

Sediment storage and severity of contamination in a shallow reservoir affected by historical lead and zinc mining

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Abstract A combination of sediment-thickness measurement and bottom-sediment coring was used to investigate sediment storage and severity of contamination in Empire Lake (Kansas), a shallow reservoir affected by historical Pb and Zn mining. Cd, Pb, and Zn concentrations in the contaminated bottom sediment typically exceeded baseline concentrations by at least an order of magnitude. Moreover, the concentrations of Cd, Pb, and Zn typically far exceeded probable-effects guidelines, which represent the concentrations above which toxic biological effects usually or frequently occur. Despite a pre-1954 decrease in sediment concentrations likely related to the end of major mining activity upstream by about 1920, concentrations have remained relatively stable and persistently greater than the probable-effects guidelines for at least the last 50 years. Cesium-137 evidence from sediment cores indicated that most of the bottom sediment in the reservoir was deposited prior to 1954. Thus, the ability of the reservoir to store the contaminated sediment has declined over time. Because of the limited storage capacity, Empire Lake likely is a net source of contaminated sediment during high-inflow periods. The contaminated sediment that passes through, or originates from, Empire Lake will be deposited in downstream environments likely as far as Grand Lake O' the Cherokees (Oklahoma).

Keywords Trace elements · Mining · Sediment · Contamination · Empire Lake · Kansas

Introduction

Mining and smelting can have a substantial and persistent effect on the chemical quality of sediment in the aquatic environment (Davies 1983). For example, such activities can increase trace element concentrations in lake-bottom sediment by at least an order of magnitude above baseline concentrations (Horowitz and Elrick 1995; Blais et al. 1999; Vermillion et al. 2005). Sediment quality is an important environmental concern because sediment can act as a sink for various contaminants (including trace elements) and, under certain conditions, as a source of contaminants to the overlying water column and biota (Baudo et al. 1990; Zoumis et al. 2001). Most, if not all, trace elements may be toxic in animals and humans if the concentrations are sufficiently large (Forstner and Wittmann 1981; Pais and Jones Jr 1997; Smol 2002). Remediation of areas affected by historical mining activity requires an understanding of the magnitude and extent of contamination as well as the transport and storage of contaminated sediment in the environment.

Empire Lake is a shallow reservoir that was formed with the completion of a dam on the Spring River at Lowell, Kansas, in 1905 (Fig. 1). In response to a washout believed to have occurred in 1909, a second dam was completed north of the original dam. The lake has a surface area of about 2.6 km². Water depths range from about 0.3 to 8 m and typically are <4 m. Throughout most of its history, Empire Lake has served as a cooling lake for a coal-fired powerplant located on the lake's west shore. The lake also is used for recreation and provides habitat for fish and wildlife.

Ongoing trace element contamination of Empire Lake has resulted from historical Pb and Zn mining. The Spring River Basin drains most of the Tri-State Mining District

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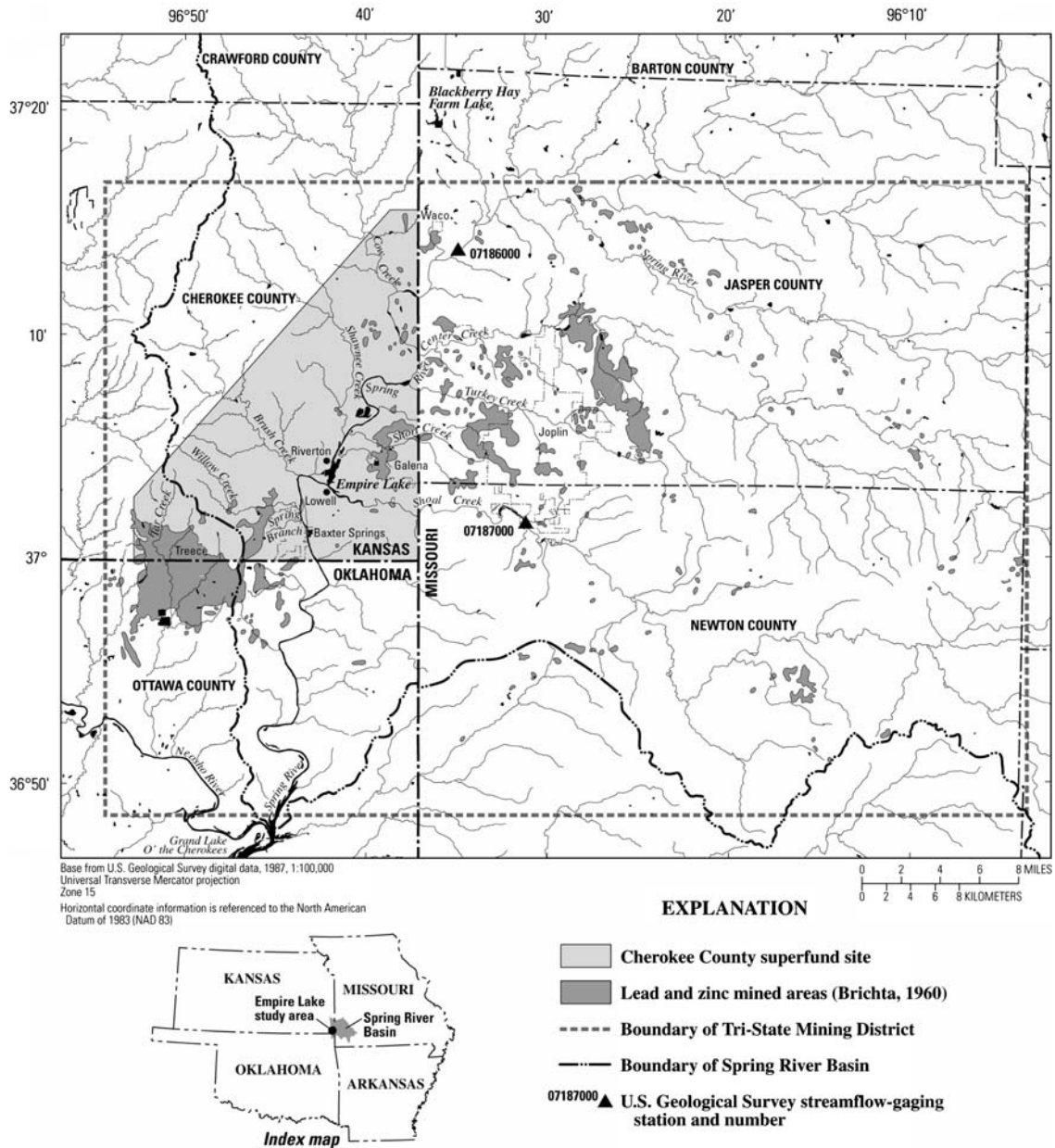


Fig. 1 Location of Empire Lake, Blackberry Hay Farm Lake, the Spring River system, the Cherokee County superfund site, and lead and zinc mined areas in the Tri-State Mining District, Kansas, Missouri, and Oklahoma

(hereafter referred to as the Tri-State District) that includes parts of southeast Kansas, southwest Missouri, and northeast Oklahoma (Fig. 1). For about 100 years (1850–1950), the Tri-State District was one of the primary sources of Pb and Zn ore in the world (Brosius and Sawin 2001). Until 1945, the area was the world’s largest producer of Pb and Zn concentrates, accounting for 10% of the Pb and 50% of the Zn produced in the United States (Gibson 1972). In the Kansas part of the Tri-State District, mining began with the discovery of Pb and Zn ore near Galena, Kansas (Fig. 1), in the 1870s and continued for about a century (Clark 1970;

Brosius and Sawin 2001). Over time, particularly in and near the town of Galena, the landscape in parts of Cherokee County, Kansas, became dominated by open pits, tailings piles, and ore-smelter waste dumps. So disturbed was the landscape by mining activity in the vicinity of Galena that it came to be known as “Hell’s Half Acre” (Brosius and Sawin 2001).

Although the mining has stopped and some remediation has occurred, the legacy of contaminated sediment in the Spring River Basin, including Empire Lake, remains. The environmental contamination caused by the decades of

mining activity resulted in southeast Cherokee County being listed on the U.S. Environmental Protection Agency's (USEPA) National Priority List as a superfund hazardous waste site in 1983 (U.S. Environmental Protection Agency 2004). Concern about environmental contamination in the area also was evidenced by the fact that the State of Kansas established a total maximum daily load (TMDL) for the Spring River Valley in 2004 to address sediment and water-quality issues caused by trace element contamination (Kansas Department of Health and Environment 2004). The Kansas Department of Health and Environment (KDHE), as part of its 2006 fish-consumption advisories, recommended not eating shellfish (mussels, clams, and crayfish) from the Spring River (Center Creek confluence to Oklahoma State line) and Shoal Creek (Missouri State line to Empire Lake) because of Cd and Pb contamination (Fig. 1) (Kansas Department of Health and Environment 2006).

The Spring River Basin is home to the Neosho madtom (*Noturus placidus*), a species of catfish listed as threatened under the Endangered Species Act (U.S. Fish and Wildlife Service 1991, 2004). Although still found in the Spring River downstream from Empire Lake and in upstream reaches in Missouri, the madtom apparently has been eliminated from the Spring River immediately upstream from Empire Lake in Kansas (John Miesner, U.S. Fish and Wildlife Service, oral communication, 2003). The absence of the madtom may be attributable to habitat degradation or toxicological effects caused by increased concentrations of Cd, Pb, and Zn in water and sediment resulting from the historical mining activity (Wildhaber et al. 1998, 1999, 2000). Other species (e.g., mussels) also are at risk (Angelo et al. 2005).

Historical mining activity also has affected human health. For example, Neuberger et al. (1990) reported an increased occurrence of several health problems for residents of Galena, Kansas that was attributed to mining-related contamination.

Several previous studies have examined the effects of Pb and Zn mining on water and sediment quality, as well as biota, in or near Empire Lake (Barks 1977; Spruill 1987; Ferrington et al. 1989; U.S. Fish and Wildlife Service 1992; Davis and Schumacher 1992; Angelo et al. 2005; Pope 2005). These studies, which provided either limited data for Empire Lake or complimentary data for nearby areas, are summarized by Juracek (2006).

The study described herein was completed by the U.S. Geological Survey (USGS) in cooperation with the U.S. Fish and Wildlife Service (USFWS) and KDHE. The objectives of the study were to: (1) estimate the thickness, total volume, and total mass of contaminated bottom sediment in Empire Lake; (2) estimate the total mass of Cd, Pb, and Zn in the bottom sediment of Empire Lake; (3)

assess the spatial and temporal variability of Cd, Pb, and Zn concentrations in the bottom sediment of Empire Lake; (4) estimate baseline concentrations in sediment in the Spring River Basin; (5) assess the quality of the Empire Lake bottom sediment with respect to available guidelines; and (6) relate, to the extent possible, any observed temporal trends in bottom-sediment concentrations to documented changes in human activity in the Spring River Basin. Together, these types of information are important for the prioritization, planning, and undertaking of restoration projects designed to improve the ecological health of Empire Lake and the Spring River Basin. Cd, Pb, and Zn were of primary interest in this study because they are the major contaminants input to the environment as a result of the historical mining activity.

Basin description

Empire Lake is nested within the Spring River Basin that drains about 6,500 km² of southwestern Missouri, southeastern Kansas, and northeastern Oklahoma (Seaber et al. 1987) (Fig. 1). Principal sources of flow into Empire Lake are the Spring River and Shoal Creek. Other important tributaries to the Spring River or Empire Lake in Cherokee County, Kansas, include Center, Cow, Shawnee, Short, and Turkey Creeks. Center, Short, and Turkey Creeks drain areas that have been substantially affected by historical Pb and Zn mining (Fig. 1).

The Spring River Basin overlaps two physiographic provinces as defined by Fenneman (1938, 1946). The southeast two-thirds of the 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). The northwest one-third of the 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). Topographically, the basin is characterized by gently rolling uplands dissected by streams.

The Pb and Zn ores in the Tri-State District occur in cherty limestone of Mississippian age. The ores are believed to have resulted from hydrothermal solutions that originated from deep within the earth. As these solutions moved vertically into the porous and permeable cherty limestone, an overlying impermeable layer of shale forced them to migrate laterally. As they spread, the solutions deposited sphalerite (ZnS), galena (PbS), and other associated minerals (Brosius and Sawin 2001).

Land use in the Spring River Basin is predominantly a mix of cropland, grassland, and woodland (Davis and Schumacher 1992). Historically, numerous sites within the basin were mined for coal, Pb, and Zn. The distribution of

the major Pb- and Zn-mined areas within the basin is shown in Fig. 1.

The climate in the Spring River Basin is characterized as subhumid continental (Stringer 1972). Long-term, mean annual precipitation at Joplin, Missouri (period of record 1948–2004) averages about 107 cm (High Plains Regional Climate Center 2005) (Fig. 1).

Methods

The study objectives were accomplished through the measurement of bottom-sediment thickness and the collection and analysis of bottom-sediment cores. A bottom-sediment core from nearby Blackberry Hay Farm Lake, northwest Jasper County, MO (Fig. 1) was collected and analyzed to provide an indication of baseline Cd, Pb, and Zn concentrations (Juracek 2006). Flood-plain soils also were sampled and analyzed.

To provide the information necessary for estimating the total volume of bottom sediment in Empire Lake, a survey was conducted to estimate bottom-sediment thicknesses throughout the reservoir. For this purpose, a series of transects were established. Along each transect, multiple measurements of bottom-sediment thickness were made using a specially designed aluminum sediment pole (designed and constructed by the College of Engineering Shops, University of Wisconsin, Madison, WI). A measurement was made by lowering the pole vertically down to the lakebed and recording the water depth as indicated on the pole. Then, the pole was pushed through the sediment to refusal. Sediment thickness was estimated as refusal depth minus water depth. Bottom-sediment thickness was measured at a total of 428 sites. At submerged channel sites, the sediment pole also provided information on the type of bed material (i.e., gravel or rock).

Total bottom-sediment volume in Empire Lake was estimated using a partitioning approach in which the reservoir was divided into segments as determined by the location of the sediment-thickness transects. The bottom-sediment volume for each reservoir segment was computed as the total surface area multiplied by the mean thickness of the bottom sediment. The segment results were combined to provide an estimate of the total volume of bottom sediment in the reservoir.

Total bottom-sediment mass (dry weight) in Empire Lake was estimated using the same segments. For each segment, a representative bulk density was computed using the bulk densities that were determined from sediment cores. Bottom-sediment mass was computed for each segment as the bottom-sediment volume multiplied by the representative bulk density. The segment results then were combined to provide an estimate of the total mass of bottom

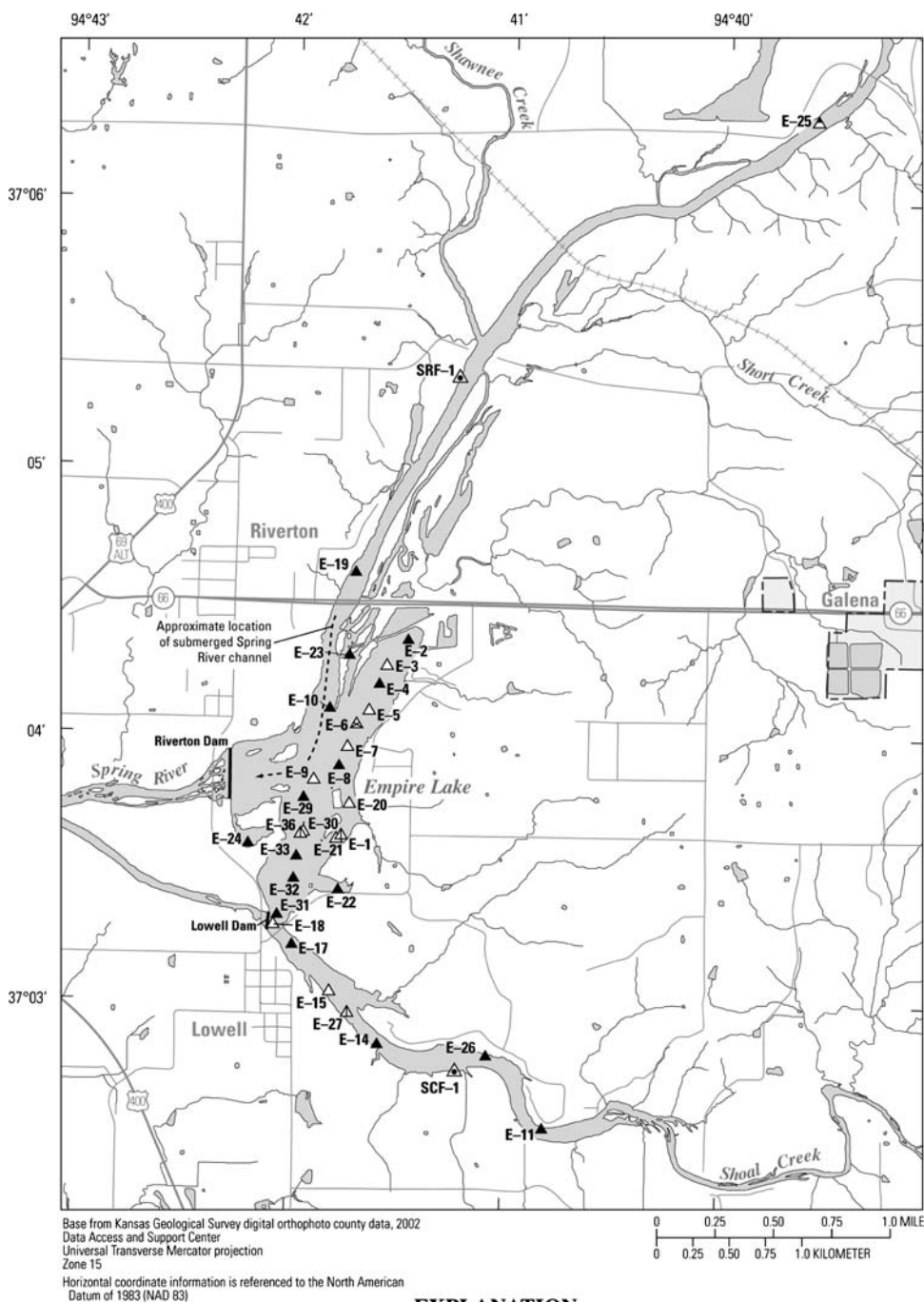
sediment in the reservoir. Additional information on bottom sediment thickness, volume, and mass estimation is provided in Juracek (2006). Total mass of Cd, Pb, and Zn in the bottom sediment of Empire Lake was estimated as the median concentration of each trace element multiplied by the total mass of bottom sediment.

Bottom-sediment cores were collected with a gravity corer in the spring and summer of 2005 at 30 sites (Fig. 2) within Empire Lake. The cores ranged in length from 0.3 to 2.1 m. The liner used in the corer was cellulose acetate butyrate transparent tubing with a 6.67 cm inside diameter. The coring sites were located to provide a spatially representative sample of bottom sediment in the reservoir. Of the 30 cores, 9 were used for bulk-density determinations only, 4 were used for chemical analysis only, and 17 were used for both bulk-density determinations and chemical analysis. Of the 21 cores used for chemical analysis, 17 were analyzed as composite samples. Cores E-1, E-6, E-27, and E-36 (hereafter referred to as trend cores) were divided into intervals, sampled, and analyzed to assess trends in constituent deposition over the life of the reservoir. Respectively, trend cores E-1, E-6, E-27, and E-36 were divided into 3, 5, 14, and 15 intervals. A sample of the original flood-plain soil at the bottom of core E-36, as well as a surficial soil sample from the Spring River (site SRF-1) and Shoal Creek (site SCF-1) flood plains (Fig. 2), also were collected for chemical analysis. Additional information on core-interval sampling and bulk-density determination and results is provided in Juracek (2006).

The sediment and soil samples were analyzed for nutrients (total nitrogen and total phosphorus), organic and total carbon, and 26 trace elements. In this paper, only the results for Cd, Pb, and Zn are presented. Results for the other constituents are provided in Juracek (2006). Prior to chemical analysis, the sediment and soil samples were wet sieved to isolate the <0.063-mm fraction (i.e., the silt and clay) using a 0.063-mm polyester screen held in a polycarbonate frame. Chemical analysis of the sediment and soil samples was performed at the USGS Sediment Trace Element Partitioning Laboratory in Atlanta, GA. Analysis for trace elements was performed using the methods described by Fishman and Friedman (1989), Arbogast (1996), and Briggs and Meier (1999).

Age dating of the bottom sediment was accomplished by determining the activity of cesium-137 (^{137}Cs). ^{137}Cs is a radioactive isotope that is a by-product 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

Fig. 2 Location of bottom-sediment coring sites in Empire Lake and flood-plain soil sampling sites



EXPLANATION

- E-11▲** Coring site and identifier—Samples collected for bulk-density determination and chemical composite analysis
- E-15△** Coring site and identifier—Samples collected for bulk-density determination only
- E-27▲** Coring site and identifier—Samples collected for chemical trend analysis
- E-6▲** Coring site and identifier—Samples collected for bulk-density determination and chemical trend analysis
- E-25▲** Coring site and identifier—Sample collected for chemical composite analysis
- SCF-1▲** Soil sampling site and identifier

1963–64. 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 ¹³⁷Cs activity follows the peak (Van Metre et al. 1997). Age dating of sediment using ¹³⁷Cs was attempted for

Empire Lake trend cores E-27 and E-36 (Fig. 2). Analysis of sediment samples for ¹³⁷Cs activity was performed at the USGS National Water-Quality Laboratory in Denver, CO, using gamma-ray spectrometry (American Society for Testing and Materials 2004).

Three trend cores (E-6, E-27, and E-36) collected from Empire Lake were used for statistical trend analyses. Temporal trends in constituent concentrations (versus 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). Temporal trends were considered to be significantly positive (constituent concentration increased toward the top of the sediment core) or negative (constituent concentration decreased toward the top of the sediment core) if the probability (two-sided *p*-value) of rejecting a correct hypothesis (in this case, no trend) was ≤ 0.05 . In the results, a possible temporal trend was considered meaningful only if the change in trace element concentration was beyond the variability that could be explained by analytical variance (defined here as the mean trace element concentration in the core $\pm 10\%$).

The U.S. Environmental Protection Agency has adopted nonenforceable sediment-quality guidelines (SQGs) in the form of level-of-concern concentrations for several trace elements (U.S. Environmental Protection Agency 1997). These level-of-concern concentrations were derived from biological-effects correlations made on the basis of paired onsite and laboratory data to relate incidence of adverse biological effects in aquatic organisms to dry-weight sediment concentrations. Two such level-of-concern guidelines adopted by USEPA are referred to as the threshold-effects level (TEL) and the probable-effects level (PEL). The TEL represents the concentration below which toxic biological effects rarely occur. In the range of concentrations between the TEL and PEL, toxic effects occasionally occur. Toxic effects usually or frequently occur at concentrations above the PEL.

The U.S. Environmental Protection Agency cautions that TEL and PEL guidelines are intended for use as screening tools for possible hazardous levels of chemicals and are not regulatory criteria. This cautionary statement is made because, although biological-effects correlation identifies level-of-concern concentrations associated with the likelihood of adverse organism response, the comparison may not demonstrate that a particular chemical is solely responsible. In fact, biological-effects correlations may not indicate direct cause-and-effect relations because sediment may contain a mixture of chemicals that contribute to the adverse effects to some degree. Thus, for any given site, these guidelines may be over- or underprotective (U.S. Environmental Protection Agency 1997).

MacDonald et al. (2000) developed consensus-based SQGs that were computed as the geometric mean of several previously published SQGs. The consensus-based SQGs consist of a threshold-effect concentration (TEC) and a

probable-effect concentration (PEC). The TEC represents the concentration below which adverse effects are not expected to occur, whereas 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 et al. 2000).

A comparison of the two SQGs indicated that the differences were small for Cd and Pb but large for Zn (Table 1). The Zn PEC (459 mg/kg) was about 69% larger than the PEL (271 mg/kg). For this study, the SQG values used were selected to provide a less-stringent assessment. Thus, for each trace element, the larger of the two SQG values for threshold effects and probable effects was selected for the purpose of assessing sediment quality (Table 1). In this paper, the SQG values used to assess sediment quality are referred to as the threshold-effects guideline and the probable-effects guideline.

Results and discussion

Sediment storage

The total volume and mass of bottom sediment in Empire Lake were estimated to be about 1.2 million m³ and 1,100 million kg, respectively. However, as will be explained, the amount of deposited sediment is not representative of the total influx of sediment over the 100-year life of the reservoir. Measured sediment thicknesses ranged from 0 to 2.3 m. The silt and (or) clay content of the sediment averaged 92%.

Age dating of the bottom sediment in Empire Lake was accomplished by determining the activity of ¹³⁷Cs in trend cores E-27 and E-36. For trend core E-27 (Fig. 3a), the absence of ¹³⁷Cs activity in the lower (older) part of the core (intervals 1 through 9) indicated pre-1954 (date approximate) sediment that was deposited prior to atmospheric fallout of ¹³⁷Cs. The ¹³⁷Cs activity measured for

Table 1 Sediment-quality guidelines (SQGs) for Cd, Pb, and Zn

Trace element	USEPA (1997)		MacDonald et al. (2000)	
	TEL	PEL	TEC	PEC
Cd	0.676	4.21	<i>0.99</i>	<i>4.98</i>
Pb	30.2	112	<i>35.8</i>	<i>128</i>
Zn	<i>124</i>	271	121	459

Values in milligrams per kilogram. Italics represents guidelines to which sediment concentrations were compared in this paper

USEPA U.S. Environmental Protection Agency, TEL threshold-effects level, PEL probable-effects level, TEC threshold-effects concentration, PEC probable-effects concentration

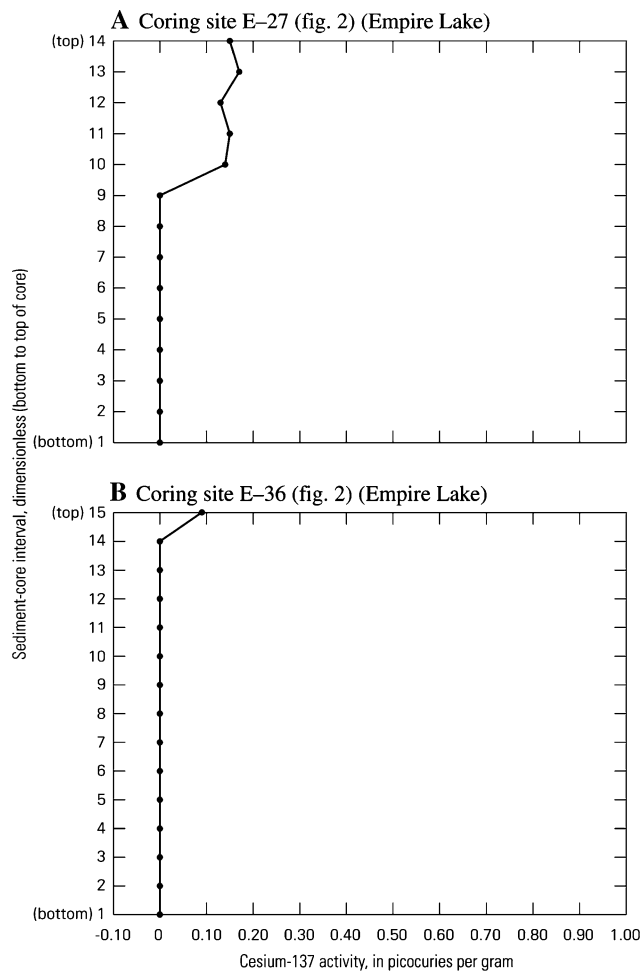


Fig. 3 Variation in cesium-137 activity with depth of bottom-sediment samples collected from coring sites E-27 and E-36 in Empire Lake

the upper (most-recent) part of the core (intervals 10 through 14) indicated post-1954 sediment. The relatively uniform ¹³⁷Cs activity in the upper part of the core may be accounted for by two possible explanations. One possibility is that the upper part of the core provides a complete record of sediment deposition since 1954. However, the lack of a well-defined 1963–64 peak is indicative of substantial post-depositional mixing (possible causes include wave action and bioturbation). A second possibility is that the upper part of the core only represents sediment deposition that postdates the 1963–64 peak. In other words, part of the depositional record at this location may have been removed (e.g., by one or more floods). Given the relatively low level of ¹³⁷Cs activity measured compared to nearby Blackberry Hay Farm Lake (Juracek 2006), the second possibility was considered more likely.

For trend core E-36 (Fig. 3b), the absence of ¹³⁷Cs activity throughout most of the core (intervals 1 through 14) indicated pre-1954 sediment. Only the top (most-

recent) interval had measurable ¹³⁷Cs activity. At this location, it appears that most of the post-1954 sediment either was not deposited or was deposited and subsequently removed. Given the relatively shallow water depth at this location (about 1.2 m), it is possible that historic sediment deposition only occurred until a threshold water depth was reached after which little additional deposition of fine-grained sediment particles was possible (i.e., flow currents and wind-induced turbulence kept the sediment in suspension until it was transported out of the reservoir). If suspended sediment is uniformly distributed and settles vertically, sediment deposition is directly proportional to water depth (Morris and Fan 1998). Additional evidence in support of the interpretation that a substantial amount of sediment was transported through Empire Lake was the elevated concentrations of Cd, Pb, and Zn in recently deposited channel-bed sediment of the Spring River immediately downstream from Empire Lake (Pope 2005).

As evidenced by the ¹³⁷Cs results for trend cores E-27 and E-36, the bottom sediment in Empire Lake does not appear to provide a complete and undisturbed record of sediment deposition over the life of the reservoir. This observation is based on the ¹³⁷Cs profile for both cores, which lacks a well-defined peak followed by a uniform, exponential decrease. Also, the limited relative thickness of post-1954 sediment in both cores, compared to the thickness of pre-1954 sediment, indicated that post-1954 sediment is underrepresented in the reservoir. For these reasons, any trends in Cd, Pb, and Zn concentrations for these two cores likely are not representative of changes that occurred over the entire history of the reservoir.

On the basis of the ¹³⁷Cs evidence, it appears that the sediment trap efficiency of Empire Lake has decreased over the life of the reservoir. This is the expected consequence as water-storage capacity is lost because of sedimentation (Morris and Fan 1998). During low-inflow periods, some sediment deposition may occur in Empire Lake. However, during high-inflow periods, most of the suspended-sediment load may be transported through the reservoir and deposited downstream. Also, the turbulence caused by the high inflows likely resuspends and transports some of the previously deposited sediment in the reservoir. Thus, during high-inflow periods, Empire Lake may be a net source of sediment.

Sediment contamination

This section describes the occurrence of, and trends in, Cd, Pb, and Zn in bottom-sediment samples collected from Empire Lake and Blackberry Hay Farm Lake (Fig. 1). Additionally, sediment quality is assessed with reference to available SQGs.

Cadmium

The Empire Lake composite cores had Cd concentrations that ranged from 7.3 mg/kg for core E-25 to 72 mg/kg for core E-29 (Table 2). For the trend cores E-1, E-6, E-27, and E-36, Cd concentrations for the sampled intervals ranged from 18 to 76 mg/kg (Table 2). Overall, using the Cd concentrations for all 17 composite cores and the mean Cd concentrations for the four trend cores (Fig. 4), the respective mean and median cadmium concentrations for the Empire Lake sediment cores were 35 and 29 mg/kg. The total mass of Cd in the Empire Lake bottom sediment was estimated to be 35,000 kg.

To provide an indication of the effects of the historical Pb and Zn mining on trace element concentrations in the bottom sediment of Empire Lake, the median concentrations were compared to baseline conditions as represented by the median concentrations in core BHF-1 collected from nearby Blackberry Hay Farm Lake (Fig. 1). The median Cd concentration in core BHF-1 was 0.4 mg/kg (Juracek 2006). Using 0.4 mg/kg as the baseline concentration, the historical mining activity increased the median Cd concentration in the bottom sediment of Empire Lake by about 7,200%.

Sediment quality was assessed by comparing the trace element concentrations in the bottom sediment with available SQGs. For Empire Lake, all bottom-sediment samples analyzed had Cd concentrations that exceeded both the threshold- and probable-effects guidelines (0.99 and 4.98 mg/kg, respectively). The Cd concentrations exceeded the probable-effects guideline by anywhere from about 50 to 1,400%. The Cd concentrations for the top (most recently deposited) interval of trend cores E-1, E-6, E-27, and E-36 ranged from 27 to 37 mg/kg (Fig. 4) (i.e., about 440–640% larger than the probable-effects guideline). In comparison, all bottom-sediment samples analyzed for Blackberry Hay Farm Lake core BHF-1 had Cd

concentrations that were less than the threshold-effects guideline (Juracek 2006).

Trend analyses indicated statistically significant negative trends for Empire Lake trend cores E-6 (Fig. 5a) and E-36 (Fig. 5c) (Table 3). Because most of the intervals were not within 10% of the mean Cd concentration for each core, the negative trends do not appear to be due to analytical variance. A negative trend also was indicated for the three-interval core E-1. A statistically significant negative trend was not indicated for trend core E-27 (Fig. 5b). No trend in Cd concentrations was indicated for Blackberry Hay Farm Lake core BHF-1 (Table 3).

Lead

Pb concentrations in the Empire Lake composite cores ranged from 100 mg/kg for core E-25 to 950 mg/kg for core E-29 (Table 2). For the trend cores, Pb concentrations for the sampled intervals ranged from 170 to 730 mg/kg (Table 2). Overall, using the Pb concentrations for all 17 composite cores and the mean Pb concentrations for the four trend cores (Fig. 6), the respective mean and median Pb concentrations for the Empire Lake sediment cores were 290 and 270 mg/kg. Compared to a baseline of 33 mg/kg (Juracek 2006), the historical mining activity increased the median Pb concentration in the bottom sediment of Empire Lake by about 720%. The total mass of Pb in the Empire Lake bottom sediment was estimated to be 290,000 kg.

For Empire Lake, all bottom-sediment samples analyzed had Pb concentrations that exceeded the threshold-effects guideline (35.8 mg/kg). With the exception of composite core E-25 (100 mg/kg), the Pb concentrations also exceeded the probable-effects guideline (128 mg/kg) by anywhere from about 10 to 640%. The Pb concentrations for the top (most recently deposited) interval of trend cores E-1, E-6, E-27, and E-36 ranged from 180 to 230 mg/kg (Fig. 6) (i.e., about 40–80% larger than the probable-

Table 2 Summary of Cd, Pb, and Zn concentrations in bottom-sediment samples collected from Empire Lake composite and trend cores, southeast Kansas, and Blackberry Hay Farm Lake trend core BHF-1, southwest Missouri, 2005

Trace element	Empire Lake			Blackberry Hay Farm Lake	
	Range in concentrations for composite cores ^a (Fig. 2)	Range in concentrations for trend cores ^b (Fig. 2)	Median concentration ^c	Range in concentrations for trend core BHF-1	Median concentration ^d
Cd	7.3–72	18–76	29	0.1–0.5	0.4
Pb	100–950	170–730	270	24–40	33
Zn	1,300–11,000	3,100–13,000	4,900	38–120	92

Values in milligrams per kilogram

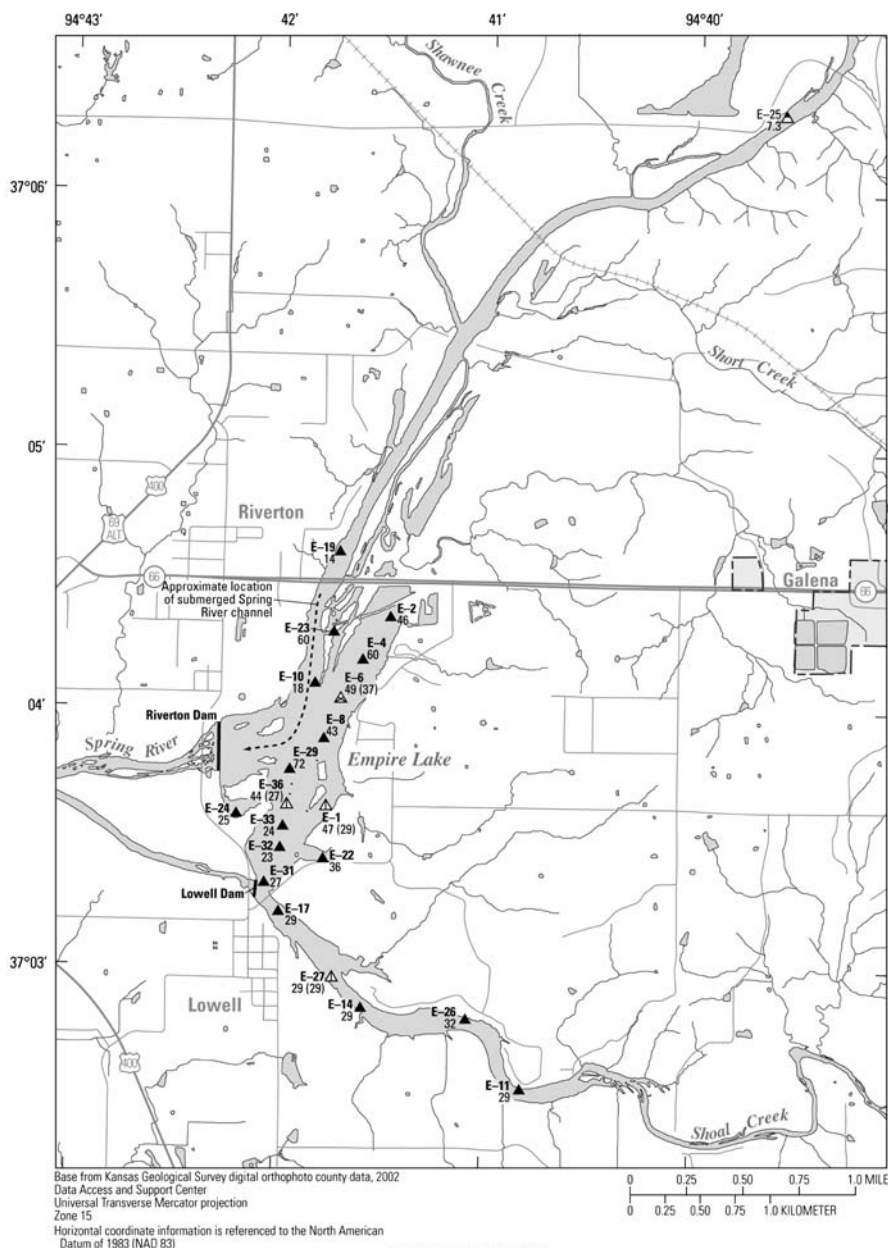
^a Seventeen composite cores analyzed

^b Four trend cores (37 core intervals) analyzed

^c Median concentration computed using the trace element concentrations for the 17 composite cores and the mean trace element concentrations for the four trend cores

^d Median concentration computed for 13-interval trend core BHF-1

Fig. 4 Cadmium concentrations for the composite cores and mean cadmium concentrations for the trend cores collected from Empire Lake



EXPLANATION

- E-11** \blacktriangle **Composite coring site and identifier**—Bulk-density determination and chemical composite analysis. Number is estimated mean cadmium concentration, in milligrams per kilogram
- E-25** \blacktriangle **Composite coring site and identifier**—Chemical composite analysis only. Number is estimated mean cadmium concentration, in milligrams per kilogram
- E-1** \triangle **Trend coring site and identifier**—Chemical trend analysis only. Number is estimated mean cadmium concentration, in milligrams per kilogram. Number in parentheses () is cadmium concentration for most recently deposited sediment, in milligrams per kilogram
- E-6** \triangle **Bulk-density and trend coring site and identifier**—Bulk-density determination and chemical trend analysis. Number is estimated mean cadmium concentration, in milligrams per kilogram. Number in parentheses () is cadmium concentration for most recently deposited sediment, in milligrams per kilogram

effects guideline). In comparison, the bottom-sediment samples analyzed for Blackberry Hay Farm Lake core BHF-1 had Pb concentrations that were ≤ 40 mg/kg, and most were less than the threshold-effects guideline (Juracek 2006).

Trend analyses indicated statistically significant negative trends for Empire Lake trend cores E-6, E-27, and E-

36 (Fig. 7) (Table 3). The negative trends do not appear to be due to analytical variance as all or most of the intervals were not within 10% of the mean Pb concentration for each core. A possible negative trend was indicated for the three-interval core E-1. No trend in Pb concentrations was indicated for Blackberry Hay Farm Lake core BHF-1 (Table 3).

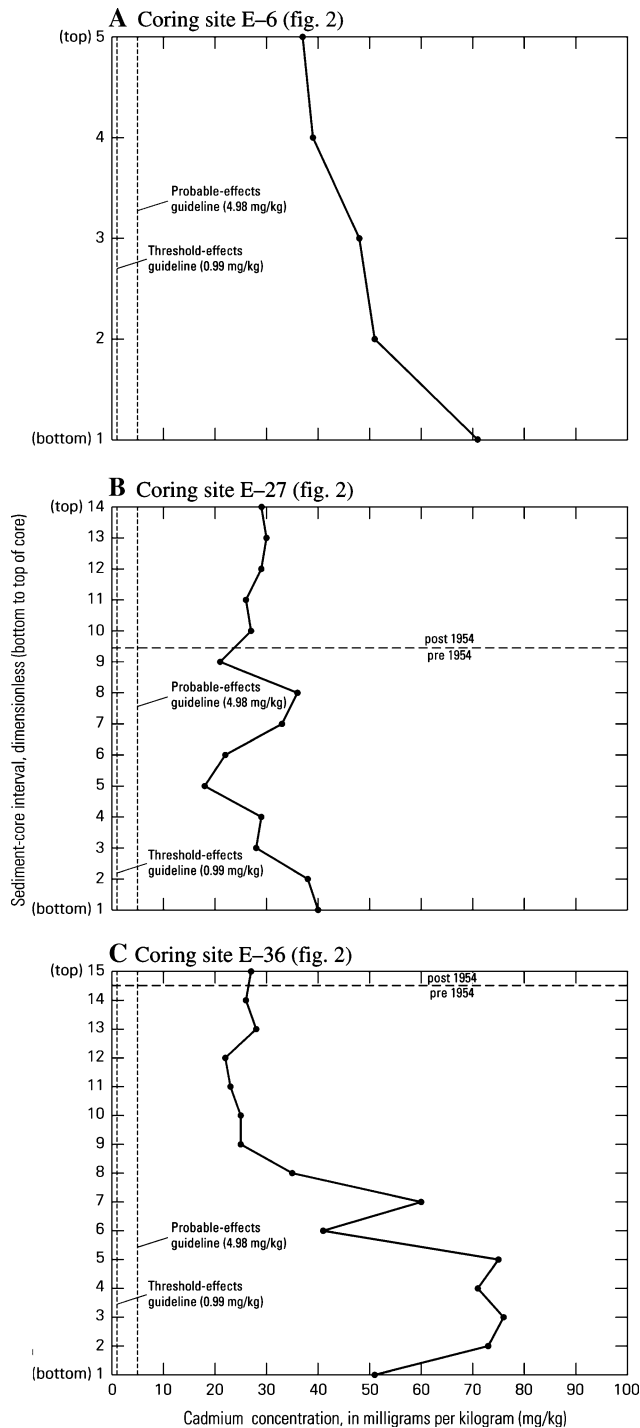


Fig. 5 Variation in cadmium concentrations with depth of bottom-sediment samples collected from coring sites E-6, E-27, and E-36 in Empire Lake

Zinc

The Empire Lake composite cores had Zn concentrations that ranged from 1,300 mg/kg for core E-25 to 11,000 mg/kg for core E-29 (Table 2). For the trend cores, Zn concentrations for the sampled intervals ranged from 3,100 to

13,000 mg/kg (Table 2). Overall, using the Zn concentrations for all 17 composite cores and the mean Zn concentrations for the four trend cores (Fig. 8), the respective mean and median Zn concentrations for the Empire Lake sediment cores were 5,600 and 4,900 mg/kg. Compared to a baseline of 92 mg/kg (Juracek 2006), the historical mining activity increased the median Zn concentration in the bottom sediment of Empire Lake by about 5,200%. Thus, for all three trace elements, concentrations generally increased by at least an order of magnitude. The total mass of Zn in the Empire Lake bottom sediment was estimated to be 5.4 million kg.

All bottom-sediment samples analyzed for Empire Lake had Zn concentrations that exceeded both the threshold- and probable-effects guidelines (124 and 459 mg/kg, respectively). The Zn concentrations exceeded the probable-effects guideline by anywhere from about 180 to 2,700%. The Zn concentrations for the top (most recently deposited) interval of trend cores E-1, E-6, E-27, and E-36 ranged from 3,100 to 4,900 mg/kg (Fig. 8) (i.e., about 580–970% larger than the probable-effects guideline). For Blackberry Hay Farm Lake core BHF-1, all of the bottom-sediment samples analyzed had Zn concentrations that were ≤ 120 mg/kg and less than the threshold-effects guideline (Juracek 2006).

Trend analyses indicated statistically significant negative trends for Empire Lake trend cores E-6, E-27, and E-36 (Fig. 9, Table 3). The negative trends do not appear to be due to analytical variance as all or most of the intervals were not within 10% of the mean Zn concentration for each core. A negative trend also was indicated for the three-interval core E-1. A statistically significant positive trend was indicated for Blackberry Hay Farm Lake core BHF-1 (Table 3). A possible explanation for the increase in Zn concentrations is increased vehicular traffic in the basin because tire wear is a known source of zinc (Callender and Rice 2000). In Empire Lake, the Zn contributed by tire wear in the bottom sediment is considered negligible compared to the Zn contributed by historical mining activity. In areas with no history of mining, Zn (and other trace elements) also may originate from road and railroad beds where chat (mill tailings) was used.

Interpretation of spatial and temporal patterns of contamination

Cd, Pb, and Zn concentrations in the bottom sediment of Empire Lake varied both spatially and temporally in relation to historical mining activity and other factors. Spatially, variability was assessed using the trace element concentrations for the 17 composite cores along with the mean concentrations for the four trend cores. Temporally, variability was assessed using the four trend cores.

Table 3 Results of trend tests on concentrations of Cd, Pb, and Zn in bottom-sediment samples collected from Empire Lake cores E-6, E-27, and E-36, southeast Kansas, and Blackberry Hay Farm Lake core BHF-1, southwest Missouri, 2005

Trace element	Spearman's rho	Trend test at 0.05 level of significance (two-sided <i>p</i> -value)
Empire Lake core E-6 (Fig. 2)		
Cd	-1.00	Negative trend (0)
Pb	-1.00	Negative trend (0)
Zn	-1.00	Negative trend (0)
Empire Lake core E-27 (Fig. 2)		
Cd	-0.23	No trend (0.434)
Pb	-0.78	Negative trend (0.001)
Zn	-0.84	Negative trend (0.0002)
Empire Lake core E-36 (Fig. 2)		
Cd	-0.77	Negative trend (0.0009)
Pb	-0.83	Negative trend (0.0001)
Zn	-0.87	Negative trend (0.00003)
Blackberry Hay Farm Lake core BHF-1 (Fig. 1)		
Cd	0.36	No trend (0.227)
Pb	-0.20	No trend (0.517)
Zn	0.64	Positive trend (0.018)

Spatially, several patterns were indicated. Within the Spring River arm of the reservoir, three cores (in downstream order, E-25, E-19, and E-10) indicated increasing Cd, Pb, and Zn concentrations in the downstream direction (Figs. 4, 6, 8). The downstream increase in concentrations likely was caused by tributary inflow from Short Creek, which drains an area that has been substantially affected by historical Pb and Zn mining (Fig. 1). Similarly, Pope (2005) determined that streambed-sediment concentrations of Cd, Pb, and Zn increased in the downstream direction along the 35-km length of the Spring River sampled within the Cherokee County superfund site. Along the Spring River, the downstream increase in concentrations likely was caused, in part, by the successive tributary inflows from Center, Turkey, and Short Creeks, which drain areas that have been substantially affected by historical Pb and Zn mining (Fig. 1). Streambed-sediment samples for these three creeks contained concentrations of Cd, Pb, and Zn that were much larger than baseline concentrations (Barks 1977; Pope 2005).

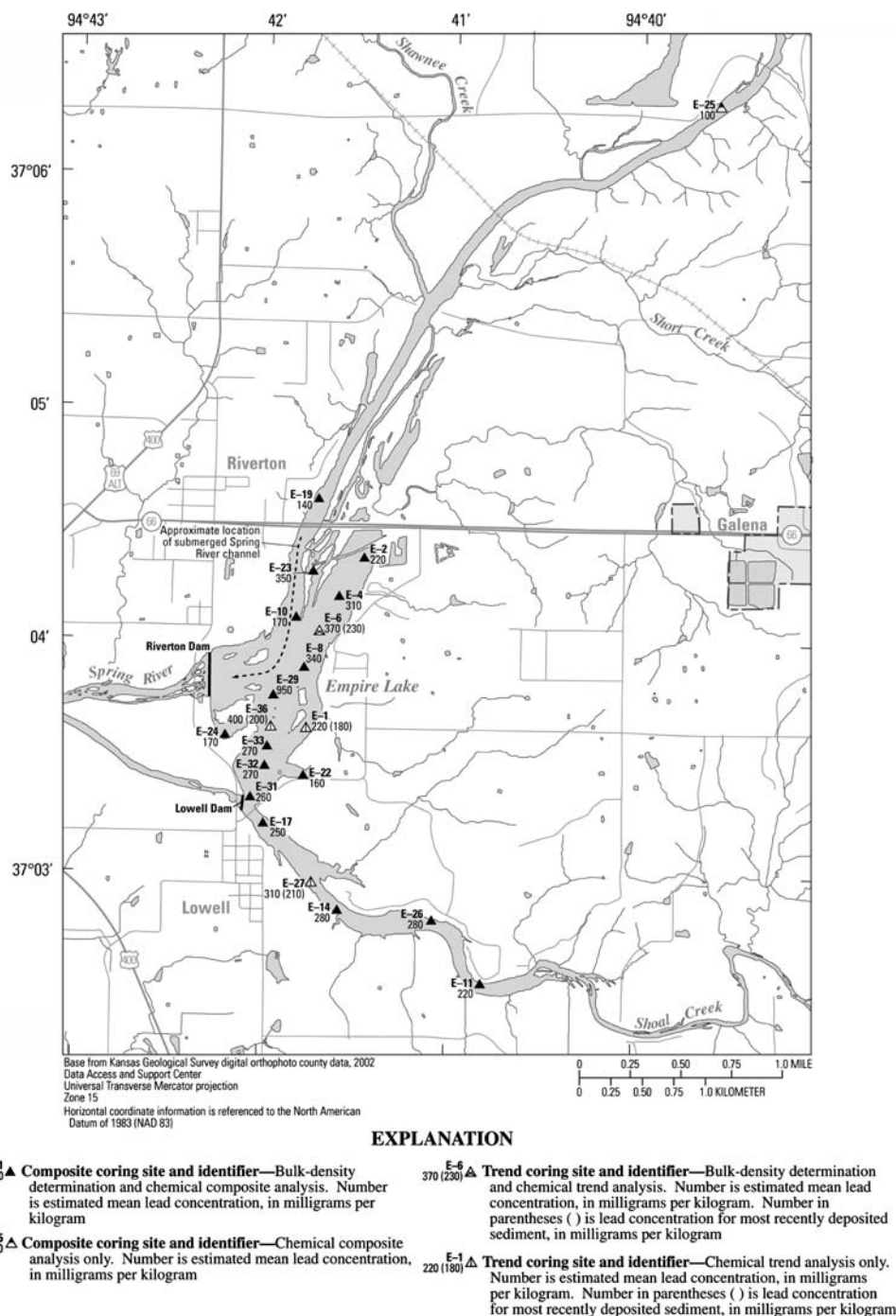
Within the Shoal Creek arm, five cores (in downstream order, E-11, E-26, E-14, E-27, and E-17) indicated uniform Cd concentrations in the downstream direction (Fig. 4). Pb and Zn concentrations increased in the downstream direction in the first four cores then decreased for core E-17 (Figs. 6, 8). A possible explanation for the downstream increase in Pb and Zn concentrations in the first four cores is related to the particle-size composition of the sediment.

Because fine particles (i.e., clay) are preferentially transported and deposited farther downstream in a reservoir than relatively coarse particles (i.e., silt) and because trace element concentrations generally increase as particle size decreases (Horowitz 1991), the downstream increase in Pb and Zn concentrations may be indicative of increasing amounts of fine particles in the sediment. The decreased Pb and Zn concentrations in core E-17 possibly represent an influx of compositionally different sediment from a minor tributary, shoreline erosion, and (or) the main body of Empire Lake.

In terms of relative magnitude, the concentrations of Cd, Pb, and Zn in the Spring River arm of the reservoir were substantially less than concentrations in the main body and the Shoal Creek arm (Figs. 4, 6, 8). Results of the sediment-thickness mapping indicated that minimal bottom sediment was deposited within the Spring River arm. The evidence obtained from the bottom-sediment thickness measurements (i.e., bare gravel or rock) indicated that the Spring River, despite the backwater imposed by Empire Lake, maintains sufficient flow velocity to prevent sediment accumulation within its channel both upstream from and through the main body of the reservoir (Juracek 2006). Thus, the sediment that was sampled may be representative of recently deposited material that is only stored temporarily before being remobilized and transported downstream. If this interpretation is valid, then the relatively small concentrations of Cd, Pb, and Zn in the Spring River arm may be indicative of less-contaminated sediments originating from the mining-affected areas of this part of the Spring River Basin (possibly due, in part, to remediation efforts and landscape stabilization) and (or) a relative increase in the contribution of minimally contaminated sediment from such sources as Shawnee Creek (Fig. 1).

Several lines of evidence indicate the transport of contaminated sediment downstream from Empire Lake. The evidence includes: (1) minimal sediment deposition in the Spring River arm of the reservoir; (2) underrepresented post-1954 sediment in Empire Lake trend cores E-27 and E-36; (3) relatively small concentrations of Cd, Pb, and Zn in the sediment sampled for the Spring River arm of the reservoir; and (4) elevated concentrations of Cd, Pb, and Zn in recently deposited channel-bed sediment of the Spring River immediately downstream from Empire Lake. These elevated concentrations typically exceeded the probable-effects guidelines (Pope 2005) and were within the range of concentrations measured for the bottom sediment in Empire Lake. Some of the contaminated sediment transported through Empire Lake during high-inflow periods will be deposited in downstream environments likely as far as Grand Lake O' the Cherokees in Oklahoma (Fig. 1). Previously, Pita and Hyne (1975) documented

Fig. 6 Lead concentrations for the composite cores and mean lead concentrations for the trend cores collected from Empire Lake



increased Pb and Zn concentrations in the uppermost layer of bottom sediment in Grand Lake O' the Cherokees.

The largest Cd, Pb, and Zn concentrations were measured for bottom sediment in the main body of Empire Lake (Figs. 4, 6, 8). As evidenced by the ^{137}Cs activity for trend core E-36 (Fig. 3b), the bottom sediment in the main body of the reservoir does not represent a complete record of deposition. Instead, with the exception of the top (most-recent) interval, trend core E-36 consisted of pre-1954

sediment. Similarly, most of trend core E-27 in the Shoal Creek arm of the reservoir consisted of pre-1954 sediment. The pre-1954 sediment included inputs of Cd, Pb, and Zn that were deposited during and after the historical peak period of Pb and Zn mining in the Kansas and Missouri parts of the Tri-State District. In the Kansas part, major production of Pb and Zn concentrates occurred from about 1920 to 1950. Major production in the Galena area ended by about 1920, but it continued until about 1950 down-

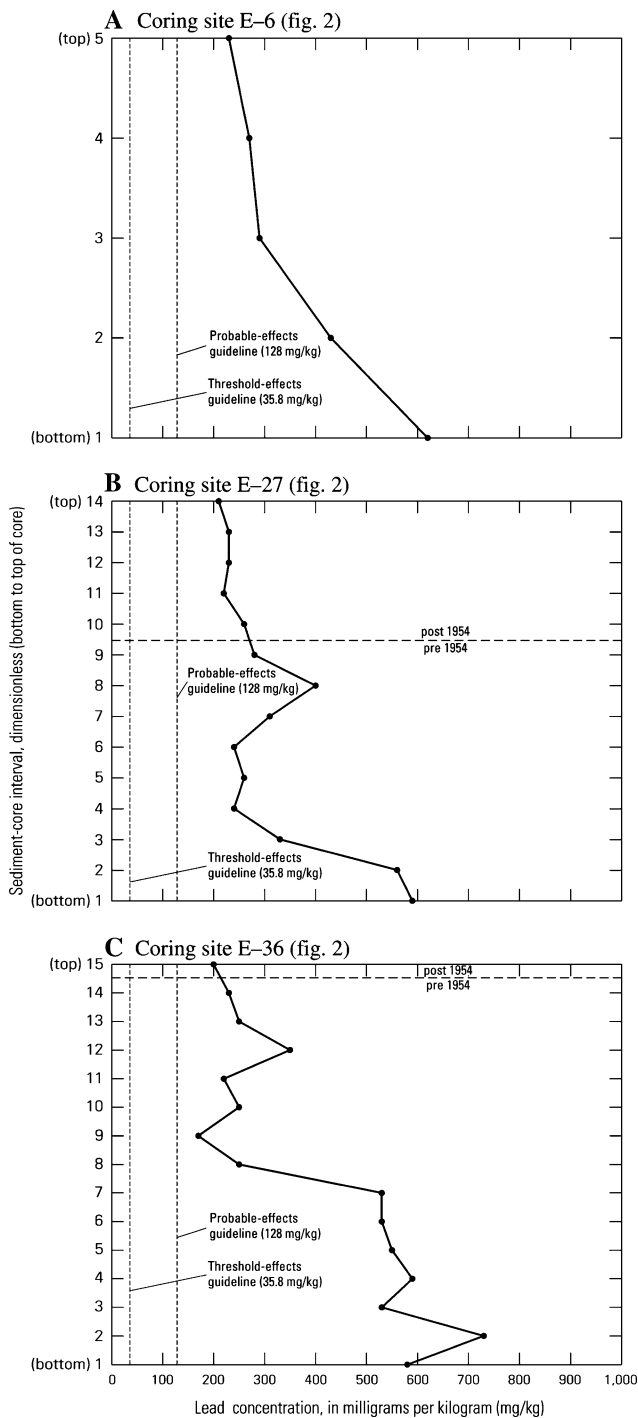


Fig. 7 Variation in lead concentrations with depth of bottom-sediment samples collected from coring sites E-6, E-27, and E-36 in Empire Lake

stream from Empire Lake in the vicinity of Baxter Springs and Treece (Fig. 1). In the Missouri part, major production occurred from about 1880 to 1920 (Spruill 1987).

The occurrence of the largest Cd, Pb, and Zn concentrations in the main body of Empire Lake indicated that, historically, sources contributing these trace elements to

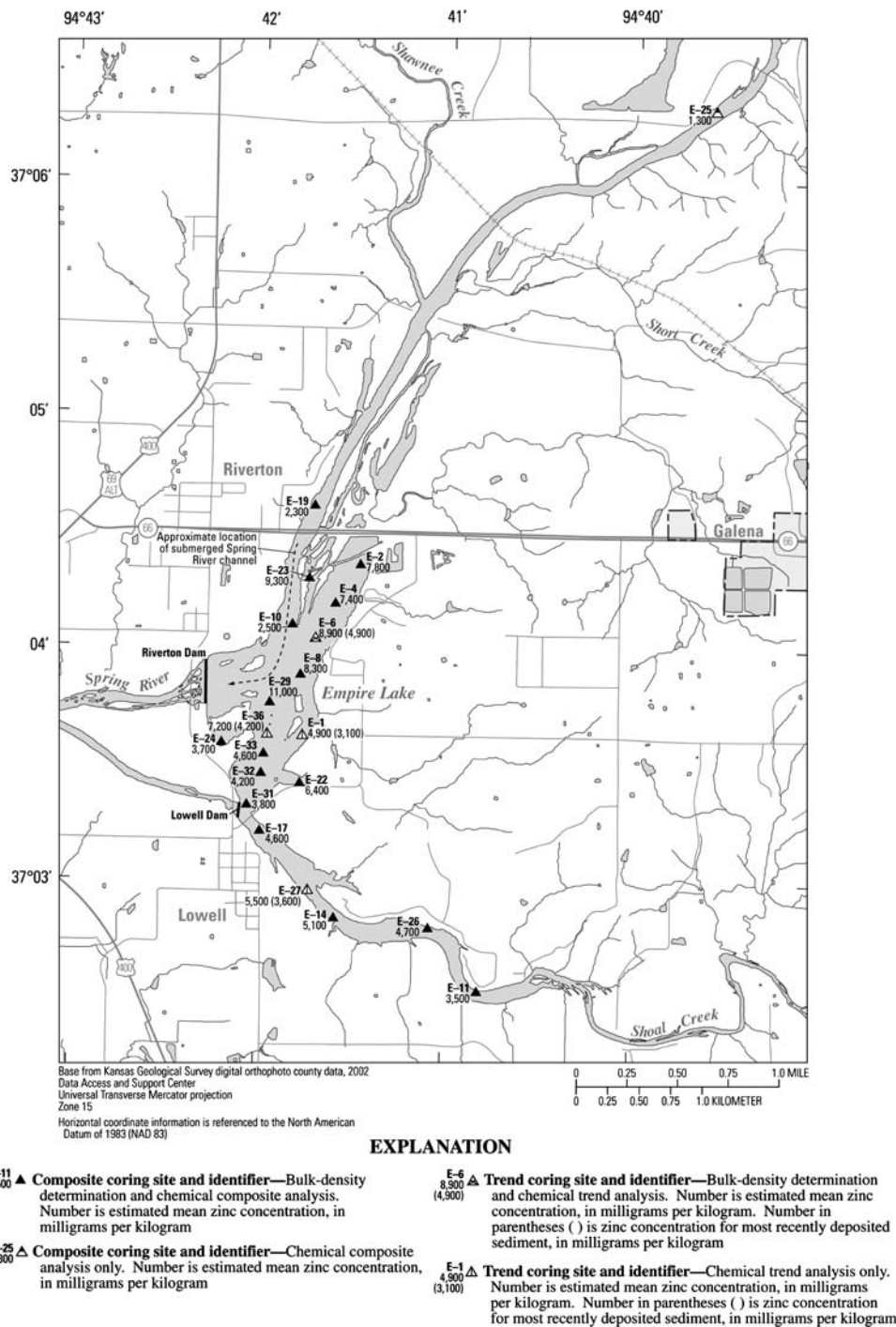
the Spring River probably provided larger inputs than sources contributing to Shoal Creek. The probable larger historical trace element concentrations in the sediment delivered by the Spring River may be indicative of the proximity of the main stem and tributaries to areas that were affected substantially by Pb and Zn mining. For example, the channel networks of Center, Turkey, and Short Creeks (tributaries of the Spring River) flow through or near more mining-affected areas than does the channel network of Shoal Creek (Fig. 1). However, possibly due in part to landscape stabilization over time as well as remediation efforts, the concentrations in the most recently deposited sediment in the main body of Empire Lake (core E-36) were similar to the most recently deposited sediment in the Shoal Creek arm of the reservoir (core E-27) (Figs. 4, 6, 8).

Temporally, the four trend cores indicated negative trends for Cd, Pb, and Zn concentrations. With the exception of the Cd trend for core E-27, the trends for cores E-6, E-27, and E-36 were statistically significant (Table 3). However, as indicated by the ¹³⁷Cs results for cores E-27 (Fig. 3a) and E-36 (Fig. 3b), the trends likely are not representative of changes that occurred over the entire history of the reservoir. Instead, the trends may be mostly indicative of pre-1954 changes.

Inspection of the concentration profiles for the more-detailed trend cores E-27 and E-36 (14 and 15 intervals, respectively) indicated that the negative trends for Cd, Pb, and Zn were not continuous as suggested by the less-detailed trend core E-6 (five intervals) (Figs. 5a, 7a, 9a). For trend core E-27, an initial negative trend (intervals 1–6) was interrupted by a period of increased concentrations (intervals 7 and 8). Then, following a decrease (interval 9), the concentrations essentially were uniform (intervals 10–14) (Figs. 5b, 7b, 9b). For trend core E-36, concentrations initially were variable with no well-defined trend (intervals 1–7). Then, there was a pronounced decrease (interval 8) after which the concentrations essentially were uniform (intervals 9–15) (Figs. 5c, 7c, 9c). The abrupt decrease in concentrations in the middle of trend core E-36 created a bimodal distribution consisting of larger concentrations for the older sediment and smaller concentrations for the more-recent sediment.

The absence of a well-defined ¹³⁷Cs profile in trend cores E-27 and E-36 (Figs. 3a, b) limited the ability to assign a date to the decrease in Cd, Pb, and Zn concentrations that was most pronounced in core E-36. Moreover, uncertainty as to how much sediment removal and mixing have occurred further restricted the ability to assign a date. However, given that the decrease occurred in both cores prior to the first detection of ¹³⁷Cs activity, it appears that the decrease happened before 1954. With the available information it is not possible to assign a more exact date

Fig. 8 Zinc concentrations for the composite cores and mean zinc concentrations for the trend cores collected from Empire Lake



and the explanation for the decrease is necessarily uncertain. Although, it is reasonable to propose that historical changes in mining activity, in part, would account for the decrease. As previously stated, major Pb and Zn production in areas upstream from Empire Lake ended about 1920. Other factors that may affect trace element concentrations include precipitation, runoff, vegetation, remediation, and landscape stabilization.

One specific possibility that could account for the pre-1954 decreases in Cd, Pb, and Zn concentrations is as follows. With the end of major Pb and Zn production in areas upstream from Empire Lake by about 1920, sediment concentrations of Cd, Pb, and Zn declined. A major flood, during the period of declining concentrations, removed some of the previously deposited sediment in Empire Lake. The missing record in the sediment profile potentially

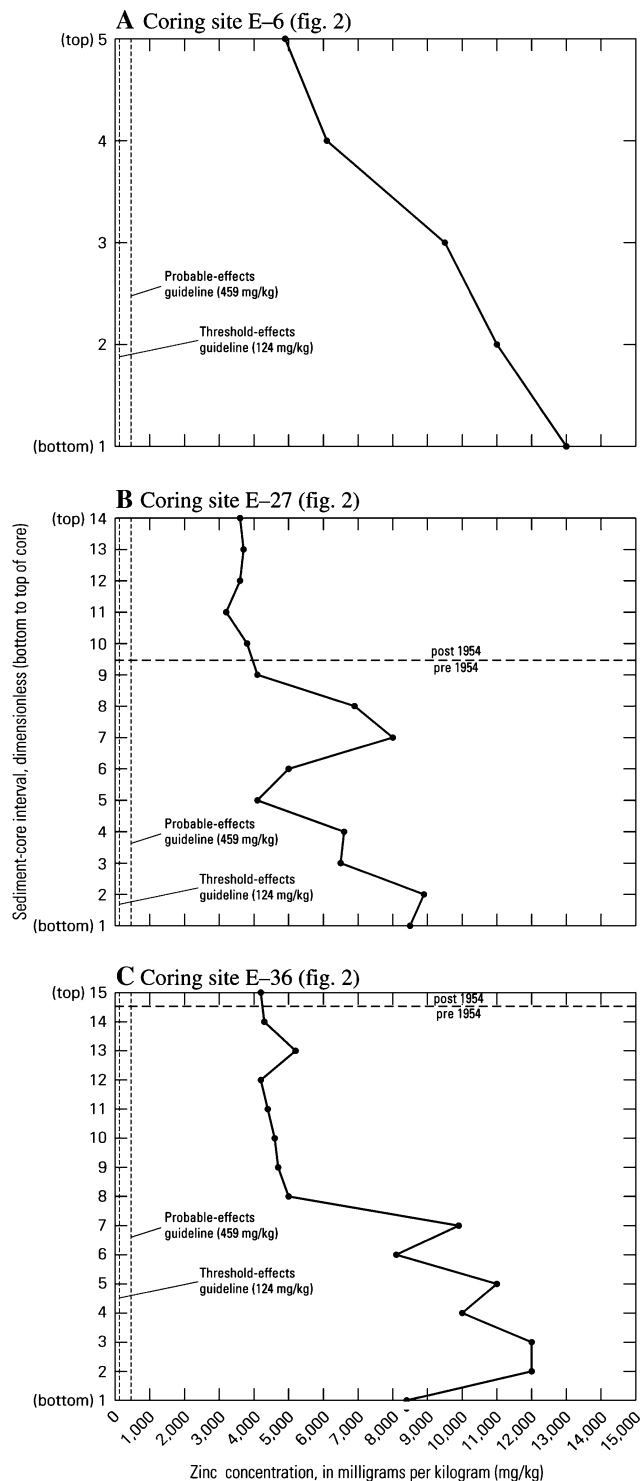


Fig. 9 Variation in zinc concentrations with depth of bottom-sediment samples collected from coring sites E-6, E-27, and E-36 in Empire Lake

would be evidenced by pronounced decreases in Cd, Pb, and Zn concentrations. Between 1923 and 1954, the largest flood measured for the Spring River near Waco, MO (USGS streamflow-gaging station 07186000, period of

record 1923–2005) (Fig. 1) occurred on May 19, 1943, with a peak discharge of 2,920 m³/s. This flood was the second largest for the period of record, exceeded only by the peak of September 26, 1993 (4,280 m³/s). The largest flood measured during the period of record for Shoal Creek above Joplin, MO (USGS streamflow-gaging station 07187000, period of record 1924–2005) (Fig. 1) occurred on May 18, 1943, with a peak discharge of 1,760 m³/s (U.S. Geological Survey 2006). Thus, if the proposed possibility is valid, a potential date for the pronounced decreases in Cd, Pb, and Zn concentrations is 1943.

To further assess temporal changes in Cd, Pb, and Zn concentrations, the most recently deposited pre-1954 sediment was compared with the post-1954 sediment in trend cores E-27 and E-36. For trend core E-27, the post-1954 concentrations (intervals 10–14) generally were similar to the most-recent pre-1954 concentrations (interval 9) (Figs. 5b, 7b, 9b). Likewise, for trend core E-36, the post-1954 concentrations (interval 15) were similar to the most-recent pre-1954 concentrations (interval 14) (Figs. 5c, 7c, 9c). This comparison indicated that Cd, Pb, and Zn concentrations in the sediment deposited in Empire Lake may not have changed substantially over the past 50 or more years. However, the concentrations may have been affected by sediment removal and (or) mixing.

Although the focus of this study was the bottom sediment in Empire Lake, three additional samples were collected to assess trace element contamination on the flood plain. The concentrations of Cd, Pb, and Zn for all three flood-plain samples exceeded baseline concentrations (Juracek 2006). For the Spring River flood plain (site SRF-1, Fig. 2), the concentrations of Cd and Pb were greater than the threshold-effects guidelines (0.99 and 35.8 mg/kg, respectively) but less than the probable-effects guidelines (4.98 and 128 mg/kg, respectively). The Zn concentration was greater than the probable-effects guideline (459 mg/kg). For the Shoal Creek flood plain (site SCF-1, Fig. 2), the Cd concentration was slightly less than the threshold-effects guideline, the Pb concentration was slightly greater than the threshold-effects guideline, and the Zn concentration was between the threshold- (124 mg/kg) and probable-effects guidelines. For both the Spring River and Shoal Creek flood-plain samples, the concentrations of Cd, Pb, and Zn were substantially smaller than the concentrations in Empire Lake bottom sediment. This observation may be indicative of a larger percentage of relatively coarse particles (i.e., silt) in the flood-plain samples compared to the bottom-sediment samples. The sample of original flood-plain material collected from the bottom of trend core E-36 (Fig. 2) contained concentrations of Cd, Pb, and Zn that, although substantially less than the concentrations in the immediately overlying sediment, still exceeded the

probable-effects guidelines. Concentrations of Cd, Pb, and Zn that exceeded the probable-effects guidelines also were found in recently deposited channel-bed sediment in the Spring River immediately downstream from Empire Lake (Pope 2005). Thus, Cd, Pb, and Zn contamination in the vicinity of Empire Lake was not confined to the reservoir bottom sediment.

Summary and conclusions

A combination of sediment-thickness mapping and bottom-sediment coring completed in 2005 was used to investigate sediment storage and Cd, Pb, and Zn contamination in bottom sediment of Empire Lake, a shallow reservoir in Cherokee County, Kansas, that has been affected by historical Pb and Zn mining. The major results of this study are listed below:

1. The total estimated volume and mass of contaminated bottom sediment in Empire Lake were 1.2 million m³ and 1,100 million kg, respectively.
2. Most of the bottom sediment in Empire Lake was deposited prior to 1954 thus indicating that the trap efficiency of the reservoir has declined over time.
3. The total estimated mass of Cd, Pb, and Zn in the bottom sediment of Empire Lake was 35,000 kg, 290,000 kg, and 5.4 million kg, respectively.
4. Cd, Pb, and Zn concentrations in the bottom sediment of Empire Lake typically exceeded baseline concentrations by at least an order of magnitude.
5. Cd, Pb, and Zn concentrations in bottom-sediment samples from Empire Lake typically far exceeded the probable-effects guidelines, which represent the concentrations above which toxic biological effects usually or frequently occur.
6. Cd, Pb, and Zn concentrations in the bottom sediment of Empire Lake decreased prior to 1954 and have remained relatively constant since.
7. Mining-related Cd, Pb, and Zn contamination in the vicinity of Empire Lake was not confined to the reservoir bottom sediment as elevated concentrations of the three trace elements were measured in flood-plain soils near the reservoir.
8. During high-inflow periods, Empire Lake may be a net source of contaminated sediment.
9. The presence of contaminated sediment in the Spring River immediately downstream from Empire Lake indicated that contaminated sediment that passes through, or originates from, Empire Lake during high-inflow periods will be deposited in downstream environments likely as far as Grand Lake O' the Cherokees in Oklahoma.

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