REPRESENTATIVENESS OF SOIL SAMPLES COLLECTED TO ASSESS MINING-RELATED CONTAMINATION OF FLOOD PLAINS IN SOUTHEAST KANSAS

Kyle Juracek, Research Hydrologist, U.S. Geological Survey, Lawrence, Kansas, kjuracek@usgs.gov

INTRODUCTION

Historical lead and zinc mining in the Tri-State Mining District (TSMD), located in parts of southeast Kansas, southwest Missouri, and northeast Oklahoma, has resulted in a substantial ongoing input of lead and zinc to the environment (Juracek, 2006; Juracek and Becker, 2009). In response to concern about the mining-related contamination, southeast Cherokee County, Kansas, was listed on the U.S. Environmental Protection Agency's (USEPA) National Priority List as a Superfund hazardous waste site (fig. 1). To provide some of the information needed to support remediation efforts in the Cherokee County Superfund site, a study was begun in 2009 by the U.S. Geological Survey (USGS) that was requested and funded by USEPA. As part of the study, surficial-soil sampling was used to investigate the extent and magnitude of mining-related lead and zinc contamination in the flood plains of the Spring River and several tributaries within the Superfund site. In mining-affected areas, flood-plain soils had lead and zinc concentrations that far exceeded background levels as well as probable-effects guidelines for toxic aquatic biological effects (Juracek, 2013). Lead- and zinc-contaminated flood plains are a concern, in part, because they represent a long-term source of contamination to the fluvial environment.

An important issue is the within-site representativeness of the surficial-soil samples collected. Specifically, the question is whether or not the samples collected provide an acceptable representation of the lead and zinc concentrations at each site for the purpose of characterizing and comparing sites. The distribution of mining-contaminated sediment on flood plains is determined by several factors including the size and density of the contaminated particles, flood-plain width and topography, flood characteristics (frequency, magnitude, duration), and fluvial geomorphic processes. To evaluate within-site representativeness, additional samples were simultaneously collected to assess within-site variability. In this paper, the specific objectives were to:

(1) Describe the collection and analysis of surficial-soil samples using a 5-point sampling technique;
(2) Describe the collection and analysis of additional surficial-soil samples to assess within-site variability; and
(3) Evaluate the within-site representativeness of the original 5-point samples for assessing mining-related contamination.

DESCRIPTION OF STUDY AREA

The Cherokee County Superfund site is a 115 square mile area located within the TSMD (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). Mining activity in the TSMD ended in the 1970s. Background sediment concentrations of lead and zinc in the Superfund site were estimated by Pope (2005) to be 20 and 100 milligrams per kilogram, respectively.

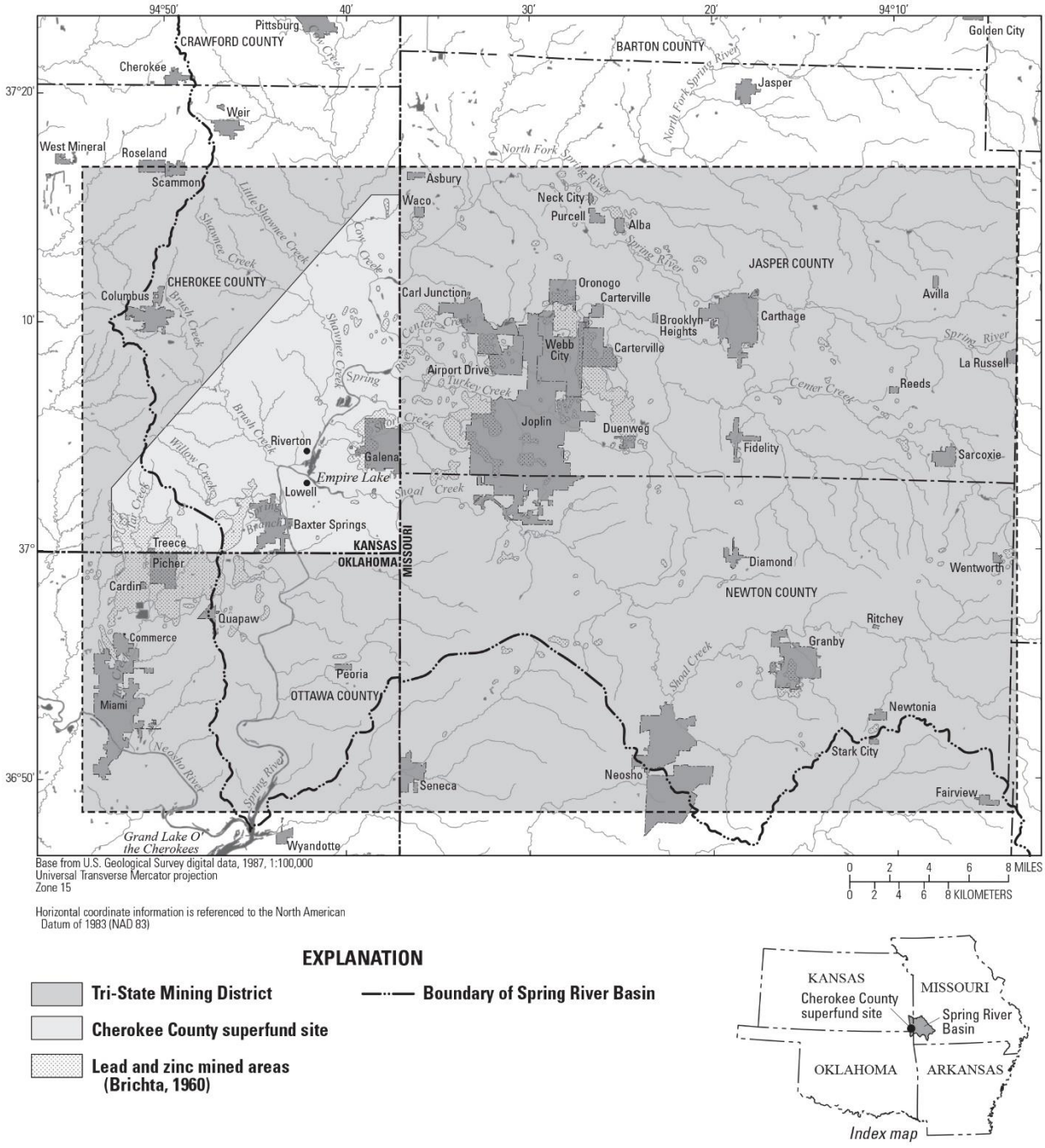

Figure 1. Location of the Spring River and its tributaries, the Cherokee County Superfund site, and lead- and zinc-mined areas in the Tri-State Mining District, Kansas, Missouri, and Oklahoma.

The Superfund site is drained by the Spring River, its tributaries, and Tar Creek. Principal tributaries to the Spring River in Cherokee County include Brush Creek, Cow Creek, Center Creek, Shawnee Creek, Shoal Creek, Short Creek, Turkey Creek, and Willow Creek. Several of the tributaries, as well as Tar Creek, drain areas that were substantially affected by historical lead and

zinc mining (fig. 1). On average, the width of the Spring River flood plain in the Superfund site is about 1 to 1.5 miles. The width of the tributary and Tar Creek flood plains generally is about 0.5 mile or less.

METHODS

As part of a study to assess the extent and magnitude of mining-related lead and zinc contamination (Juracek, 2013), information was obtained through an analysis of surficial-soil samples collected from the Spring River flood plain, tributary flood plains, and the Tar Creek flood plain in the Superfund site. Sampling sites for the Spring River flood plain, as compared to the other flood plains, were selected using different schemes as described below.

Sampling site selection: The selection of surficial-soil sampling sites for the Spring River flood plain involved several steps. First, all one-square-mile sections that were located mostly (that is, at least 50 percent) or completely in the Spring River flood plain were identified using USGS 1:24,000-scale topographic quadrangle maps. Second, the selected sections were divided into quadrants. Third, for each section, a quadrant was randomly selected for sampling. The random-selection process involved the use of coin flips to determine if the quadrant was north or south and east or west. Using this process, either the northwest, northeast, southwest, or southeast quadrant was selected for each section. If the randomly selected quadrant for a section was unusable, either because it was located mostly out of the flood plain or because access permission from the land owner was not granted, the next quadrant was selected using a clockwise rotation. A total of 30 Spring River flood-plain surficial-soil sampling sites were selected. Typically, the flood-plain soil was sampled at the center of each randomly selected quadrant.

Tributary streams for which flood-plain surficial soils were sampled included Brush Creek, Cow Creek, Shawnee Creek, Shoal Creek, Short Creek, Spring Branch, Tar Creek, Turkey Creek, and Willow Creek (fig. 1). Tar Creek is not a direct tributary of the Spring River. It flows into the Neosho River, which subsequently joins the Spring River at Grand Lake O' the Cherokees in Oklahoma. Tar Creek was included because it drains a part of Cherokee County that was substantially affected by historical lead and zinc mining activity (fig. 1). Along each stream, one to three transects were established for the purpose of sampling. Each transect extended perpendicularly away from the channel on one or both sides as dictated by the location of the flood plain and site accessibility. Twenty transects were established. Along each transect, two to four flood-plain sampling sites were selected. The distance between successive sampling sites (when two or more sites were sampled on the same side of the channel) ranged from about 10 to about 300 feet depending on flood-plain width, number of sites, and site conditions. A total of 59 tributary flood-plain surficial-soil sampling sites were selected.

Sample Collection and Preparation: The Spring River flood-plain surficial-soil samples were collected in the fall of 2009. The tributary flood-plain surficial-soil samples (including Tar Creek) were collected in the spring of 2011. All flood-plain surficial-soil samples were collected to a depth of about 1 inch. At each Spring River flood-plain site, the soil was sampled at the selected center location and typically at a distance (hereafter referred to as the sampling radius) of 100 feet north, south, east, and west of the center. This sampling method is referred to as the 5-point sampling technique (fig. 2). For the tributary flood-plain sites, the 5-point technique was used with

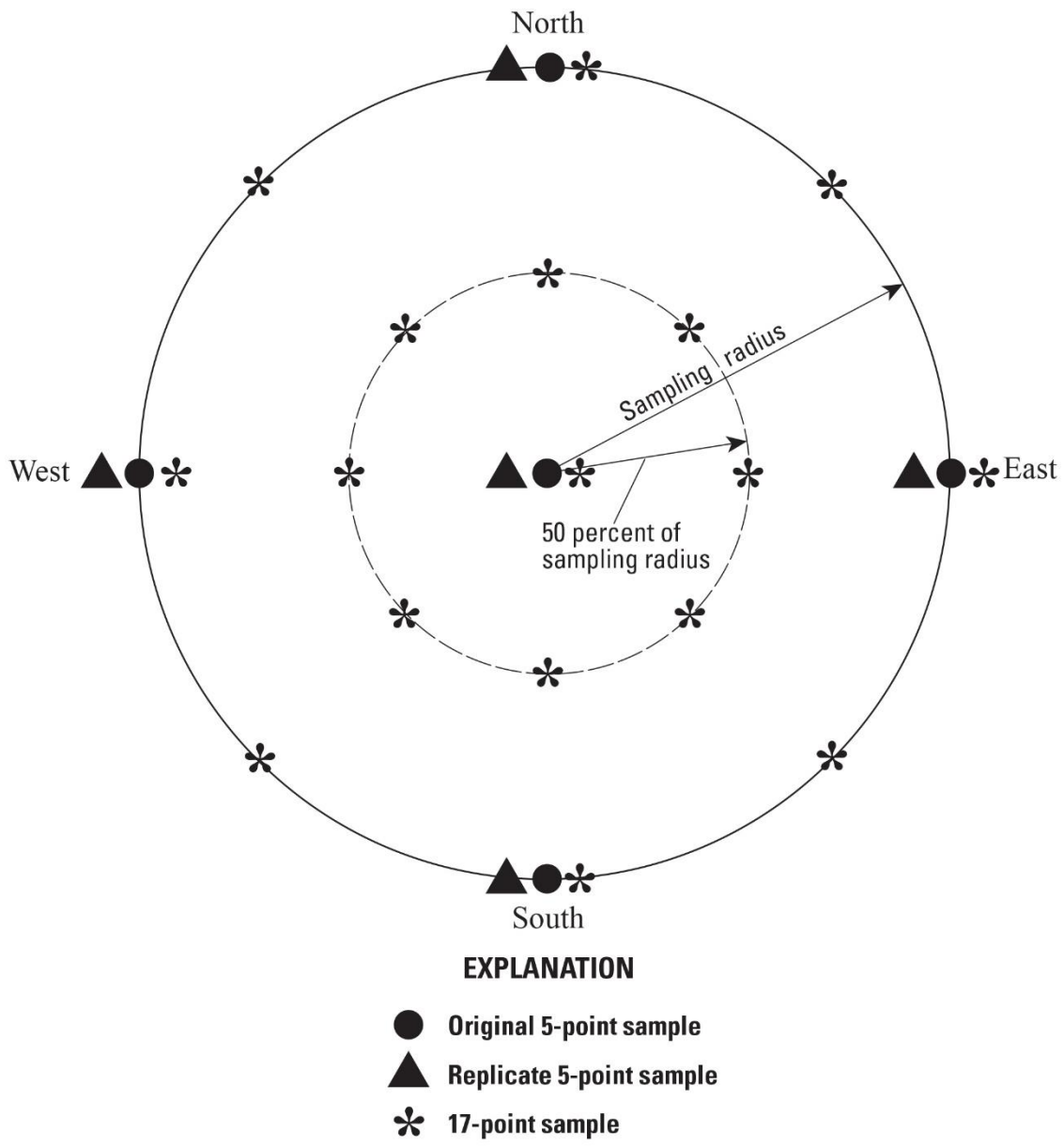

Figure 2. Diagram showing the 5- and 17-point sampling techniques.

a sampling radius that ranged from 5 to 50 feet depending on the width of flood plain available for sampling and the number of sampling sites per transect. Along each transect, samples collected using the 5-point technique were non-overlapping.

At each sampling site, an equal volume of soil was collected at the five locations using a 5-inch long section of cellulose acetate butyrate transparent tubing (2.6-inch inside diameter) that was pushed by hand into the soil. The tubing was thoroughly cleaned with a clean paper towel prior to each reuse. For each site, the soil from the five locations was combined in a plastic bag and transported back to the USGS laboratory in Lawrence, Kansas, for subsequent sample preparation.

Following air drying, each bulk sample was spread out on a clean plastic sheet and all visible organics (for example, plant fragments, seed pods, and roots) were removed using stainless steel tweezers. Each sample was disaggregated using a rubber-tipped pestle until the entire sample passed through a 4-millimeter stainless steel sieve. Then, each disaggregated sample was placed in a glass bowl and homogenized using a plastic spoon to provide a composite sample for each site. All utensils used in sample preparation were thoroughly cleaned with deionized water and wiped dry with a clean paper towel before each reuse.

Sample Collection to Assess Representativeness: To evaluate the within-site representativeness of the 5-point samples collected, two additional sets of samples (each set representing about 10 percent of the total samples collected) were simultaneously collected to assess within-site variability. First, replicate 5-point samples were collected in juxtaposition with the original 5-point samples (fig. 2) at three Spring River and six tributary flood-plain sampling sites. Second, 17-point samples were collected at three Spring River and five tributary flood-plain sampling sites. In the 17-point technique, the soil was sampled at the center and at 100 and 50 percent of the selected sampling radius north, northeast, east, southeast, south, southwest, west, and northwest from the center (fig. 2). Following collection, these additional samples were prepared for analysis in the same manner as the original samples.

Chemical Analyses: The flood-plain surficial-soil samples were analyzed for lead and zinc concentration at USEPA facilities using x-ray fluorescence (XRF) (U.S. Environmental Protection Agency, 2007). All samples were analyzed as bulk samples. The samples collected from the Spring River flood plain were analyzed using a handheld XRF instrument. The samples collected from the tributary flood plains were analyzed using a stationary XRF instrument.

XRF analytical variability was assessed by the triplicate analysis of multiple samples to determine the deviation from the mean concentration. For the Spring River flood-plain samples, the analytical variability for lead ranged from $\pm$2 to $\pm$38 percent with a mean variability of $\pm$17 percent (9 samples). For zinc, the analytical variability ranged from $\pm$2 to $\pm$33 percent with a mean variability of $\pm$11 percent (10 samples). For the tributary flood-plain samples, the analytical variability for lead ranged from $\pm$1 to $\pm$12 percent with a mean variability of $\pm$4 percent (70 samples). The analytical variability for zinc ranged from 0 to $\pm$12 percent with a mean variability of $\pm$3 percent (70 samples). The larger variability for the Spring River flood-plain samples likely was caused, in part, by the use of a handheld XRF instrument.

To assess the comparability of the XRF analyses with another method, split-replicate samples from three Spring River and six tributary flood-plain surficial-soil sampling sites were analyzed at a USGS laboratory for lead and zinc concentration using spectroscopic methods (Fishman and Friedman, 1989; Arbogast, 1996; Briggs and Meier, 1999). For each site, the composite sample was split to provide the original and split-replicate samples. The spectroscopic methods used provided total (at least 95 percent of the element present) rather than total-recoverable concentrations. Analytical variability for the spectroscopic methods was about 10 percent or less (Juracek, 2013).

Overall, including the results for both the Spring River and tributary flood plains, lead and zinc concentrations determined by spectroscopic methods typically were larger. Lead and zinc concentrations for the three Spring River split-replicate samples averaged 55 and 28 percent larger, respectively. Lead concentrations for the six tributary split-replicate samples ranged from 56 percent smaller to 94 percent larger. Zinc concentrations for the six tributary split-replicate samples ranged from 3 to 70 percent larger.

RESULTS AND DISCUSSION

Within-site representativeness of the original 5-point surficial-soil samples was evaluated using two additional sets of samples that were simultaneously collected. On average, lead and zinc concentrations in the replicate 5-point samples collected from the Spring River flood plain were within about ±11 and ±15 percent of the concentrations in the original 5-point samples, respectively (table 1). For lead, the average variability for the replicate samples was computed using only two of the three sampling sites because the lead concentration was less than the XRF limit of detection for one of the original samples. On average, lead and zinc concentrations in the replicate 5-point samples collected from the tributary flood plains were within about ±8 and ±4 percent, respectively (table 1). The larger variability measured for the Spring River samples possibly was caused, in part, by the use of a handheld (as opposed to stationary) XRF instrument for the chemical analyses.

Lead and zinc concentrations in the 17-point samples collected from the Spring River flood plain were, on average, within about ±27 and ±23 percent of the concentrations in the original 5-point samples, respectively (table 1). Lead and zinc concentrations in the 17-point samples collected from the tributary flood plains were, on average, within about ±11 and ±14 percent, respectively (table 1). The larger variability documented for the Spring River 17-point samples may be indicative of greater spatial variability associated with the use of a larger sampling radius. Also, the larger variability for the Spring River samples possibly was caused, in part, by the use of a handheld XRF instrument for the chemical analyses. Finally, the larger variability measured for the 17-point samples, compared to the replicate 5-point samples, may be indicative of the fact that more spatial complexity in flood-plain lead and zinc concentrations is being captured by the 17-point samples.

SUMMARY AND CONCLUSIONS

To assess the within-site representativeness of flood-plain surficial-soil samples collected using a 5-point sampling technique to characterize the extent and magnitude of mining-related lead and zinc contamination in the Cherokee County (Kansas) Superfund site, additional 5- and 17-point samples were simultaneously collected and analyzed. On the basis of the similarity of the chemical results obtained, it was concluded that, for the flood-plain sampling sites selected, the 5-point samples provided representative data for the purpose of assessing lead and zinc contamination.

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Table 1. Lead and zinc concentrations for original 5-point samples, replicate 5-point samples, and 17-point samples collected from the Spring River and tributary flood plains, Cherokee County, Kansas. [mg/kg, milligrams per kilogram; %, percent; <, less than; --, not available. Each parenthetical percentage indicates the difference from the original sample concentration.]

Surficial-soil sample	Lead, in mg/kg	Zinc, in mg/kg
Spring River flood plain		
SRF-1, original 5-point	24	56
SRF-1, replicate 5-point	22 (-8%)	48 (-14%)
SRF-3, original 5-point	<19	78
SRF-3, replicate 5-point	19 (--)	67 (-14%)
SRF-7, original 5-point	21	186
SRF-7, replicate 5-point	18 (-14%)	155 (-17%)
SRF-4, original 5-point	16	53
SRF-4, 17-point	19 (+19%)	45 (-15%)
SRF-9, original 5-point	29	75
SRF-9, 17-point	13 (-55%)	41 (-45%)
SRF-29, original 5-point	47	200
SRF-29, 17-point	50 (+6%)	216 (+8%)
Tributary flood plains		
BC2-2, original 5-point	66	200
BC2-2, replicate 5-point	63 (-5%)	173 (-14%)
CC1-3, original 5-point	55	158
CC1-3, replicate 5-point	45 (-18%)	159 (+1%)
SB2-1, original 5-point	697	3,515
SB2-1, replicate 5-point	638 (-8%)	3,456 (-2%)
TrC1-2, original 5-point	5,363	25,500
TrC1-2, replicate 5-point	4,943 (-8%)	24,900 (-2%)
TkC1-3, original 5-point	475	2,839
TkC1-3, replicate 5-point	483 (+2%)	2,725 (-4%)
WC1-1, original 5-point	210	927
WC1-1, replicate 5-point	218 (+4%)	954 (+3%)
BC1-2, original 5-point	50	90
BC1-2, 17-point	52 (+4%)	118 (+31%)
CC1-2, original 5-point	63	165
CC1-2, 17-point	50 (-21%)	148 (-10%)
ShC2-1, original 5-point	281	2,007
ShC2-1, 17-point	291 (+4%)	1,887 (-6%)
SB2-3, original 5-point	233	973
SB2-3, 17-point	272 (+17%)	1,161 (+19%)
TrC3-1, original 5-point	62	290
TrC3-1, 17-point	69 (+11%)	302 (+4%)