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

Occurrence and Trends of Selected Chemical Constituents in Bottom Sediment, Grand Lake O' the Cherokees, Northeast Oklahoma, 1940–2008

Scientific Investigations Report 2009–5258

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

Cover Photographs—

Front cover: Grand Lake O’ the Cherokees, Oklahoma (photograph taken by Kyle Juracek, USGS)

Back cover: USGS personnel collecting a sediment core from Grand Lake O’ the Cherokees, Oklahoma (photograph taken by Kyle Juracek, USGS)

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Conversion Factors, Abbreviations, and Datum

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
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	0.004047	square kilometer (km^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	
acre-foot (acre-ft)	1,233	cubic meter (m^3)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Mass	
milligram per kilogram (mg/kg)	1.0	part per million (ppm)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C=(°F-32)/1.8$$

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

Occurrence and Trends of Selected Chemical Constituents in Bottom Sediment, Grand Lake O' the Cherokees, Northeast Oklahoma, 1940-2008

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Abstract

After over 100 years of continuous activity, lead and zinc mining in the Tri-State Mining District (hereafter referred to as the TSMD) in parts of southeast Kansas, southwest Missouri, and northeast Oklahoma ended in the 1970s. The mining activity resulted in substantial historical and ongoing input of cadmium, lead, and zinc to the environment including Grand Lake O' the Cherokees (hereafter referred to as Grand Lake), a large reservoir in northeast Oklahoma. To help determine the extent and magnitude of contamination in Grand Lake, a one-year study was conducted by the U.S. Geological Survey in cooperation with the U.S. Fish and Wildlife Service. Bottom-sediment coring at five sites was used to investigate the occurrence of cadmium, lead, zinc, and other selected constituents in the bottom sediment of Grand Lake.

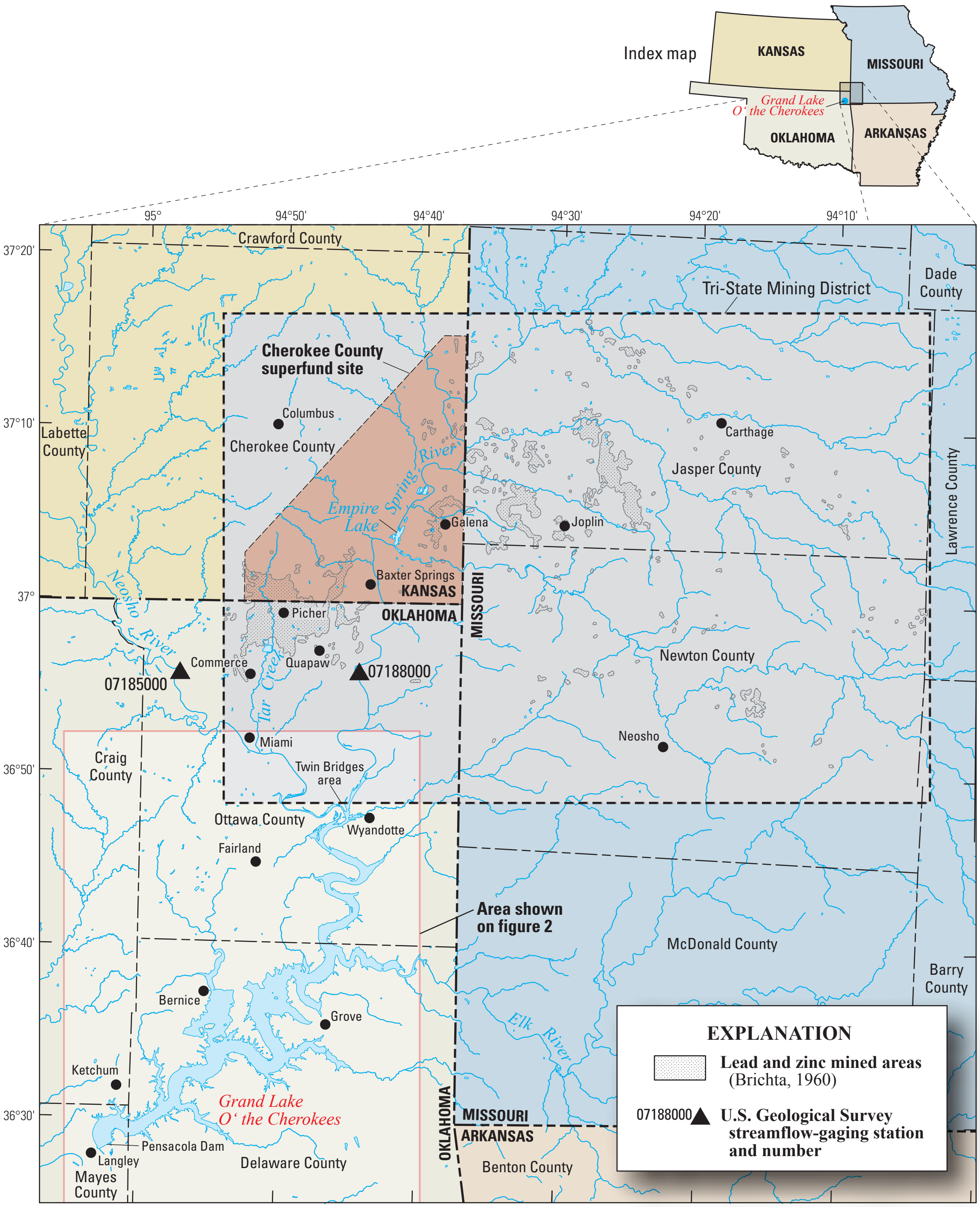
Cadmium concentrations in the bottom sediment of Grand Lake ranged from 2.3 to 3.6 mg/kg (milligrams per kilogram) with a median of 3.5 mg/kg (5 samples). Compared to an estimated local background concentration of 0.6 mg/kg, the historical mining activity increased cadmium concentrations by about 280 to 500 percent. Lead concentrations ranged from 35 to 102 mg/kg with a median of 59 mg/kg (50 samples). Compared to an estimated local background concentration of 20 mg/kg, the historical mining activity increased lead concentrations by about 75 to 410 percent. The range in zinc concentrations was 380 to 986 mg/kg with a median of 765 mg/kg (50 samples). Compared to an estimated local background concentration of 100 mg/kg, the historical mining activity increased zinc concentrations by about 280 to 890 percent. With the exception of the most upstream coring site, the lead and zinc depositional profiles generally were similar in terms of the range in concentrations measured and the temporal pattern observed. Depositional profiles for lead and zinc indicated mid-core peaks followed by concentrations that decreased since about the 1980s. The depositional profiles reflect the complex interaction of several factors including historical mining and related activities, mine drainage, remediation, landscape stabilization, precipitation and associated runoff, and the erosion and transport of contaminated and clean sediments within the basin.

Compared to sediment-quality guidelines, the Grand Lake samples had cadmium concentrations that were substantially less than the general probable-effects concentration (PEC) (4.98 mg/kg) and a TSMD-specific PEC (11.1 mg/kg). The PECs represent the concentration above which toxic biological effects are likely to occur. Likewise, all sediment samples had lead concentrations that were substantially less than the general PEC (128 mg/kg) and a TSMD-specific PEC (150 mg/kg). Zinc concentrations typically exceeded the general PEC (459 mg/kg), but were substantially less than a TSMD-specific PEC (2,083 mg/kg). Throughout the history of Grand Lake, lead and zinc concentrations in the deposited sediment did not approach or exceed the TSMD-specific PECs.

As of 2008, legacy effects of mining still included the delivery of contaminated sediment to Grand Lake by the Spring and Neosho Rivers. The Neosho River, with its larger flows and less-contaminated sediment, likely dilutes the load of contaminated sediment delivered to Grand Lake by the Spring River. The information contained in this report provides a baseline of Grand Lake conditions with which to compare future conditions that may represent a response to changes in mining-related activity in the Grand Lake Basin.

Introduction

Grand Lake O' the Cherokees (hereafter referred to as Grand Lake) is a large reservoir on the Grand River in northeast Oklahoma (fig. 1). Primary tributaries to the reservoir are the Spring and Neosho Rivers which together drain the Tri-State Mining District (hereafter referred to as the TSMD) that covers part of Jasper and Newton Counties in southwest Missouri, Cherokee County in southeast Kansas, and Ottawa County in northeast Oklahoma (fig. 1). For about 100 years (1850–1950), the TSMD was one of the primary sources of lead and zinc ore in the world (Brosius and Sawin, 2001). Although the mining has ended and some remediation has occurred, the legacy of environmental contamination remains (Juracek, 2006). Stream sediments within and downstream from mined areas in the TSMD contain concentrations of cadmium, lead, and zinc that often exceed estimated local



Base from U.S. Geological Survey digital data, 1:100,000, 2008
Universal Transverse Mercator projection,
Zone 15

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

Figure 1. Location of Grand Lake O’ the Cherokees in relation to lead and zinc mined areas in the Tri-State Mining District, Kansas, Missouri, and Oklahoma.

background concentrations by one to two orders of magnitude or more (Pope, 2005). Sediment quality is an important environmental concern because sediment may be a sink for some water-quality constituents and a source of constituents to the overlying water column and biota (Baudo and others, 1990; Zoumis and others, 2001). Once in the food chain, sediment-derived constituents may pose an even greater concern due to bioaccumulation (that is, the accumulation of constituents in biological tissues of living organisms) (Smol, 2002).

In addition to the environmental degradation caused by the mining, processing, and smelting of the lead and zinc ores, contamination also has resulted from other related activities and processes. For example, as extraction technologies improved, “chat” piles (that is, processed ore-bearing waste rock also known as mine tailings) sometimes were reprocessed. The reprocessing resulted in additional volumes of fine-grained waste material (tailings) that were susceptible to erosion and transport by water and wind. Chat also has been processed and shipped to various locations for use as aggregate for roads. Sometimes, the chat is screened and washed to remove the fine-grained material prior to shipment. The fine-grained material left behind can have large concentrations of cadmium, lead, and zinc (Schaider and others, 2007; U.S. Environmental Protection Agency, 2008). Another pathway for contamination has been mine drainage from the abandoned mines. Mine drainage can have large dissolved concentrations of cadmium, lead, and zinc (Parkhurst, 1987; Spruill, 1987).

The ongoing mining-related environmental contamination has adversely affected biota including mussels (Angelo and others, 2007), waterfowl (Beyer and others, 2004), and possibly the endangered Neosho madtom (Wildhaber and others, 1998, 1999, 2000). In recent years, a shellfish consumption advisory was issued in Kansas (Kansas Department of Health and Environment, 2006) and a fish consumption advisory was issued in Oklahoma (Oklahoma Department of Environmental Quality, 2007) because of cadmium and (or) lead contamination. Human health problems also have been attributed to mining-related contamination (Neuberger and others, 1990).

The environmental contamination caused by the decades of mining activity resulted in the listing of several sites within the TSMD on the U.S. Environmental Protection Agency’s (USEPA) National Priority List as superfund hazardous waste sites (U.S. Environmental Protection Agency, 2009a, 2009b, 2009c). Authority for the establishment of superfund sites was given to the USEPA through provisions of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA; U.S. Code Title 42, Chapter 103). Provisions of this act provide a means to assess injured public natural resources through the direction and oversight of natural resource trustees. The process by which the trustees assess the injured resources is known as the Natural Resource Damage Assessment (NRDA). For Grand Lake, the U.S. Department of the Interior (DOI) is one of the trustees.

CERCLA required the promulgation of regulations for NRDAs, and the responsibility for rule making was given to the DOI by Presidential Executive Order 12580 (January 23, 1987). DOI regulations and processes for conducting a NRDA are detailed in the Code of Federal Regulations Title 43, Part 11, which describes the following five major steps: (1) preassessment, (2) assessment planning, (3) injury determination and quantification, (4) pathway determination, and (5) damage determination and restoration. The study described in this report was conducted by the U.S. Geological Survey (USGS) in cooperation with the U.S. Fish and Wildlife Service (USFWS) to assist the DOI with the injury determination and quantification for Grand Lake.

Grand Lake is a reservoir on the Grand River that was formed with the 1940 completion of Pensacola Dam near the town of Langley, Oklahoma (fig. 1). The dam was constructed by the Grand River Dam Authority, a state agency that continues to operate the dam. From the dam, the reservoir extends upstream to the confluence of the Spring and Neosho Rivers (fig. 1). Primary uses of Grand Lake include hydroelectric power generation, flood control, and recreation. The reservoir is home to several species of fish, amphibians, and shellfish, and supports several species of migratory waterfowl. At the normal pool elevation of 742 ft (feet) above sea level, Grand Lake has a surface area of about 46,500 acres (Grand River Dam Authority, 2009) and a water-storage capacity of about 1,537,000 acre-ft (acre feet) (U.S. Army Corps of Engineers, 2009).

The trustees require several types of information including: (1) a determination of trace element concentrations in bottom sediment in Grand Lake and the Grand River Basin; (2) an assessment of the spatial variability of trace element concentrations in bottom sediment in Grand Lake and the Grand River Basin; and (3) an assessment of the temporal variability of trace element concentrations in bottom sediment that may reflect changes caused by mining-related activity.

Previous Investigations

In a comparative study of five Oklahoma reservoirs, Pita and Hyne (1975) documented increased lead and zinc concentrations in the uppermost layer of bottom sediment in Grand Lake. The increased concentrations were attributed to historical mining activity in the TSMD.

Spruill (1987) conducted an extensive study of the effects of abandoned lead and zinc mines on hydrology and surface- and ground-water quality in Cherokee County, Kansas, and adjacent areas. Water from mines located mostly in the vicinity of Galena, Kansas (fig. 1), had median concentrations of 180 μg/L (micrograms per liter) for dissolved cadmium, 240 μg/L for dissolved lead, and 37,600 μg/L for dissolved zinc. It also was reported that mine drainage in the Tar Creek Basin, Kansas (fig. 1), had large concentrations of dissolved cadmium, lead, and zinc. Information on water and sediment quality in the Tar Creek Basin in northeast Oklahoma was provided by Parkhurst (1987) and Parkhurst and others (1988).

Cope and others (2008) investigated the loading potential following rainfall of the suspended-sediment load from a short stream segment of Tar Creek that was bordered by mine tailings and received mine discharge. Seven samples were collected over 14 days following a rain event and the mean total instantaneous loads for cadmium, lead, and zinc were 0.156 lb/day (pound per day), 0.039 lb/day, and 142 lb/day, respectively. This study demonstrated that the contributions from a very small reach of a stream within the mining-affected area could be substantial and indicated the potential for overall contributions from the entire area.

Pope (2005) provided an assessment of sediment quality along the main stem and major tributaries for both the Spring River and Tar Creek systems within the boundary of the Cherokee County, Kansas, superfund site (fig. 1). All sediment samples were collected to a depth of 0.8 in. (inch) and sieved to isolate the less than 63-µm (micron) fraction (that is, silt- and clay-size particles) for analysis. Concentrations ranged from 0.6 to 460 mg/kg (milligrams per kilogram) for cadmium, 22 to 7,400 mg/kg for lead, and 100 to 45,000 mg/kg for zinc, with respective median concentrations of 13, 180, and 1,800 mg/kg. The largest concentrations were measured for sampling sites in the Short Creek, Tar Creek, and Spring Branch Creek Basins. The locations of Short and Spring Branch Creeks are provided in Pope (2005). Proceeding downstream along the 22-mile length of the Spring River within the superfund site (fig. 1), sediment concentrations of cadmium, lead, and zinc increased about 18, 7, and 17 times, respectively.

Juracek (2006) investigated mining-related sediment contamination in Empire Lake, Kansas, which is located upstream from Grand Lake along the Spring River within the TSMD (fig. 1). All bottom-sediment samples were sieved to isolate the less than 63-µm fraction for analysis. Cadmium concentrations ranged from 7.3 to 76 mg/kg with a median concentration of 29 mg/kg. Lead concentrations ranged from 100 to 950 mg/kg with a median concentration of 270 mg/kg. Zinc concentrations ranged from 1,300 to 13,000 mg/kg with a median concentration of 4,900 mg/kg. In general, the cadmium, lead, and zinc concentrations were one to two orders of magnitude larger than estimated local background concentrations with the largest concentrations in the older sediments that corresponded to when the mines were in operation. Despite a decrease in concentrations over time, the concentrations of cadmium, lead, and zinc in the most recently deposited bottom sediment still exceeded probable-effects guidelines (U.S. Environmental Protection Agency, 1997; MacDonald and others, 2000) for toxic biological effects.

In 2007, sediment samples collected by the U.S. Environmental Protection Agency at 70 locations in the TSMD were analyzed by USGS with objectives that included an evaluation of sediment contamination and sediment toxicity. Concentrations of trace elements, including cadmium, lead and zinc, varied widely in the samples analyzed. Likewise, laboratory sediment toxicity tests conducted using the samples demonstrated a wide range in responses of amphipods, midge, and mussels (Ingersoll and others, 2008).

In 2008, USFWS collected surficial samples of bottom sediment along 12 transects within Grand Lake from downstream near the dam to upstream at the confluence of the Spring and Neosho River arms of the reservoir. The samples were not sieved prior to analysis. Median concentrations for the transects ranged from 44 to 65 mg/kg for lead and from 454 to 767 mg/kg for zinc. Results for the transect at the confluence of the Spring and Neosho River arms of the reservoir indicated that the bottom sediment in the Spring River arm was more contaminated. Specifically, lead and zinc concentrations in the Spring River arm were about 5 and 12 times larger, respectively (Suzanne Dudding, U.S. Fish and Wildlife Service, written commun., 2009).

Based on the results of the 12 transects, 40 sites were resampled by USFWS in 2008 to provide sediment samples that represented a range in trace-element chemistry for use in sediment toxicity testing by USGS. Sediment toxicity was determined by assessing the effects of trace elements including cadmium, lead, and zinc on the survival or growth of the amphipod *Hyalella azteca* (a species known to be sensitive to trace element contamination). The toxicity tests indicated that concentrations of trace elements including cadmium, lead, and zinc in the Grand Lake sediment samples were not sufficient to reduce the survival or growth of amphipods (Ingersoll and others, 2009).

Andrews and others (2009) summarized several sets of sediment and water-quality data collected from 2000 through 2006 within the basin upstream from Grand Lake. Data collected included a sediment core transect across the Tar Creek flood plain that was analyzed for trace elements. Results indicated spatial variability in trace element concentrations and that the flood-plain sediments were repositories for trace elements of concern. Routine annual base-flow and high-flow water samples illustrated the importance of total trace element loads to Grand Lake during high flows.

MacDonald and others (2009a), using data collected in 2006 and 2007, developed and evaluated sediment and pore-water toxicity thresholds to support sediment-quality assessments in the TSMD. Many of the toxicity thresholds developed, including those for cadmium, lead and zinc, were found to provide a reliable and predictive basis for classifying sediment samples from the TSMD as either toxic or not toxic.

MacDonald and others (2009b) conducted an ecological risk assessment to determine if exposure to contaminants, including cadmium, lead and zinc, in aquatic habitats within the TSMD present potential risks to aquatic biota. Results indicated that contaminant concentrations in surface water, sediment, and pore water do present potential risks to aquatic biota. It was determined that cadmium, lead, and (or) zinc concentrations in surficial sediment samples frequently were sufficient to present moderate to high risks to benthic invertebrates. Sediment toxicity tests with amphipods, midge, or freshwater mussels confirmed that sediment samples with elevated levels of these trace elements were toxic to sediment-dwelling organisms.

Numerous other studies also have investigated the effects of mining activity in the TSMD on sediment quality, water quality, and biota. Several such studies are summarized by Pope (2005) and Juracek (2006).

Current Investigation

A one-year study by USGS, in cooperation with USFWS, was begun in 2008 to investigate the deposition of selected chemical constituents in the bottom sediment of Grand Lake. Specific objectives of the study were to:

1. assess the spatial and temporal variability of cadmium, lead, and zinc concentrations in the bottom sediment of Grand Lake;
2. assess the quality of Grand Lake bottom sediment with respect to background conditions and available sediment-quality guidelines;
3. relate, to the extent possible, any observed temporal trends in bottom-sediment constituent concentrations to documented changes in mining-related activity and other factors in the Grand Lake Basin; and
4. provide a baseline of information on Grand Lake conditions with which to compare future conditions that may represent a response to changes in mining-related activity in the basin.

The purpose of this report is to present the results of the USGS study to determine the occurrence of, and temporal trends for 1940 to 2008 in, selected chemical constituents in the bottom sediment of Grand Lake. In November 2008, sediment cores were collected at five sites along the length of the reservoir and analyzed for selected chemical constituents. Cadmium, lead, and zinc concentrations in the bottom sediment were of primary interest to DOI because they are the major contaminants input to the environment as a result of historical upstream mining activity (Juracek, 2006). Other chemical constituents, including additional trace elements and nutrients, were analyzed to provide a more comprehensive assessment of sediment quality in the reservoir. Data for the additional constituents are presented but not discussed in this report.

Results presented in this report will assist USFWS in efforts to evaluate injury to natural resources in Grand Lake. From a national perspective, the methods and results presented in this report provide guidance and perspective for future reservoir studies concerned with the issues of sediment-associated contaminant transport and deposition.

Description of Grand Lake O′ the Cherokees Basin

The Grand Lake Basin is about 10,298 mi^2 (square miles) (U.S. Army Corps of Engineers, 2009) and drains part of Arkansas, Kansas, Missouri, and Oklahoma. The primary tributaries to Grand Lake are the Spring and Neosho Rivers, which join to form the Grand River (at an area locally known as “Twin Bridges”) in northeast Oklahoma (fig. 1). Together, the Spring and Neosho Rivers drain the TSMD. A third important tributary is the Elk River, which flows into Grand Lake upstream from Grove, Oklahoma (fig. 1). Several other lesser tributaries also contribute flow directly to Grand Lake.

The Grand Lake Basin is located within two physiographic provinces as defined by Fenneman (1938, 1946). The western part of the basin, which includes all of the Neosho River Basin and part of the Spring River Basin, is located in the Osage Plains Section of the Central Lowland Province. This part of the basin is underlain by shale with interbedded sandstone and limestone of Pennsylvanian age (Fenneman, 1938). The eastern part of the basin, which includes the remainder of the Spring River Basin, is located in the Springfield Plateau Section of the Ozark Plateaus Province. This part of the basin is underlain by limestone of Mississippian age (Fenneman, 1938). Topographically, the basin is characterized by gently rolling uplands dissected by streams.

The lead and zinc ores in the TSMD occur in Mississippian-age cherty limestones. The Mississippian-age rock contained numerous fractures and solution cavities prior to the migration of hydrothermal (hot, metal bearing) fluids (McKnight and Fischer, 1970) from deep within the earth. As these fluids moved vertically into the porous and permeable cherty limestones, an overlying impermeable layer of shale forced them to migrate laterally. The primary ore and gangue minerals precipitated out from the hydrothermal fluids. Ores deposited were sulfide-type minerals consisting largely of sphalerite (zinc sulfide) and galena (lead sulfide) (Brosius and Sawin, 2001).

The climate in the Grand River Basin is characterized as subhumid continental (Stringer, 1972). Long-term, mean annual precipitation at Joplin, Missouri (period of record 1948–2007) averages about 42 in. (High Plains Regional Climate Center, 2009). Joplin is located within the TSMD (fig. 1).

Land use in the Grand Lake Basin is predominantly a mix of cropland, grassland, and woodland. The largest urban area in the basin is Joplin, Missouri, with a 2007 population for the entire metropolitan area of about 170,000 (U.S. Census Bureau, 2009). Historically, numerous locations within the basin were mined for coal, lead, and zinc. The locations of the major lead- and zinc-mined areas within the basin are shown in figure 1.

Methods

The study objectives described in this report mostly were accomplished using newly collected information. Chemical data for Grand Lake were obtained through the collection and analysis of bottom-sediment cores. The following sections describe the methods of sediment-core collection and analysis.

Sediment-Core Collection, Handling, and Processing

Bottom-sediment cores were collected in November 2008 at five sites within Grand Lake (fig. 2). The coring sites, located in areas of the submerged flood plain, provide a spatially representative sample of bottom sediment along the length of the reservoir. The bottom-sediment cores were collected from a pontoon boat using a gravity corer. The liner used for all cores was cellulose acetate butyrate transparent tubing with a 2.625-in. inside diameter. The latitude and longitude for each coring site, obtained using a global positioning system (GPS), are provided in table A1 in the "Supplemental Information" section at the back of this report.

When using a gravity corer, a phenomenon referred to as "core shortening" occurs that results in a recovered sediment core the length of which is less than the actual thickness of sediment penetrated (Emery and Hulsemann, 1964). Core shortening is caused by the friction of the sediment against the inner wall of the core liner as the corer penetrates the sediment (Emery and Hulsemann, 1964; Hongve and Erlandsen, 1979; Blomqvist, 1985; Blomqvist and Bostrom, 1987). In "normal" lake-bottom sediment, which is characterized by uniform texture with decreasing water content at depth, core shortening results in a core that provides a thinned but complete representation of all of the sediment layers that were penetrated (Emery and Hulsemann, 1964; Hongve and Erlandsen, 1979). In this study, a comparison of the length of core recovered by gravity coring to the thickness of sediment penetrated (penetration of the entire sediment thickness was achieved for all cores) indicated that core recovery averaged about 90 percent. The thickness of sediment penetrated was computed as the total depth of corer penetration (as measured from the water surface) minus the water depth. Estimated sediment thickness, length of core recovered, and estimated recovery percentage for the coring sites are provided in table A1.

Upon collection, the bottom and top of each sediment core was covered with a plastic end cap that was secured to the liner with electrical tape. Both ends of each core were sealed with a chain-of-custody sticker. The cores were transported to the USGS laboratory in Lawrence, Kansas, where they were stored vertically and refrigerated (at 4–5 ºC) in a locked walk-in cooler. The cores were processed within about 1 month of collection. The core liners were cut lengthwise in two places 180 degrees apart. The cuts were completed with a 4-in. hand-held circular saw with its blade set at a depth to minimize penetration of the cores. The cores were split in half by pulling a tightly held nylon string through the length of the cores and allowing the halves to separate. Once split, the relatively undisturbed inner parts of the cores were exposed for examination and sampling. Based on differences in moisture content, texture, and organic matter content (for example, root hairs and sticks), the boundary between the sediment deposited in the reservoir and the underlying original (pre-reservoir) flood-plain soil was determined. Typically, the reservoir bottom sediment was characterized by higher moisture content, finer texture, and little if any visible organic matter as compared to the original flood-plain soil.

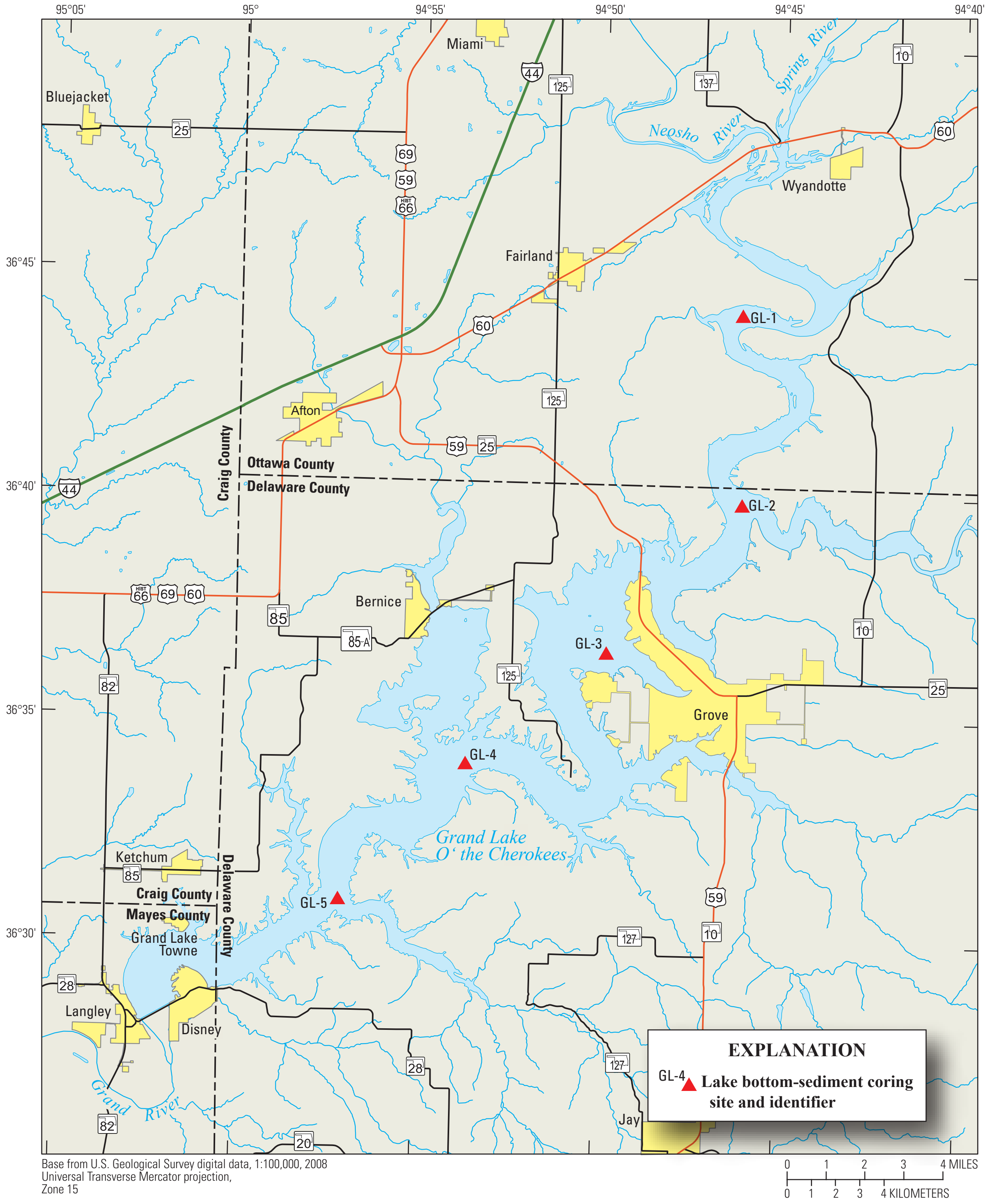
All cores were divided into 10 intervals of equal length, sampled, and analyzed to assess the magnitude of, and trends in, constituent deposition over the life of the reservoir. Also, samples of the original flood-plain soil at the bottom of two cores (sites GL-4 and GL-5, fig. 2) were collected for constituent analyses. The flood-plain soil samples were used to provide an indication of pre-reservoir conditions.

From each core interval, an approximately equal volume of sediment was removed lengthwise from both halves and combined. In all cases, care was taken to avoid sampling the sediment that came into contact with the core liner and the saw blade. The combined sediment volume for each interval was homogenized and samples were taken for subsequent chemical and age-dating analyses. Plastic utensils were used for the sediment removal, homogenization, and sampling. The utensils were thoroughly cleaned with deionized water and wiped dry with a clean paper towel prior to each reuse. The sediment was homogenized in a glass bowl that also was thoroughly cleaned (as previously described) prior to each reuse. All samples for chemical analyses were placed in plastic jars that were labeled and sealed with a chain-of-custody sticker prior to shipment to other laboratories for analyses.

Chemical Analyses, Quality Control, and Age Dating

The sediment samples for chemical analyses were dried completely at 40 ºC, ground, and analyzed for cadmium, lead, and zinc using x-ray fluorescence (XRF) methods (U.S. Environmental Protection Agency, 2007). A total of 52 samples were analyzed by XRF methods at the USFWS laboratory in Manhattan, Kansas. Chain-of-custody procedures were followed at the USFWS laboratory during sample storage, processing, and analysis.

To verify comparability of results with other recent studies (for example, see the study of Empire Lake, Kansas, by Juracek (2006) in the Previous Investigations section of this report), a randomly selected split-replicate sample from each of the five cores was analyzed by combustion and various spectroscopic methods. Also, split-replicate samples of the original flood-plain soil for two cores (sites GL-4 and GL-5) were analyzed by combustion and various spectroscopic methods. In addition to 26 trace elements, these seven samples were analyzed for nutrients (total nitrogen and total phosphorus) and organic and total carbon (table 1). The five sediment samples were analyzed as bulk (unsieved) samples given the expectation that they consisted mostly (at least 90 percent) of particles less than 63 µm in size (that is, the silt and (or) clay fraction). The two soil samples were analyzed as bulk samples and as the less than 63-µm fraction. Analyses of the sediment and soil samples by combustion and various spectroscopic methods were performed at the USGS Sediment Trace Element Partitioning Laboratory in Atlanta, Georgia.



Base from U.S. Geological Survey digital data, 1:100,000, 2008
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Figure 2. Location of bottom-sediment coring sites in Grand Lake O' the Cherokees, northeast Oklahoma.

Table 1. Chemical analyses for bottom-sediment samples from Grand Lake O’ the Cherokees, northeast Oklahoma, 2008.

[Number in parentheses is the detection limit or method reporting limit for each constituent. mg/kg, milligrams per kilogram; %, percent dry weight; dpm/g, disintegrations per minute per gram]

Analyses using x-ray fluorescence methods[1]			
Cadmium (50–150 mg/kg)	Lead (10–100 mg/kg)	Zinc (10–100 mg/kg)	
Analyses using combustion and various spectroscopic methods[2]			
Aluminum (0.1%)	Chromium (1.0 mg/kg)	Molybdenum (1.0 mg/kg)	Sulfur (0.01%)
Antimony (0.1 mg/kg)	Cobalt (1.0 mg/kg)	Nickel (1.0 mg/kg)	Thallium (50 mg/kg)
Arsenic (0.1 mg/kg)	Copper (1.0 mg/kg)	Nitrogen, total (100 mg/kg)	Tin (1.0 mg/kg)
Barium (1.0 mg/kg)	Iron (0.1%)	Phosphorus, total (50 mg/kg)	Titanium (0.01%)
Beryllium (0.1 mg/kg)	Lead (1.0 mg/kg)	Selenium (0.1 mg/kg)	Uranium (50 mg/kg)
Cadmium (0.1 mg/kg)	Lithium (1.0 mg/kg)	Silver (0.5 mg/kg)	Vanadium (1.0 mg/kg)
Carbon, organic (0.1%)	Manganese (10.0 mg/kg)	Strontium (1.0 mg/kg)	Zinc (1.0 mg/kg)
Carbon, total (0.1%)	Mercury (0.01 mg/kg)		
Radionuclide			
Cesium-137 (0.05 dpm/g)			

[1] The detection limit varies depending on several factors including the constituent of interest, the type of detector used, the type and strength of excitation source, count time used to irradiate the sample, physical matrix effects, chemical matrix effects, and interelement spectral interferences (U.S. Environmental Protection Agency, 2007).

[2] Carbon and nitrogen analyzed by combustion. Mercury analyzed by cold vapor atomic absorption. Antimony, arsenic, and selenium analyzed by hydride generation inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Cadmium, lead, and silver analyzed by flame atomic absorption. Remaining constituents analyzed by ICP-AES (Fishman and Friedman, 1989; Arbogast, 1996; Briggs and Meier, 1999; Horowitz and others, 2001).

Chain-of-custody procedures were followed at the laboratory during sample storage, processing, and analysis. Analyses of samples for total nitrogen and carbon concentrations were performed using the methods described by Horowitz and others (2001). Analyses for total phosphorus and trace elements were performed using the methods described by Fishman and Friedman (1989), Arbogast (1996), and Briggs and Meier (1999). For cadmium, lead, and zinc, analysis of a duplicate sample indicated that the analytical variability for the spectroscopic methods was less than 4 percent.

Quality control for the XRF chemical analysis of the sediment samples involved several parts. Each individual sample was analyzed three times to determine the analytical variability of the XRF method. Additional verification was provided by the analysis of a randomly selected split-replicate sample from each of the five cores using various spectroscopic methods. Finally, the accuracy of the XRF method was evaluated through an analysis of standard reference samples.

Cadmium concentrations were less than the XRF limit of detection (LOD) (table 1) for all samples analyzed. Thus, an evaluation of XRF analytical variability for cadmium was not possible. For lead and zinc, XRF-measured concentrations typically were within ±10 percent of the mean concentration for each sample.

A comparison of cadmium concentrations determined by XRF and spectroscopic methods was not possible because the cadmium concentrations were less than the XRF LOD for all five of the split-replicate samples. Lead and zinc concentrations determined by spectroscopic methods averaged 8 and 16 percent larger, respectively (table 2). Given the close agreement for lead and zinc, the XRF-measured concentrations were considered reliable and were used for interpretive purposes in this report. A complete list of results for the five split-replicate samples analyzed using spectroscopic methods is provided in table A2 in the “Supplemental Information” section.

The analyses of four reference samples (one blank plus three samples that covered a range of trace element concentrations) from the National Institute of Standards and Technology were completed prior to, repeatedly during, and subsequent to the triplicate analyses of the 52 samples. The four reference samples were analyzed an average of 17 times. Results for the analyses of the reference samples are provided in table A3 in the “Supplemental Information” section. A target goal for acceptable results of the analyses of the reference samples was within the published limits for each constituent or ±10 percent of the most probable value for the constituent (whichever was greater), except when constituent concentrations were near or less than method reporting limits. For cadmium, an assessment of analytical variability was not possible for two of the non-blank reference samples because the concentrations were less than the XRF LOD. For the third non-blank reference sample, mean cadmium concentrations determined by XRF differed from the most probable value of 41.7 ± 0.25 mg/kg by an average of about 31 percent. The average difference between the mean lead concentrations determined by XRF and the reported lead value for the three non-blank reference samples was less than 4 percent. For zinc, the average difference between the mean concentrations determined by XRF and the reported value for the three non-blank reference samples was about

Table 2. Cadmium, lead, and zinc concentrations for five randomly selected bottom-sediment samples collected from Grand Lake O' the Cherokees, northeast Oklahoma, and analyzed by x-ray fluorescence (XRF) and spectroscopic methods.

[mg/kg, milligrams per kilogram; <, less than; LOD, limit of detection]

Sample identifier	XRF concentration[1] (mg/kg)	Spectroscopic concentration (mg/kg)
	Cadmium	
GL-1A9	<LOD	2.7
GL-2A7	<LOD	3.6
GL-3A10	<LOD	2.3
GL-4A5	<LOD	3.5
GL-5A3	<LOD	3.6
	Lead	
GL-1A9	35	39
GL-2A7	58	61
GL-3A10	53	54
GL-4A5	67	73
GL-5A3	59	66
	Zinc	
GL-1A9	401	440
GL-2A7	818	960
GL-3A10	486	570
GL-4A5	777	960
GL-5A3	895	1,000

[1] The limit of detection (LOD) for XRF analyses varies depending on several factors. See footnote on table 1 for more information.

10 percent or less. Without exception, analyses of the blank samples by XRF consistently indicated that cadmium, lead, and zinc concentrations were less than the LOD.

Age dating of the bottom sediment was achieved by determining the activity of cesium-137 (^{137}Cs). ^{137}Cs is a radioactive isotope that is a byproduct of aboveground nuclear weapons testing. Measurable activity of this isotope first appeared in the atmosphere about 1952, peaked during 1963–64, and has since declined (Ritchie and McHenry, 1990). Measurable activity in soils began about 1954 (Wise, 1980). ^{137}Cs is an effective marker for age dating bottom sediment in reservoirs constructed before 1963–64 (Van Metre and others, 1997). It also can be used to demonstrate that the sediment is relatively undisturbed if the 1963–64 peak is well-defined and a generally uniform, exponential decrease in ^{137}Cs activity follows the 1963–64 peak. Age dating of sediment using ^{137}Cs was attempted for all five Grand Lake cores (fig. 2). Analysis of sediment samples for ^{137}Cs activity was performed at the USGS Florida Integrated Science Center in St. Petersburg, Florida, using gamma-ray spectrometry (Holmes and others, 2001).

The ^{137}Cs activity had a well-defined 1963–64 peak followed by a uniform, exponential decrease for coring sites GL-2, GL-3, GL-4, and GL-5 (figs. 3*B*–3*E*). Thus, for these four sites, it was concluded that the bottom sediment was relatively undisturbed and any trends in constituent deposition may be considered meaningful. However, for upstream coring site GL-1 (fig. 3*A*), a well-defined peak in ^{137}Cs activity was absent. Thus, substantial postdepositional disturbance, including possible removal, of the bottom sediment was indicated for this site and any trends in constituent deposition may not be meaningful. The fact that the greatest ^{137}Cs activity was measured at the bottom of core GL-1 provided evidence that the bottom sediment sampled may only be representative of post 1963–64 deposition (as the underlying older sediment may have been removed). Coring site GL-1 was located in an area of shallow water (about 7 ft deep on the day of coring) where the bottom sediment was more susceptible to disturbance (for example, by wind-induced turbulence and lake-level fluctuations). The other four downstream coring sites were located in much deeper water (ranging from 28 to 82 ft on the day of coring) where the depositional environment was more isolated from disturbance.

Trend Analysis

Temporal trends in constituent concentrations (in relation to depth in the sediment profile) were examined by computing a nonparametric Spearman's rho correlation coefficient. An advantage of Spearman's rho is that, because it is based on ranks, it is more resistant to outlier effects than the more commonly used Pearson's r correlation coefficient (Helsel and Hirsch, 1992). Measures of correlation are dimensionless and scaled to range from -1.0 to 1.0. A value of 0 indicates no relation between two variables. Temporal trends were considered to be significant if the probability (two-sided p-value) of rejecting a correct hypothesis (in this case, no trend) was less than or equal to 0.05. A value between 0 and 1.0 indicated that the constituent concentration increased toward the top of the sediment core whereas a value between 0 and -1.0 indicated that the constituent concentration decreased toward the top of the sediment core. A possible temporal trend was only considered meaningful if the change in constituent concentration was beyond the variability that could be explained by analytical variance (defined here as the mean constituent concentration in the sediment core ± 10 percent). The possibility must be recognized that sediment-associated trace element concentrations in the cores may have been affected by post-depositional remobilization and subsequent diffusion (Smol, 2002).

Sediment-Quality Assessment

MacDonald and others (2000) developed consensus-based sediment-quality guidelines (SQGs) for cadmium, lead, and zinc (table 3) that were computed as the geometric mean of several previously published SQGs. The consensus-based SQGs consist of a threshold-effect concentration (TEC) and

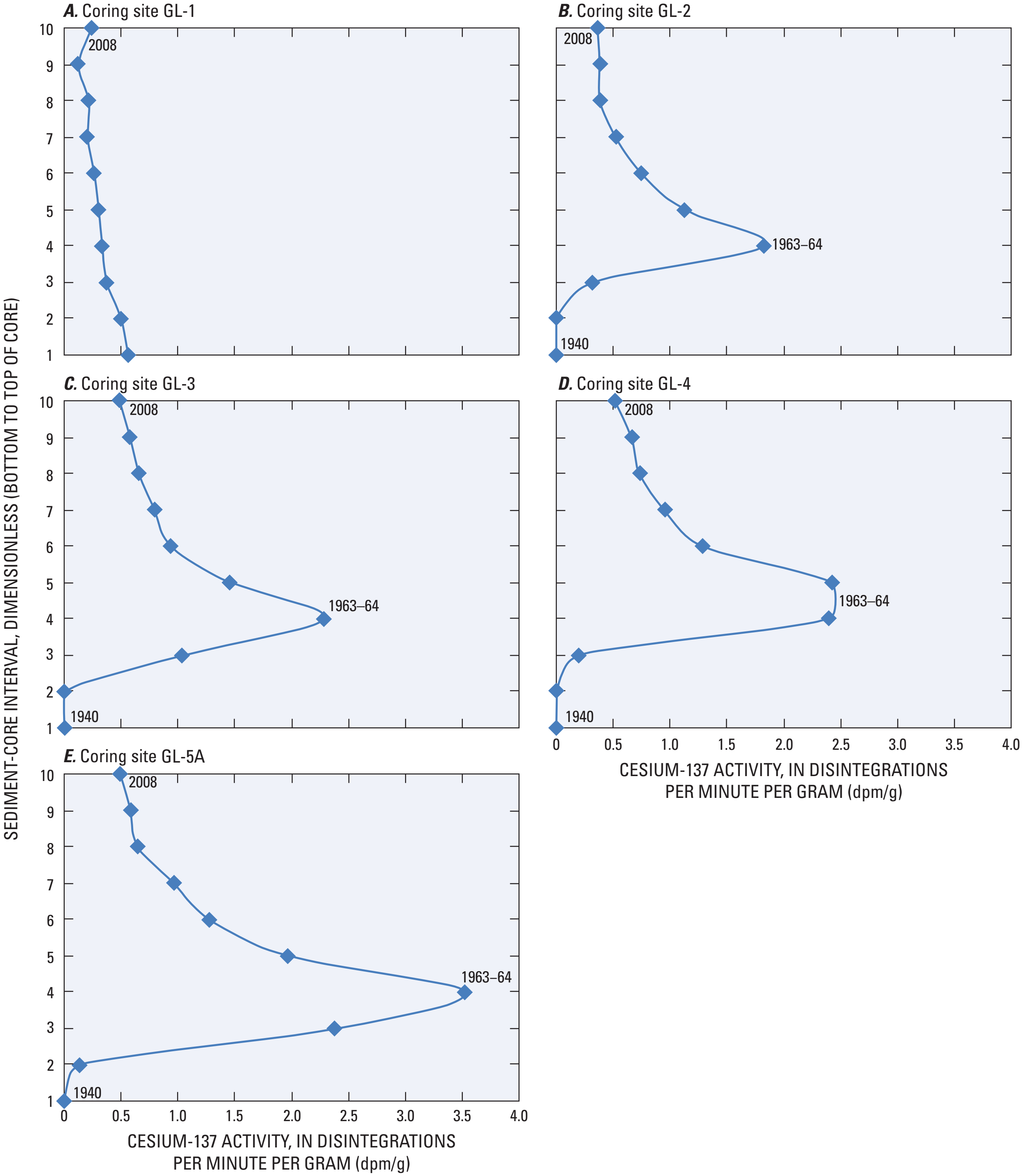

Figure 3. Variation in cesium-137 activity with depth of bottom-sediment samples collected from coring sites GL-1, GL-2, GL-3, GL-4, and GL-5 in Grand Lake O’ the Cherokees, northeast Oklahoma, November 2008.

a probable-effect concentration (PEC). The TEC represents the concentration below which adverse biological effects are not expected to occur. The PEC represents the concentration above which adverse effects are expected to occur more often than not. An evaluation of the reliability of the SQGs indicated that most of the individual TECs and PECs provide an accurate basis for predicting the presence or absence of sediment toxicity (MacDonald and others, 2000).

In 2009, TSMD-specific PECs for cadmium, lead and zinc were developed. The TSMD-specific PECs represent sediment concentrations predicted to reduce the survival of the amphipod *Hyalella azteca* (a species known to be sensitive to trace element contamination) by 10 percent relative to reference conditions in the TSMD (Ingersoll and others, 2009). In this study, both the general PECs provided by MacDonald and others (2000) and the TSMD-specific PECs provided by Ingersoll and others (2009) were used to assess sediment quality. A comparison of the PECs is provided in table 3.

Table 3. Sediment-quality guidelines for cadmium, lead, and zinc and associated bioaccumulation index.

[Concentrations in milligrams per kilogram. TSMD, Tri-State Mining District; TEC, threshold-effects concentration; PEC, probable-effects concentration]

Trace element	General[1]		TSMD-specific[2]	Bioaccumulation index[3]
	TEC	PEC	PEC	
Cadmium	0.99	4.98	11.1	moderate
Lead	35.8	128	150	moderate
Zinc	121	459	2,083	high

[1] General sediment-quality guidelines from MacDonald and others (2000).

[2] TSMD-specific sediment-quality guidelines from Ingersoll and others (2009).

[3] Bioaccumulation index information for trace elements from Pais and Jones (1997).

Background Information for Trace Elements

Trace elements are important determinants of sediment quality because of their potential toxicity to living organisms (Forstner and Wittmann, 1981; Smol, 2002; Luoma and Rainbow, 2008). Trace elements may be defined as elements that typically are detected in the environment in relatively low (less than 0.1 percent) concentrations (Adriano, 1986; Pais and Jones, 1997). Using this definition, most of the elements analyzed in this study can be considered trace elements. Exceptions include aluminum and iron, which are some of the abundant rock-forming elements (Adriano, 1986).

Trace elements in sediment originate naturally from the rock and soil within a basin. Elevated concentrations of sediment-associated trace elements may be attributable to several human-related sources including fertilizers, liming materials, pesticides, irrigation water, animal and human wastes, coal-combustion residues, leaching from landfills, mining, metal-smelting industries, and automobile emissions (Forstner and Wittmann, 1981; Davies, 1983; Adriano, 1986; Luoma and Rainbow, 2008).

The health of living organisms is dependent on a sufficient intake of various trace elements. Many elements, such as cobalt, copper, iron, manganese, and zinc, are essential for plants, animals, and humans. Other elements, such as arsenic and chromium, are required by animals and humans but are not essential for plants. Nonessential elements for plants, animals, and humans include cadmium, mercury, and lead (Adriano, 1986; Lide, 1993; Pais and Jones, 1997).

Toxicity is a function of several factors including the type of organism, availability of a trace element in the environment, and its potential to bioaccumulate once in the food chain. The daily intake of trace elements by animals and humans may be classified as deficient, optimal, or toxic. Most, if not all, trace elements may be toxic in animals and humans if the concentrations are sufficiently large (Pais and Jones, 1997; Smol, 2002; Luoma and Rainbow, 2008). Information on the bioaccumulation index (Pais and Jones, 1997) for cadmium, lead, and zinc is provided in table 3.

Occurrence and Trends of Selected Trace Elements

This section describes the occurrence and trends of cadmium, lead, and zinc concentrations in bottom-sediment samples collected from Grand Lake. In addition, sediment quality was assessed with reference to general and TSMD-specific PECs for cadmium, lead, and zinc (table 3). In the following summaries, the mean trace element concentrations determined by XRF were used for all samples (that is, the average of the three XRF analyses completed for each sample). The mean XRF results for all samples are provided in tables A4 through A8 in the “Supplemental Information” section. If one or two of the three XRF results for a sample was less than the LOD, the final result was reported as less than the largest value that was measured. If all three XRF results for a sample were less than the LOD, the final result was reported as “<LOD”. Results for the five randomly selected samples (that is, one per core) and the two flood-plain soil samples, analyzed by combustion and various spectroscopic methods, are provided in table A2 in the “Supplemental Information” section.

Cadmium

Cadmium concentrations in the bottom sediment of Grand Lake were less than the XRF LOD for all 50 samples.

Thus, the assessment of cadmium contamination was limited to the five randomly selected split-replicate samples analyzed by spectroscopic methods, which represent 10 percent of the total bottom-sediment sample set. For these five samples, cadmium concentrations ranged from 2.3 to 3.6 mg/kg (table 2) with a median of 3.5 mg/kg. In comparison, cadmium concentrations in the bottom sediment of Empire Lake (located upstream on the Spring River within the TSMD) ranged from 7.3 to 76 mg/kg with a median concentration of 29 mg/kg (Juracek, 2006).

Based on streambed-sediment concentrations for sites minimally affected by mining activity in Cherokee County, Kansas, Pope (2005) estimated the local background cadmium concentration to be 0.6 mg/kg. In comparison, Horowitz and Stephens (2008) estimated the national background concentration of cadmium in sediment to be 0.4 mg/kg. Compared to the local background concentration provided by Pope (2005), the historical mining activity increased the cadmium concentration in the five split-replicate samples by about 280 to 500 percent. Cadmium concentrations for the five samples were substantially less than the general PEC (4.98 mg/kg) and the TSMD-specific PEC (11.1 mg/kg).

Lead

Lead concentrations for Grand Lake coring site GL-1 (fig. 2) ranged from 35 to 102 mg/kg (tables 4 and A4). For the other four downstream coring sites, lead concentrations ranged from 46 to 84 mg/kg (tables 4, A5–A8). Excluding coring site GL-1, the coring sites generally were similar in terms of the range in lead concentrations measured and the lead concentration in the most recently deposited sediment. The range in mean and median lead concentrations for the five coring sites was 55 to 63 mg/kg and 51 to 62 mg/kg, respectively (table 4). The overall median lead concentration was 59 mg/kg. In comparison, lead concentrations in the bottom sediment of Empire Lake ranged from 100 to 950 mg/kg with a median concentration of 270 mg/kg (Juracek, 2006).

Table 4. Summary of lead and zinc concentrations determined by x-ray fluorescence methods in bottom-sediment samples collected from coring sites GL-1, GL-2, GL-3, GL-4, and GL-5 in Grand Lake O' the Cherokees, northeast Oklahoma, November 2008.

[All concentrations are in milligrams per kilogram]

Coring site (fig. 2)	Concentration range	Mean concentration	Median concentration
		Lead	
GL-1	35–102	55	51
GL-2	47–71	59	60
GL-3	53–75	63	62
GL-4	46–84	61	60
GL-5	48–81	61	59
		Zinc	
GL-1	401–966	676	701
GL-2	516–897	753	786
GL-3	486–986	786	835
GL-4	380–941	708	746
GL-5	438–983	693	641

The local background lead concentration in sediment estimated by Pope (2005) was 20 mg/kg. Likewise, the national background concentration of lead in sediment was estimated to be 20 mg/kg (Horowitz and Stephens, 2008). Compared to the background concentration, the historical mining activity increased the lead concentration in the 50 bottom-sediment samples by about 75 to 410 percent. Lead concentrations at the bottom of the sediment cores (that is, the oldest sediment estimated to date from the early to mid 1940s) ranged from 46 mg/kg (130 percent larger than background) for coring site GL-4 to 67 mg/kg (235 percent larger than background) for coring site GL-2. Subsequently, lead concentrations were largest in the middle of the cores (during the 1970s based on the location of the 1963–64 peak of ^{137}Cs activity in the cores, see fig. 3) and ranged from 71 mg/kg (255 percent larger than background) for coring site GL-2 to 84 mg/kg (320 percent larger than background) for coring site GL-4. The increase in lead concentration from the bottom of the cores to the largest concentrations ranged from 6 percent (coring site GL-2) to 83 percent (coring site GL-4). Following the peak, lead concentrations decreased to the top of the cores by 28 percent (coring site GL-2) to 43 percent (coring site GL-4). Lead concentrations for the most recently deposited sediment ranged from 48 mg/kg (140 percent larger than background) for coring sites GL-4 and GL-5 to 53 mg/kg (165 percent larger than background) for coring site GL-3 (fig. 4, tables A5–A8). Overall, compared to the background concentration, lead concentrations in the cores were about two to four times larger. Coring site GL-1 (table A4) was not included in the temporal comparison to background concentration because ^{137}Cs activity in the core (fig. 3*A*) indicated substantial postdepositional disturbance.

All 50 bottom-sediment samples analyzed for Grand Lake had lead concentrations that were substantially less than the general PEC (128 mg/kg) and the TSMD-specific PEC (150 mg/kg) (fig. 4). Restated, samples from the five coring sites indicated that lead concentrations in the sediment deposited in Grand Lake have not approached or exceeded the PECs during the life of the reservoir.

Temporal trend analyses, with a significance level of 0.05, indicated no statistically significant trends in lead deposition for any of the five Grand Lake coring sites (table 5). For coring site GL-1 (fig. 4*A*), a negative trend was significant at the 0.1 level. However, because ^{137}Cs activity in the core indicated substantial postdepositional disturbance (fig. 3*A*), the trend may not be meaningful. Downstream, a mid-core peak in lead concentrations (circa 1970s) emerged at coring site GL-2 and became pronounced at coring sites GL-3, GL-4, and GL-5 (fig. 4).

Zinc

Zinc concentrations for the five Grand Lake coring sites ranged from 380 to 986 mg/kg with a median of 765 mg/kg (tables 4, A4–A8). The five coring sites generally were similar in terms of the range in zinc concentrations measured. Excluding coring site GL-1, the coring sites generally were similar with respect to the zinc concentrations in the most recently deposited sediment. The range in mean and median zinc concentrations for the five coring sites was 676 to 786 mg/kg and 641 to 835 mg/kg, respectively (table 4). In comparison, zinc concentrations in the bottom sediment of Empire Lake ranged from 1,300 to 13,000 mg/kg with a median concentration of 4,900 mg/kg (Juracek, 2006).

The local background zinc concentration in sediment estimated by Pope (2005) was 100 mg/kg. Nationally, the background concentration of zinc in sediment was estimated to be 91 mg/kg (Horowitz and Stephens, 2008). Compared to the local background concentration provided by Pope (2005), the historical mining activity increased the zinc concentration in the 50 bottom-sediment samples by about 280 to 890 percent. Zinc concentrations at the bottom of the sediment cores (circa early to mid 1940s) ranged from 380 mg/kg (280 percent larger than local background) for coring site GL-4 to 875 mg/kg (about 780 percent larger than local background) for coring site GL-3. Zinc concentrations peaked in the middle of the cores with a pronounced double peak evident for coring sites GL-3, GL-4, and GL-5 (fig. 5). Based on the location of the 1963–64 peak of ^{137}Cs activity in the cores, it was estimated that the double peaks in zinc were deposited in the 1950s and (or) 1960s and the 1980s. Peak zinc concentrations ranged from 897 mg/kg (about 800 percent larger than local background) for coring site GL-2 to 986 mg/kg (about 890 percent larger than local background) for coring site GL-3. The increase in zinc concentrations from the bottom of the cores to the first peaks ranged from 13 percent (coring sites GL-2 and GL-3) to 148 percent (coring site GL-4). Following the last peaks, zinc concentrations decreased to the top of the cores by 42 percent (coring site GL-2) to 55 percent (coring site GL-5). Zinc concentrations for the most recently deposited sediment ranged from 438 mg/kg (about 340 percent larger than local background) for coring site GL-5 to 516 mg/kg (about 420 percent larger than local background) for coring site GL-2 (fig. 5; tables A5–A8). Overall, compared to the local background concentration, zinc concentrations in the cores were about 4 to 10 times larger. Coring site GL-1 (table A4) was not included in the temporal comparison to background zinc concentration because ^{137}Cs activity in the core (fig. 3*A*) indicated substantial postdepositional disturbance.

Table 5. Trend tests for lead and zinc concentrations in bottom-sediment samples collected from coring sites GL-1, GL-2, GL-3, GL-4, and GL-5 in Grand Lake O’ the Cherokees, northeast Oklahoma, November 2008.

Trace element	Spearman’s rho	Trend test at 0.05 level of significance (two-sided p-value)
	Core GL-1A	
Lead	-0.55	no trend (0.098)
Zinc	-.73	negative trend (0.016)
	Core GL-2A	
Lead	-.41	no trend (0.241)
Zinc	-.33	no trend (0.347)
	Core GL-3A	
Lead	-.52	no trend (0.121)
Zinc	-.75	negative trend (0.013)
	Core GL-4A	
Lead	.01	no trend (0.973)
Zinc	-.04	no trend (0.907)
	Core GL-5A	
Lead	.02	no trend (0.960)
Zinc	-.33	no trend (0.347)

Of the 50 bottom-sediment samples analyzed for Grand Lake, 46 (92 percent) had zinc concentrations (tables A4–A8) that exceeded the general PEC (459 mg/kg) with a range in exceedances of about 3 to 110 percent and a mean exceedance of about 60 percent. A comparison of changing zinc concentrations over time in relation to the general and TSMD-specific PECs for all five cores is provided in figure 5. Peak zinc concentrations (which occurred two or more decades ago) exceeded the general PEC by about 95 percent (coring site GL-2) to 110 percent (coring site GL-3). The zinc concentration for the top (most recently deposited) interval of the five cores ranged from 438 to 704 mg/kg (that is, about 5 percent less than to about 50 percent larger than the general PEC). However, zinc concentrations for all 50 samples were substantially less than the TSMD-specific PEC (2,083 mg/kg). Restated, samples from the five coring sites indicated that zinc concentrations in the sediment deposited in Grand Lake typically exceeded the general PEC but have not approached or exceeded the TSMD-specific PEC during the life of the reservoir.

Temporal trend analyses, with a significance level of 0.05, indicated a statistically significant negative trend in zinc deposition for coring sites GL-1 and GL-3 (table 5). However, because ^{137}Cs activity in the core indicated substantial post-depositional disturbance, the trend for coring site GL-1 may not be meaningful. A statistically significant trend was not indicated for coring sites GL-2, GL-4, and GL-5 (table 5).

The differences in the depositional profiles for lead and zinc may be caused, in part, by variability in sediment source areas over time as related to spatial differences in precipitation and runoff for storms that occurred in the basin. Even for mines extracting ore from the same mineralized zones in a given area, variations in the trace element concentration of the ores can change dramatically from mine to mine (Miller, 1997). Moreover, the differences may be caused, in part, by the delivery of contaminated sediment to Grand Lake that can occur as a series of sediment pulses (Macklin, 1996).

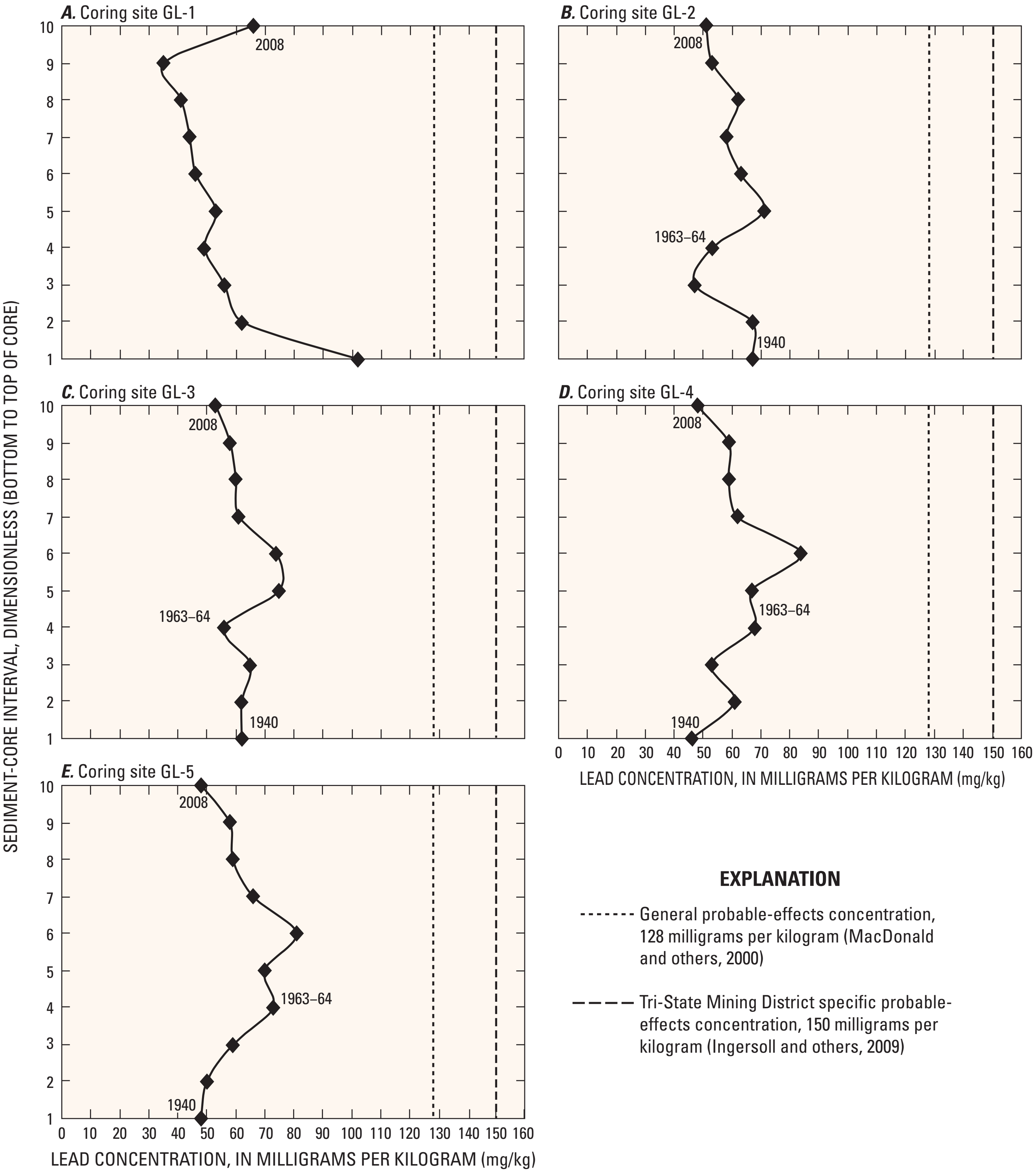

Figure 4. Variation in lead concentrations with depth of bottom-sediment samples collected from coring sites GL-1, GL-2, GL-3, GL-4, and GL-5 in Grand Lake O’ the Cherokees, northeast Oklahoma, November 2008.

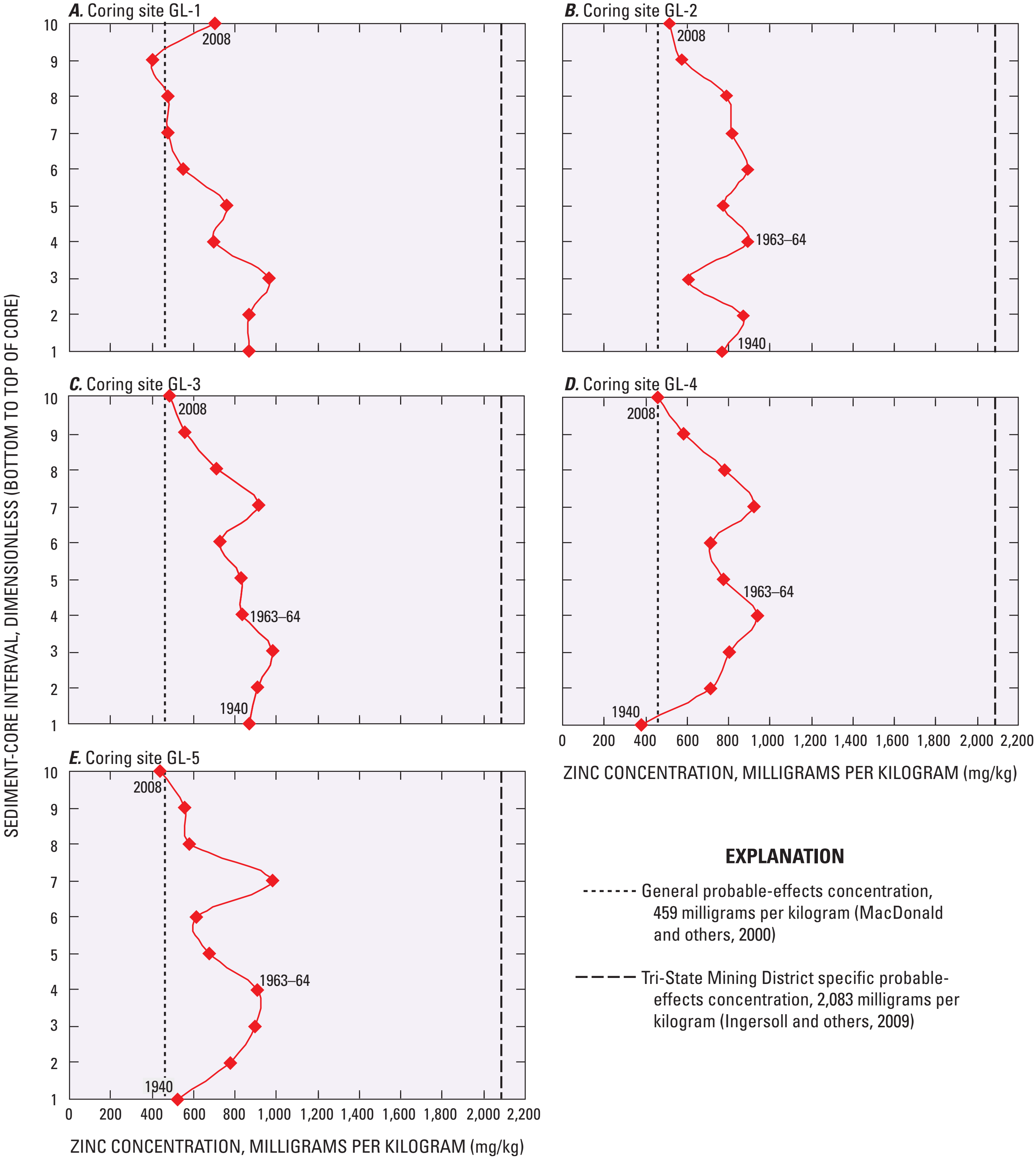

Figure 5. Variation in zinc concentrations with depth of bottom-sediment samples collected from coring sites GL-1, GL-2, GL-3, GL-4, and GL-5 in Grand Lake O' the Cherokees, northeast Oklahoma, November 2008.

Variability of Trace Element Concentrations in Relation to Mining-Related Activity and Other Factors

The variability of lead and zinc concentrations in the bottom sediment of Grand Lake was interpreted in relation to historical mining activity and other factors. Because cadmium concentration data were only available for 10 percent of the samples, emphasis was placed on an analysis of the lead and zinc data.

For Grand Lake, both the mean and median lead and zinc concentrations for the five coring sites indicated the same upstream-to-downstream pattern. Specifically, concentrations increased from coring site GL-1 (the most upstream site) to GL-3 (the mid-reservoir site) and then decreased to coring site GL-5 (the furthest downstream site) (fig. 2; table 4). The initial increase in concentrations may be related to changes in the particle-size composition of the bottom sediment (specifically, an increase in clay content). Within a large reservoir, particle size typically decreases with distance downstream as progressively smaller particles settle out (Morris and Fan, 1998). Concurrently, trace element concentrations in the sediment would be expected to increase with distance downstream because trace element concentrations typically increase as particle size decreases (Horowitz, 1991). Thus, the initial increase in concentrations appears to be consistent with what is known about reservoir sediment chemistry. However, further downstream (coring sites GL-4 and GL-5) the concentrations decreased rather than continuing to increase. A possible explanation for this trend reversal is dilution by tributaries that contribute relatively "clean" sediment directly to Grand Lake. Also, analytical variability may, in part, account for the pattern observed.

Comparison of lead and zinc concentrations in the bottom sediment of Grand Lake with upstream locations indicated less contamination with distance downstream from the mining-affected areas. For example, median lead and zinc concentrations in the bottom sediment of Empire Lake, Kansas (located immediately downstream from mining-affected areas within the TSMD) (fig. 1), were about 5 and 6 times larger than median concentrations in Grand Lake, which is located at least 13 miles downstream from the last Spring River tributary that drains a substantial mining-affected area. Grand Lake also is located about 20 miles downstream from the Cherokee County superfund site in Kansas (fig. 1). A downstream decrease in trace element concentrations may be caused by several processes including (1) hydraulic sorting of bed material; (2) dilution by mixing with "clean" sediment delivered by tributaries not affected by mining; (3) storage of contaminated sediment on the flood plain; (4) chemical solution; and (5) biological uptake (Marcus, 1987; Lewin and Macklin, 1987; Miller, 1997).

Assessment of the temporal variability in lead and zinc concentrations was focused on the downstream four coring sites (GL-2 through GL-5) (fig. 2) for which the ^{137}Cs activity indicated minimal postdepositional disturbance of the bottom sediment (fig. 3). For lead, the depositional profiles indicated that concentrations peaked in the middle of the cores and then declined (fig. 4). For zinc, the depositional profiles indicated that concentrations peaked twice before declining (fig. 5). Together, the lead and zinc depositional profiles indicated decreasing concentrations since about the 1980s.

Several factors may, in part, account for the mid-core peaks in lead and zinc concentrations. Lead and zinc deposition in Grand Lake is assumed to be directly related to the history of upstream mining activity. Within the TSMD, production of lead and zinc concentrates can be described by state. In Missouri and Kansas, major production occurred from about 1880 to 1920 and from about 1920 to 1950, respectively. In Oklahoma, major production occurred from about 1910 to 1950 (Spruill, 1987). With the closing of the mines in Oklahoma, the pumps were removed in the 1960s or 1970s resulting in flooding of the mines and subsequent mine drainage which began in 1979 (U.S. Environmental Protection Agency, 1984). The fact that the peak lead and zinc concentrations in the bottom sediment of Grand Lake postdate the periods of major production may be indicative of the time required for the contaminated sediment to be transported from the mined areas downstream to the reservoir. Recent decreases in lead and zinc deposition may be caused, in part, by several factors including remediation and landscape stabilization.

In addition to the history of mining activity, another important determinant of the deposition of contaminated sediment in Grand Lake is variability in precipitation and associated runoff, streamflow, and sediment transport within the basin. Generally, a direct relation exists between runoff and streamflow and the amount of sediment that is transported. To provide an indication of the variability in sediment transport to Grand Lake, the variability in mean annual streamflow was examined from 1940 to 2008 for two USGS streamflow-gaging stations located immediately upstream from the reservoir—the Spring River near Quapaw, Oklahoma (station 07188000), and the Neosho River near Commerce, Oklahoma (station 07185000) (fig. 1). As shown in figure 6, inflows to the reservoir from the two rivers generally were correlated over time. The Neosho River inflows, on average, were about 70 percent larger (U.S. Geological Survey, 2009). Because years of high flow occurred throughout 1940 to 2008, variability in streamflow alone cannot explain the mid-core peaks in lead and zinc concentrations. In other words, an explanation for the mid-core peaks may be less related to the quantity of sediment being transported and more related to the quality of sediment being transported. A related factor is the likely possibility that sediment sources within the basin have changed over time. Because different sources likely will be different compositionally, a change in sources over time also may partly account for the changes in lead and zinc deposition measured in the bottom sediment of Grand Lake.

Of importance, from the contaminant loading perspective, was the relative contribution of cadmium, lead, and zinc delivered to Grand Lake by the Spring and Neosho Rivers.

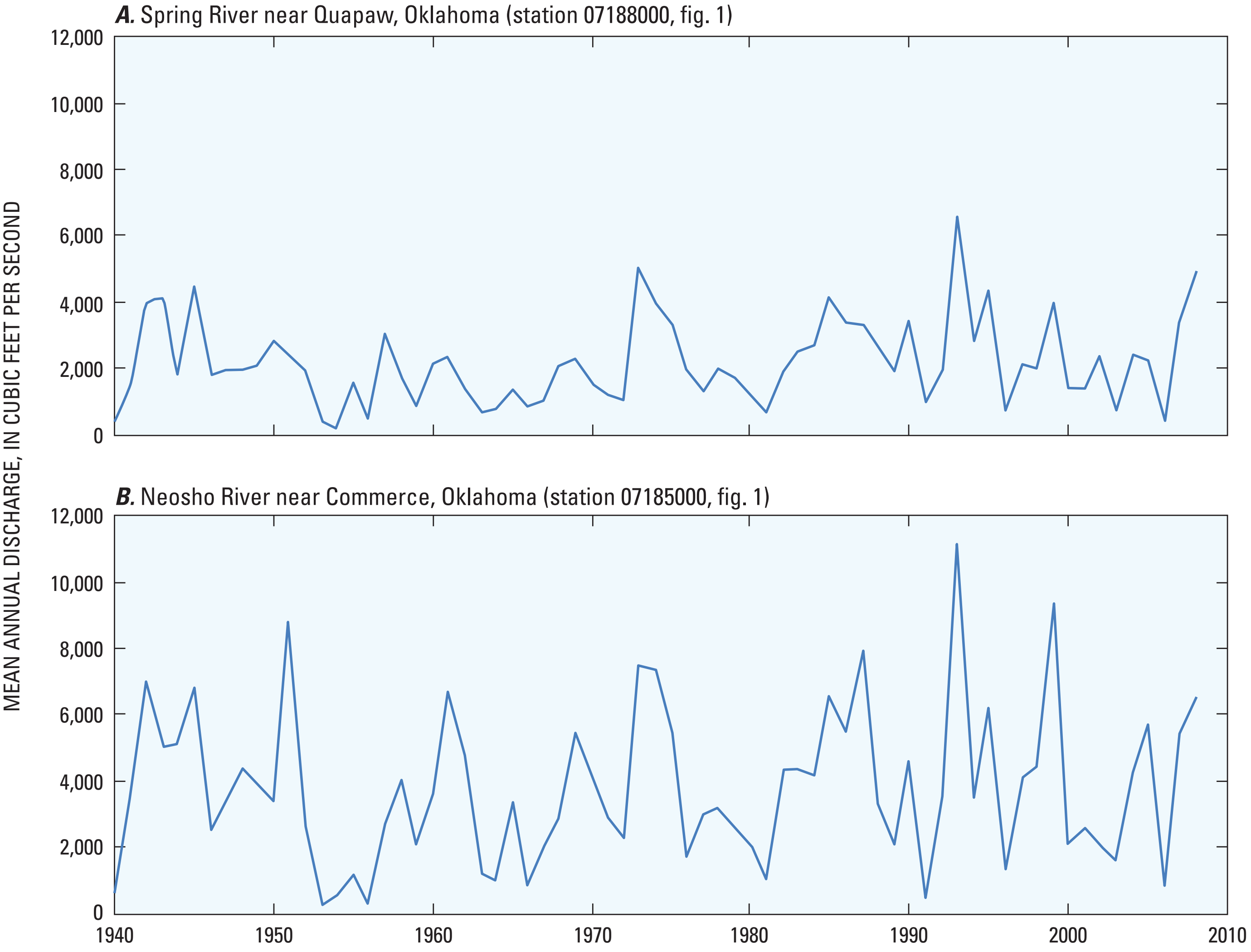

Figure 6. Variation in mean annual streamflow from 1940 to 2008 for the Spring River near Quapaw, Oklahoma, and the Neosho River near Commerce, Oklahoma.

An assessment of the relative contribution required information on sediment chemistry for the two rivers. As part of a study to assess mining-related contamination of sediments and streams in the Oklahoma part of the TSMD, Andrews and others (2009) determined that concentrations of lead and zinc in the bottom sediment of the Spring River near Wyandotte, Oklahoma, were about 3 and 5 times larger, respectively, than concentrations in the bottom sediment of the Neosho River near Wyandotte, Oklahoma. Likewise, an analysis of bottom-sediment cores collected in 2007 by the USGS determined that cadmium, lead, and zinc concentrations in the bottom sediment of the Spring River arm of Grand Lake were about 14, 5, and 8 times larger, respectively, than concentrations in the Neosho River arm of the reservoir (David Fey, U.S. Geological Survey, written commun., 2009). Finally, an analysis of surficial samples of bottom sediment collected in 2008 by USFWS along a transect that crossed the confluence of the Spring and Neosho River arms of the reservoir, indicated that lead and zinc concentrations in the Spring River arm were about 5 and 12 times larger, respectively (Suzanne Dudding, U.S. Fish and Wildlife Service, written commun., 2009). Thus, the Neosho River sediment was relatively less contaminated compared to the Spring River sediment. Because of its larger flows and less-contaminated sediment, the Neosho River likely dilutes the load of contaminated sediment delivered to Grand Lake by the Spring River.

Other factors that may have contributed to the contamination of sediment deposited in Grand Lake include mine drainage and the reprocessing and redistribution of chat. Mine drainage in the TSMD can have increased dissolved concentrations of cadmium, lead, and zinc (Parkhurst, 1987; Spruill, 1987). Once in the streams, the dissolved trace elements may increase concentrations in the sediment by the processes of precipitation and adsorption (Merefield, 1995). Chat reprocessing involved a washing and screening process whereby the fine particles were removed prior to shipment (Ed

Kehely, Kehely and Associates, oral commun., 2009). The fine particles left behind contain large concentrations of cadmium, lead, and zinc (Schaider and others, 2007; U.S. Environmental Protection Agency, 2008) and are susceptible to erosion and transport by water and wind.

In addition to the bottom-sediment samples, a sample was collected at coring sites GL-4 and GL-5 (fig. 2) to assess pre-impoundment trace element contamination of the flood-plain soils. Lead and zinc concentrations in the flood-plain samples (tables A7 and A8 at the back of this report) either were similar to or less than estimated background concentrations. For both flood-plain samples, the concentrations of lead and zinc were substantially smaller than the concentrations in the Grand Lake bottom sediment. The relatively small concentrations of lead and zinc in the flood-plain samples may, in part, be indicative of a larger percentage of coarse particles (silt) in the samples analyzed. Another possibility is that the locations sampled were nondepositional zones on the original flood plain and, therefore, did not have deposits of contaminated sediment.

Summary and Conclusions

Bottom-sediment coring completed in 2008 was used to investigate the occurrence of, and temporal trends for 1940 to 2008 in, selected chemical constituents in the bottom sediment of Grand Lake, a reservoir in northeast Oklahoma that has been affected by historical lead and zinc mining. The major results of this study are listed below:

1. The delivery of contaminated sediment to Grand Lake was still ongoing as of 2008.
2. Median cadmium, lead, and zinc concentrations in the bottom sediment of Grand Lake were 3.5, 59, and 765 mg/kg, respectively.
3. Maximum cadmium, lead, and zinc concentrations in the bottom sediment of Grand Lake were 3.6, 102, and 986 mg/kg, respectively.
4. Cadmium, lead, and zinc concentrations in the bottom sediment of Grand Lake were substantially larger than estimated local background concentrations.
5. Cadmium and lead concentrations in the bottom sediment of Grand Lake were substantially less than general and Tri-State Mining District specific probable-effects concentrations, which represent the concentrations above which toxic biological effects are likely to occur.
6. Zinc concentrations in the bottom sediment of Grand Lake typically exceeded the general probable-effects concentration but were substantially less than the Tri-State Mining District specific probable-effects concentration.
7. With the exception of coring site GL-1, the lead and zinc depositional profiles generally were similar in terms of the range in concentrations measured and the temporal pattern observed.
8. Lead and zinc depositional profiles indicated that, following peaks, concentrations in the bottom sediment of Grand Lake have decreased since about the 1980s.
9. The depositional profiles for lead and zinc reflect the complex interaction of several factors including historical mining and related activities, mine drainage, remediation, landscape stabilization, precipitation and associated runoff, and the erosion and transport of contaminated and clean sediments within the Grand Lake Basin.
10. The Neosho River, with its larger flows and less-contaminated sediment, likely dilutes the load of contaminated sediment delivered to Grand Lake by the Spring River.
11. The baseline of information on Grand Lake conditions provided in this report can be used for comparison with future conditions that may represent a response to changes in mining-related activity in the Grand Lake Basin.

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Supplemental Information

Table A1. Latitude and longitude coordinates, water depth, estimated penetration depth, length of recovered core, and estimated recovery percentage for bottom-sediment coring sites at Grand Lake O' the Cherokees, northeast Oklahoma, 2008.

Coring site identifier (fig. 2)	Date cored (month/day/year)	Latitude (decimal degrees)	Longitude (decimal degrees)	Water depth (feet)	Estimated penetration depth (feet)	Length of recovered core (feet)	Estimated recovery percentage[1]
GL-1	11/03/08	36.73444	94.76917	7	6.0	5.4	90
GL-2	11/04/08	36.66333	94.76806	28	8.0	7.5	94
GL-3	11/04/08	36.60750	94.82972	42	8.0	6.4	80
GL-4	11/04/08	36.56611	94.89389	60	5.0	4.6	92
GL-5	11/05/08	36.51528	94.95222	82	6.0	5.6	93

[1] Recovery percentage estimated as the length of recovered core divided by the estimated penetration depth and multiplied by 100.

Table A2. Percentage of silt and clay and constituent concentrations determined by combustion and spectroscopic methods for five randomly selected bottom-sediment samples (GL-1A9, GL-2A7, GL-3A10, GL-4A5, GL-5A3) and two flood-plain soil samples (GL-4A0, GL-5A0) collected from Grand Lake O' the Cherokees, northeast Oklahoma, November 2008.

[mg/kg, milligrams per kilogram; %, percent dry weight; µm, micron; <, less than]

Constituent and unit of measurement	Constituent concentration				
	Sample GL-1A9	Sample GL-2A7	Sample GL-3A10	Sample GL-4A5	Sample GL-5A3
Percentage of silt and clay	88	99	99	98	98
		Nutrients			
Total nitrogen, mg/kg	1,200	2,300	2,800	2,700	2,900
Total phosphorus, mg/kg	680	990	1,300	1,200	1,000
		Carbon			
Carbon (total organic), %	1.0	1.8	2.3	2.2	2.1
Carbon (total), %	1.0	1.9	2.4	2.3	2.1
		Trace elements			
Aluminum, %	5.0	7.9	8.6	8.8	9.0
Antimony, mg/kg	.7	.9	.9	1.0	1.1
Arsenic, mg/kg	5.8	11	12	13	14
Barium, mg/kg	530	630	610	660	690
Beryllium, mg/kg	1.5	2.5	2.6	2.7	2.8
Cadmium, mg/kg	2.7	3.6	2.3	3.5	3.6
Chromium, mg/kg	51	82	88	90	90
Cobalt, mg/kg	10	16	16	16	17
Copper, mg/kg	16	27	28	31	32
Iron, %	2.1	3.8	4.3	4.2	4.3
Lead, mg/kg	39	61	54	73	66
Lithium, mg/kg	31	54	60	60	62
Manganese, mg/kg	500	800	1,100	1,600	1,600
Mercury, mg/kg	.05	.08	.05	.09	.10
Molybdenum, mg/kg	<1	1	1	1	1
Nickel, mg/kg	20	40	38	42	44
Selenium, mg/kg	.8	1.0	1.1	1.1	.9
Silver, mg/kg	<.5	<.5	<.5	<.5	<.5
Strontium, mg/kg	110	120	120	120	110
Sulfur, %	.05	.13	.14	.17	.13
Thallium, mg/kg	<50	<50	<50	<50	<50
Tin, mg/kg	2	4	3	4	4
Titanium, %	.42	.47	.46	.46	.45
Uranium, mg/kg	<50	<50	<50	<50	<50
Vanadium, mg/kg	66	120	130	130	140
Zinc, mg/kg	440	960	570	960	1,000

Table A2. Percentage of silt and clay and constituent concentrations determined by combustion and spectroscopic methods for five randomly selected bottom-sediment samples (GL-1A9, GL-2A7, GL-3A10, GL-4A5, GL-5A3) and two flood-plain soil samples (GL-4A0, GL-5A0) collected from Grand Lake O' the Cherokees, northeast Oklahoma, November 2008.—Continued

[mg/kg, milligrams per kilogram; %, percent dry weight; µm, micron; <, less than]

Constituent and unit of measurement	Constituent concentration			
	Sample GL-4A0 (bulk)	Sample GL-4A0 (<63-µm)	Sample GL-5A0 (bulk)	Sample GL-5A0 (<63-µm)
Percentage of silt and clay	88	100	80	100
Nutrients				
Total nitrogen, mg/kg	1,200	900	1,900	1,600
Total phosphorus, mg/kg	290	240	460	380
Carbon				
Carbon (total organic), %	1.3	1.0	2.2	1.6
Carbon (total), %	1.3	1.0	2.2	1.6
Trace elements				
Aluminum, %	2.9	2.6	3.3	3.2
Antimony, mg/kg	.5	.5	.6	.6
Arsenic, mg/kg	2.7	2.1	3.6	3.0
Barium, mg/kg	510	480	550	550
Beryllium, mg/kg	1.1	.9	1.3	1.2
Cadmium, mg/kg	.2	.1	.5	.4
Chromium, mg/kg	35	32	36	35
Cobalt, mg/kg	7	5	8	6
Copper, mg/kg	11	10	14	13
Iron, %	1.0	.8	1.1	1.0
Lead, mg/kg	16	14	20	19
Lithium, mg/kg	21	19	22	22
Manganese, mg/kg	450	350	800	670
Mercury, mg/kg	.02	.01	.05	.04
Molybdenum, mg/kg	<1	<1	<1	<1
Nickel, mg/kg	11	9	16	14
Selenium, mg/kg	.8	.6	.7	.7
Silver, mg/kg	<.5	<.5	<.5	<.5
Strontium, mg/kg	73	71	79	82
Sulfur, %	.02	.02	.03	.02
Thallium, mg/kg	<50	<50	<50	<50
Tin, mg/kg	2	1	2	2
Titanium, %	.44	.47	.40	.43
Uranium, mg/kg	<50	<50	<50	<50
Vanadium, mg/kg	43	37	46	43
Zinc, mg/kg	38	30	71	66

Table A3. Chemical analyses of reference samples using x-ray fluorescence and comparison to most probable values.

[mg/kg, milligrams per kilogram; NIST, National Institute of Standards and Technology; MPV, most probable value; XRF, x-ray fluorescence; Std. Dev., standard deviation; RSD, relative standard deviation; % Diff., percent difference between NIST value and XRF mean; %, percent; <, less than; LOD, limit of detection; --, not determined]

Reference sample		Concentration, mg/kg		
		Cadmium	Lead	Zinc
NIST LOW	MPV	0.38±0.01	18.9±0.5	106±3
XRF mean		<LOD	18.4	95
Std. Dev.		--	2.8	2.9
RSD		--	15.0	3.1
% Diff.		--	-2.6	-10.3
NIST MED	MPV	41.7±0.25	1,162±31	350.4±4.8
XRF mean		54.8	1,204	328.2
Std. Dev.		27.7	23.4	8.6
RSD		50.5	1.9	2.6
% Diff.		31.4	3.6	-6.3
NIST HIGH	MPV	21.8±0.2	5,532±80	6,952±91
XRF mean		<LOD	5,716	7,182
Std. Dev.		--	58.6	98.1
RSD		--	1.0	1.4
% Diff.		--	3.3	3.3
NIST BLANK				
XRF mean		<LOD	<LOD	<LOD
Total count		18	18	18
Detects		0	0	0
% Accuracy		100	100	100

Table A4. Mean constituent concentrations determined by x-ray fluorescence methods for bottom-sediment samples collected from coring site GL-1 in Grand Lake O' the Cherokees, northeast Oklahoma, November 2008.

[mg/kg, milligrams per kilogram; <, less than; LOD, limit of detection]

Core interval	Constituent concentration, mg/kg		
	Cadmium	Lead	Zinc
GL-1A1[a]	<LOD	102	865
GL-1A2	<LOD	62	868
GL-1A3	<LOD	56	966
GL-1A4	<LOD	49	697
GL-1A5	<LOD	53	758
GL-1A6	<LOD	46	549
GL-1A7	<LOD	44	474
GL-1A8	<LOD	41	475
GL-1A9	<LOD	35	401
GL-1A10[b]	<LOD	66	704

[a] Bottom of core

[b] Top of core.

Table A5. Mean constituent concentrations determined by x-ray fluorescence methods for bottom-sediment samples collected from coring site GL-2 in Grand Lake O' the Cherokees, northeast Oklahoma, November 2008.

[mg/kg, milligrams per kilogram; <, less than; LOD, limit of detection]

Core interval	Constituent concentration, mg/kg		
	Cadmium	Lead	Zinc
GL-2A1[a]	<LOD	67	772
GL-2A2	<LOD	67	874
GL-2A3	<LOD	47	610
GL-2A4	<LOD	53	895
GL-2A5	<LOD	71	777
GL-2A6	<LOD	63	897
GL-2A7	<LOD	58	818
GL-2A8	<LOD	62	795
GL-2A9	<LOD	53	575
GL-2A10[b]	<LOD	51	516

[a] Bottom of core

[b] Top of core.

Table A6. Mean constituent concentrations determined by x-ray fluorescence methods for bottom-sediment samples collected from coring site GL-3 in Grand Lake O' the Cherokees, northeast Oklahoma, November 2008.

[mg/kg, milligrams per kilogram; <, less than; LOD, limit of detection]

Core interval	Constituent concentration, mg/kg		
	Cadmium	Lead	Zinc
GL-3A1[a]	<LOD	62	875
GL-3A2	<LOD	62	915
GL-3A3	<LOD	65	986
GL-3A4	<LOD	56	838
GL-3A5	<LOD	75	832
GL-3A6	<LOD	74	734
GL-3A7	<LOD	61	921
GL-3A8	<LOD	60	715
GL-3A9	<LOD	58	559
GL-3A10[b]	<LOD	53	486

[a] Bottom of core

[b] Top of core.

Table A7. Mean constituent concentrations determined by x-ray fluorescence methods for bottom-sediment samples collected from coring site GL-4 in Grand Lake O' the Cherokees, northeast Oklahoma, November 2008.

[mg/kg, milligrams per kilogram; <, less than; LOD, limit of detection]

Core interval	Constituent concentration, mg/kg		
	Cadmium	Lead	Zinc
GL-4A0[a]	<LOD	17	40
GL-4A1[b]	<LOD	46	380
GL-4A2	<LOD	61	713
GL-4A3	<LOD	53	803
GL-4A4	<LOD	68	941
GL-4A5	<LOD	67	777
GL-4A6	<LOD	84	714
GL-4A7	<LOD	62	925
GL-4A8	<LOD	59	781
GL-4A9	<LOD	59	583
GL-4A10[c]	<LOD	48	458

[a] Original flood-plain soil.

[b] Bottom of core.

[c] Top of core.

Table A8. Mean constituent concentrations determined by x-ray fluorescence methods for bottom-sediment samples collected from coring site GL-5 in Grand Lake O' the Cherokees, northeast Oklahoma, November 2008.

[mg/kg, milligrams per kilogram; <, less than; LOD, limit of detection]

Core interval	Constituent concentration, mg/kg		
	Cadmium	Lead	Zinc
GL-5A0[a]	<LOD	19	67
GL-5A1[b]	<LOD	48	521
GL-5A2	<LOD	50	775
GL-5A3	<LOD	59	895
GL-5A4	<LOD	73	905
GL-5A5	<LOD	70	672
GL-5A6	<LOD	81	610
GL-5A7	<LOD	66	983
GL-5A8	<LOD	59	580
GL-5A9	<LOD	58	555
GL-5A10[c]	<LOD	48	438

[a] Original flood-plain soil.

[b] Bottom of core.

[c] Top of core.

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