<35	9.9	112	136	17	19
TC-B-HD1	1–2	<260	<260	10.9	--	--	84	<35	<35	15.0	226	1,320	74	142
TC-B-HD2	0–1	<260	<260	11.8	--	--	--	<35	44.3	15.0	244	301	55	35
TC-C-HD1	2–3	<260	<260	11.1	--	--	62	37.5	41.2	17.7	809	488	3	52
TC-C-HD2	2–3	<260	<260	12.6	--	--	--	<35	<35	7.7	907	1,880	70	162
TC-C-HS1	0–1	<260	<260	10.7	--	--	--	<35	<35	8.5	129	241	102	49
TC-D-HD1	7.5–8.5	<260	<260	6.9	--	--	6	42.2	40.0	44.9	1,100	722	3	39
TC-D-HD2	3–4	<260	<260	9.9	--	--	--	<35	<35	19.8	807	687	2	14
TC-E-HD1	1–2	<260	<260	10.3	--	--	--	<35	<35	33.2	519	389	51	77
TC-E-HD2	3.5–4.5	<260	<260	10.6	--	--	--	<35	<35	24.7	465	444	86	89
TC-E-HD3	0–1	<260	<260	10.5	--	--	--	<35	<35	20.3	563	313	29	83
TC-E-WC1	0–0.7	<260	<260	9.6	--	--	--	<35	<35	5.5	495	211	80	52
TKC-CH-1	4–5	<260	<260	19.8	--	--	--	<35	47.3	36.5	2,970	2,260	37	63
TKC-CH-2	1–2	<260	<260	10.4	--	--	9	45.6	<35	41.7	537	422	38	60
TKC-CH-3	9–10	<260	<260	9.9	--	--	--	<35	<35	12.2	138	179	20	6
TKC-CH-4	10–11	<260	<260	11.1	--	--	--	<35	37.2	14.8	227	227	7	7
TKC-CH-5	2–3	<260	<260	12.9	--	--	40	40.9	45.2	25.8	317	289	23	32
TKC-CH-5P	1–2	<260	<260	12.2	--	--	76	45.5	<35	20.4	571	417	15	17
TKC-CH-6	8–8.5	<260	<260	10.3	--	--	--	<35	<35	25.6	606	594	8	6
TKC-CH-7	1–2	<260	<260	--	--	--	--	<35	--	22.5	342	--	4	--
TKC-CH-7	4–4.5	<260	<260	7.4	--	--	--	<35	<35	23.0	267	267	27	27
TKC-FP-1	0–1	<260	<260	7.7	--	--	--	<35	39.9	17.2	118	129	8	1
TKC-FP-3	0–1	<260	<260	10.9	--	--	--	<35	39.5	43.8	515	796	48	5
TKC-WC-1	3.6–4.6	<260	<260	17.4	--	--	82	40.0	<35	16.8	118	126	22	15
TKC-WC-3	2–3	<260	<260	43.2	--	--	--	<35	<35	27.6	7,520	7,500	6	6

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.—Continued

[XRF, analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Manganese				Nickel				Zinc						
		Original sample		Split sample		Original sample		Split sample		Original sample		Split sample				
		XRF	LAB	RPD-1 ^a	RPD-2 ^b	XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB			
														RPD-1 ^a	RPD-2 ^b	RPD-1 ^a
Turkey Creek—Continued																
TC-A-HD1	1–1.3	959	820	929	16	13	<65	<65	21.7	--	--	865	1,930	2,460	96	24
TC-A-HD2	1–1.8	708	728	501	3	37	<65	<65	21.0	--	--	1,830	1,210	2,310	23	63
TC-B-HD1	1–2	1,430	1,020	1,260	33	21	<65	<65	26.3	--	--	2,670	2,610	9,290	111	112
TC-B-HD2	0–1	1,040	1,050	1,270	1	19	<65	<65	72.8	--	89	2,970	2,620	3,060	3	15
TC-C-HD1	2–3	463	570	512	21	11	<65	<65	24.7	--	--	3,590	2,240	3,520	2	44
TC-C-HD2	2–3	1,440	440	398	106	10	<65	<65	24.4	--	--	1,710	2,010	2,720	46	30
TC-C-HS1	0–1	916	567	1,350	47	82	<65	<65	18.8	--	--	1,450	954	3,680	87	118
TC-D-HD1	7.5–8.5	175	315	171	57	59	67.0	<65	23.7	96	--	13,100	8,630	20,000	42	79
TC-D-HD2	3–4	729	439	763	50	54	<65	<65	31.7	--	--	11,600	7,270	15,300	28	71
TC-E-HD1	1–2	580	487	418	17	15	<65	<65	16.8	--	--	3,510	4,530	13,200	116	98
TC-E-HD2	3.5–4.5	788	525	702	40	29	<65	<65	19.8	--	--	7,960	7,880	20,900	90	90
TC-E-HD3	0–1	775	541	423	36	24	<65	<65	17.7	--	--	6,470	5,380	8,800	31	48
TC-E-WC1	0–0.7	962	611	940	45	42	<65	<65	17.1	--	--	8,960	3,260	1,310	149	85
TKC-CH-1	4–5	382	262	402	37	42	<65	82.6	50.3	--	49	27,900	21,900	42,100	41	63
TKC-CH-2	1–2	664	493	545	30	10	<65	<65	19.9	--	--	11,700	6,480	20,200	53	103
TKC-CH-3	9–10	323	342	336	6	2	<65	<65	36.0	--	--	3,120	3,940	3,930	23	0
TKC-CH-4	10–11	653	616	752	6	20	<65	<65	24.6	--	--	4,590	4,060	5,620	20	32
TKC-CH-5	2–3	525	463	533	13	14	69.8	80.9	29.7	67	93	3,740	4,400	11,600	102	90
TKC-CH-5P	1–2	555	607	929	9	42	<65	<65	23.0	--	--	6,080	7,210	9,800	47	30
TKC-CH-6	8–8.5	355	357	347	0	3	<65	<65	25.7	--	--	4,880	4,640	5,220	7	12
TKC-CH-7	1–2	341	302	--	12	--	<65	--	22.4	--	--	8,930	--	12,100	30	--
TKC-CH-7	4–4.5	259	306	311	17	2	<65	<65	16.8	--	--	7,460	5,460	15,000	67	93
TKC-FP-1	0–1	318	562	355	56	45	<65	<65	19.3	--	--	5,750	8,050	9,270	47	14
TKC-FP-3	0–1	341	543	511	46	6	<65	<65	25.6	--	--	6,620	8,170	9,880	40	19
TKC-WC-1	3.6–4.6	1,240	1,230	1,290	1	5	<65	<65	53.6	--	--	329	335	464	34	32
TKC-WC-3	2–3	620	664	629	2	5	74.7	<65	89.4	18	--	9,560	9,140	8,970	6	2

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.—Continued

[XRF, analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Arsenic				Barium				Cadmium			
		Original sample		Split sample		Original sample		Split sample		Original sample		Split sample	
		XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB	XRF	LAB
Shoal Creek													
SC-A-HD1	2.5-3.5	<11	3	--	--	<100	<100	185	--	<12	0.8	--	--
SC-A-HD2	1-2	<11	5	--	--	104	103	230	75	<12	3.3	--	--
SH-CH-1	3-4	13	6	73	--	130	<100	162	22	<12	3.5	--	--
SH-CH-11	3-4	<11	7	--	--	<100	<100	196	--	<12	4.4	--	--
SH-CH-5	0-1	<11	9	--	--	128	222	151	16	<12	3.3	--	--
SH-CH-7	2-3	15	4	117	--	<100	165	217	--	<12	4.1	--	--
SH-CH-8	4-5	<11	8	--	--	165	108	270	49	<12	2.3	--	--
SH-CH-9	2-3	<11	7	--	--	119	135	114	4	<12	6.6	--	--
SH-FB-2	1-2	<11	5	--	--	393	222	369	6	<12	1.1	170	--
SH-FB-3	0-1	<11	5	--	85	414	164	336	21	<12	1.0	181	--
SH-FB-4	7-8	<11	5	--	--	124	125	381	102	<12	9.6	--	--
SH-WC-1	2-2.8	<11	6	--	--	195	148	430	75	<12	2.4	--	--
SH-WC-2	1-2	<11	7	--	--	137	205	152	10	<12	3.6	--	--
SH-WC-3	3-4	<11	7	--	84	<100	<100	151	--	<12	2.4	--	--
Tar Creek													
TAR-FB-3	0-1	<11	9	--	--	--	150	181	--	32.1	38.0	--	17
TAR-FP1-3	4-5	<11	6	--	--	513	227	216	81	19.7	18.0	27	35
TAR-TR-1	0-0.3	24	32	30	32	125	192	87	36	14.4	14.8	61	59
TAR-TR-2	0-0.2	18	28	44	10	109	269	87	22	13.6	16.7	59	40
TAR-TR-3	0-0.7	30	38	23	58	<100	177	101	--	<12	14.9	--	39
TAR-TR-3A	1-2	34	33	4	54	<100	157	92	--	12.9	17.3	58	30
TAR-TR-4	0-1	<11	33	--	--	150	138	115	26	<12	19.5	--	--
TAR-TR-5	0-0.5	20	29	38	--	<100	103	79	--	<12	4.3	--	--
TAR-TR-6	0-1	<11	17	--	25	110	159	59	60	13.6	21.0	110	76
TAR-TR-7	0-1	<11	19	--	--	112	115	181	47	<12	13.7	--	66
TAR-TR-8	0-1	28	18	44	17	106	178	57	61	17.6	17.7	46	46
TAR-TR-9	0-1	22	15	36	66	145	187	56	88	<12	18.2	--	13

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.—Continued

[XRF, analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Manganese				Nickel				Zinc				
		Original sample		Split sample		RPD-1 ^a	RPD-2 ^b	Original sample		Split sample		RPD-1 ^a	RPD-2 ^b	
		XRF	LAB	XRF	LAB			XRF	LAB	XRF	LAB			
Shoal Creek—Continued														
SC-A-HD1	2.5–3.5	87	85	66	27	25	<65	<65	13.0	176	176	219	22	22
SC-A-HD2	1–2	391	434	380	3	13	<65	<65	16.6	628	558	633	1	13
SH-CH-1	3–4	402	450	449	11	0	65.5	<65	39.6	806	1,020	824	2	21
SH-CH-11	3–4	412	450	493	18	9	<65	<65	36.3	1,030	1,020	993	4	3
SH-CH-5	0–1	416	439	458	10	4	<65	<65	20.4	763	744	907	17	20
SH-CH-7	2–3	172	265	245	35	8	<65	<65	21.0	822	788	871	6	10
SH-CH-8	4–5	878	842	880	0	4	<65	<65	29.2	443	396	539	20	31
SH-CH-9	2–3	425	468	472	11	1	<65	<65	15.9	1,850	1,360	2,110	13	43
SH-FB-2	1–2	508	348	558	9	46	<65	<65	13.0	212	259	290	31	11
SH-FB-3	0–1	441	418	642	37	42	<65	<65	17.5	202	187	233	14	22
SH-FB-4	7–8	589	611	708	18	15	<65	<65	37.1	1,740	1,690	1,920	10	13
SH-WC-1	2–2.8	130	157	186	35	17	66.9	<65	47.2	267	221	252	6	13
SH-WC-2	1–2	841	837	689	20	19	<65	<65	22.9	970	974	1,080	11	10
SH-WC-3	3–4	494	419	427	15	2	<65	<65	33.4	901	811	799	12	1
Tar Creek—Continued														
TAR-FB-3	0–1	250	303	283	12	7	<65	<65	36.7	4,430	6,130	6,100	32	0
TAR-FP1-3	4–5	398	294	387	3	27	<65	<65	16.9	39.4	3,630	3,680	196	1
TAR-TR-1	0–0.3	417	402	449	7	11	99.4	80.4	74.0	6,970	7,490	8,010	14	7
TAR-TR-2	0–0.2	403	672	337	18	66	68.4	90.8	62.6	5,220	4,230	7,990	42	62
TAR-TR-3	0–0.7	1,190	2,410	674	55	113	83.2	157.5	97.1	5,040	5,970	7,100	34	17
TAR-TR-3A	1–2	145	184	370	87	67	79.4	97.5	73.6	3,150	3,870	6,740	73	54
TAR-TR-4	0–1	341	400	455	29	13	76.7	<65	83.6	2,730	2,550	5,910	74	79
TAR-TR-5	0–0.5	313	369	654	71	56	<65	<65	60.8	791	671	871	10	26
TAR-TR-6	0–1	1,020	2,280	283	113	156	99.2	111.8	34.1	3,230	4,980	11,300	111	78
TAR-TR-7	0–1	2,300	2,270	477	131	131	115.4	141.7	35.8	3,860	3,690	7,740	67	71
TAR-TR-8	0–1	380	344	189	67	58	96.8	117.4	25.3	4,120	3,750	7,070	53	61
TAR-TR-9	0–1	<85	127	99	--	25	79.6	122.0	18.8	2,280	4,450	6,010	90	30

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.—Continued

[XRF, analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Arsenic			Barium			Cadmium				
		Original sample		Split sample	RPD-1 ^a	RPD-2 ^b	Original sample	Split sample		RPD-1 ^a	RPD-2 ^b	
		XRF	LAB					XRF	LAB			XRF
		Spring River										
SR-CH-1	5–6	<11	13	359	305	339	6	10	<12	3.0	--	--
SR-CH-2	9–10	15	12	115	157	173	40	10	<12	12.9	5.2	85
SR-CH-3	2–3	<11	13	<100	196	154	--	24	<12	<12	2.4	--
SR-CH-4	3–4	<11	9	103	114	111	8	2	22.4	15.2	36.0	47
SR-CH-5	4–5	<11	9	116	--	129	11	--	<12	--	5.6	--
SR-CH-5	6–7	<11	11	<100	163	128	--	24	<12	<12	3.1	--

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.—Continued

[XRF, analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Colbalt			Copper			Lead						
		Original sample	Split sample		Original sample	Split sample		Original sample	Split sample					
			XRF	LAB		RPD-1 ^a	RPD-2 ^b		XRF	LAB	XRF	LAB		
Spring River—Continued														
SR-CH-1	5–6	<260	<260	17.1	--	--	<35	8.7	--	66	60.1	68.7	4	13
SR-CH-2	9–10	<260	<260	16.3	--	--	<35	10.6	--	71.7	55	69.1	4	23
SR-CH-3	2–3	<260	<260	15.2	--	--	<35	11.1	--	28.7	41.6	48.3	51	15
SR-CH-4	3–4	<260	<260	10.1	--	--	<35	13.7	--	184	135	182	1	30
SR-CH-5	4–5	<260	--	13.5	--	--	<35	--	12.2	73.9	--	86	15	--
SR-CH-5	6–7	<260	<260	23.1	--	--	<35	<35	6.8	19.6	24.2	28.7	38	17

Table 8. Concentrations of select trace element measured by two methods, with two sample preparation types, in the less than 2-millimeter size fractions of stream channel sediment samples.—Continued

[XRF, analysis was conducted using an x-ray fluorescence instrument owned and operated by U.S. Fish and Wildlife Service personnel following U.S. Environmental Protection Agency Method 6200 (EPA, 2007) at the U.S. Fish and Wildlife Service office; LAB, analysis was conducted by the U.S. Geological Survey Central Mineral and Environmental Resources Science Center laboratory in Denver, Colorado, using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry methods described in Taggart (2002); RPD, relative percent difference; <, less than; --, not calculated; shaded value indicates RPD greater than 30 percent]

Core location	Depth below land surface (foot)	Manganese				Nickel				Zinc			
		Original sample		Split sample		Original sample		Split sample		Original sample		Split sample	
		XRF		XRF	LAB	RPD-1 ^a	RPD-2 ^b	XRF	LAB	XRF		XRF	LAB
--	--	--	--	--	--	29	26	--	--	--	--	--	--
Average relative percent difference—Continued													
												49	75
Number of cases—Continued													
--	--	84	83	85	84	84	83	17	12	85	17	12	85
Maximum value—Continued													
--	--	7,460	6,950	9,340	131	156	115	157	97	101	147	27,900	42,100
Minimum value—Continued													
--	--	87	85	66	0	0	<65	<65	12	7	8	39	219
												176	219
												1	0

^aRPD between XRF results from analysis of the original sample and split sample sent for laboratory analysis.

^bRPD between XRF scan of split sample sent for laboratory chemical analysis and split sample sent for laboratory analysis.

Publishing support provided by:
Rolla Publishing Service Center

For more information concerning this publication, contact:
Director, USGS Missouri Water Science Center
1400 Independence Road
Rolla, MO 65401
(573) 308-3667

Or visit the Missouri Water Science Center Web site at:
<http://mo.water.usgs.gov/>

