Final

Rev3_8.9.04

Phase I Assessment Plan: Appendix B

QUALITY-ASSURANCE PROJECT PLAN FOR DATA COLLECTION RELATED TO AN ASSESSMENT OF METALS IN SEDIMENT IN EMPIRE LAKE AND SPRING RIVER AND TAR CREEK SYSTEMS, SOUTHEAST KANSAS

QA CATEGORY IV Basic Research and Development

APPROVALS

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USFWS Project Manager Date
John F. Miesner

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USGS Principal Investigator Date
Larry M. (Mike) Pope

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USGS Principal Investigator Date
Kyle E. Juracek

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USGS QA Official Date
Andrew C. Ziegler

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USGS Sediment Lab Director Date
Arthur J. Horowitz

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USGS Field Specialist Date
Patrick J. Finnegan

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Kansas - KDHE Co-Trustee Date
Leo Henning – NRDAR Coordinator

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PROJECT MANAGEMENT

A3. Distribution List

The following individuals will receive copies of the approved Quality Assurance Project Plan (QAPP):

John Miesner, Project Manager, U.S. Fish and Wildlife Service (USFWS)

Mike Pope, Principal Investigator/Project Leader, U.S. Geological Survey (USGS)

Kyle Juracek, Principal Investigator, USGS

Andy Ziegler, Water-Quality/Quality-Assurance Specialist, USGS

Art Horowitz, Sediment Trace Element Analytical Services Director, USGS

Pat Finnegan, Field Activities Specialist, USGS

Leo Henning, Co-Trustee, Kansas Department of Health and Environment (KHDE)

A4. Project Organization

The individuals participating in the project and their specific roles and responsibilities are discussed below:

John Miesner, Project Manager – the primary decision maker for the project and the primary user of the data to determine if further investigation in the study area is required and to what extent remediation efforts are needed. His duties are:

1. Overall responsibility for the investigation.
2. Reviewing and approving the QAPP and subsequent revisions.
3. Reviewing reports and ensuring plans are implemented according to schedule.
4. Making final project decisions with the authority to commit the necessary resources to conduct the project.

Mike Pope, Principal Investigator/Project Leader – The Project Leader will coordinate the project activities with the following specific responsibilities:

1. Develop and revise the QAPP as needed to define project goals and activities.

2. Coordinate field and laboratory activities associated with sampling of streambed sediments.
3. Conduct project activities in accordance with the QAPP and within scheduled project time frames.
4. Verify and validate field and laboratory data generated from sampling of streambed sediments.
5. Reporting to Project Manager regarding the project status and preparing interim and final project reports.
6. Preparation of report describing the extent and magnitude of contaminated streambed sediments in those parts of the Spring River and Tar Creek watersheds that lay within the defined study area.
7. Ensure that field activities are conducted with regard to approved safety protocols as presented in Wilde and Radtke (chapters variously dated).

Kyle Juracek, Principal Investigator – The Principal Investigator will be integrally involved in the formulation of project work plans and investigative techniques and methods and have the following specific responsibilities:

1. Coordinate field and laboratory activities associated with bed-sediment sampling of Empire Lake.
2. Conduct project activities in accordance with the QAPP and within scheduled project time frames.
3. Verify and validate field and laboratory data generated from sampling of lake-bed sediments.
4. Preparation of report describing the occurrence of trace elements in and historical transport of contaminated sediments to Empire Lake.
5. Ensure that field activities are conducted with regard to approved safety protocols as presented in Wilde and Radtke (chapters variously dated).

Andy Ziegler, Water-Quality/Quality-Assurance Specialist – The Water-Quality/Quality-Assurance (WQ/QA) Specialist will provide technical assistance to the project team members on matters related to geochemical processes, sampling protocols, and quality-assurance (QA) issues. The WQ/QA specialist also will be responsible for final USGS internal review and approval of the QAPP and will conduct quarterly reviews of the project status and operations and communicate results of the reviews to the principal investigators.

Art Horowitz, Sediment Trace Element Analytical Services Director – The Analytical Services Director (ASD) will be responsible for coordinating the analysis of stream and lake-bed samples for trace elements and laboratory validation of data. This coordination will include the receipt of samples at the laboratory, selection of the analytical team, the insurance that internal laboratory audits are conducted per standard operating procedures (SOP's), and the distribution of applicable sections of the QAPP to analytical team members. The ASD will coordinate internal laboratory QA procedures to include the analysis of standard reference samples (control samples) and split replicate samples. Identified laboratory problems will be reported to the project principal investigators as soon as they are determined.

Pat Finnegan, Field Activities Specialist – The field specialist will assist the principal investigators in conducting field operations associated with the collection of stream and lake-bed sediment samples. He will ensure that sampling protocols are followed and will serve as the USGS/USCG certified boat operator during bathymetric surveys and sampling of Empire Lake and a selected reference lake.

A5. Project Background and Problem Definition

That part of the Spring River that drains the Tri-state mining district includes the Cherokee County site and parts of southwest Missouri and northeast Oklahoma (fig. 1). For about 100 years beginning in 1870, the Tri-State mining district was pit and strip mined as one of the primary sources of lead and zinc ore in the United States (Clark, 1970). Over time, the landscape in large areas of Cherokee County, particularly in and near the town of Galena, Kansas, became

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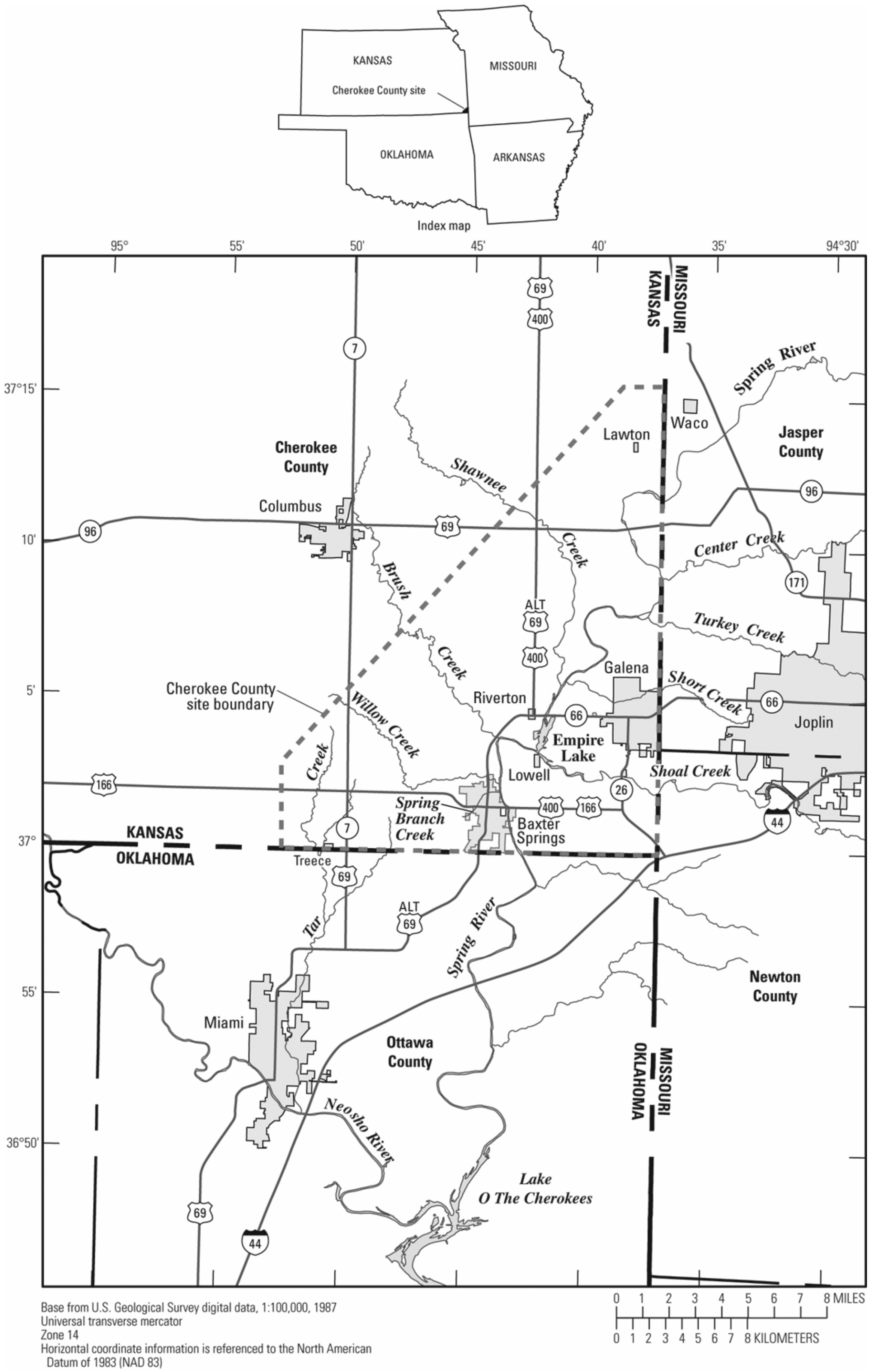

Figure 1. Map of Cherokee County project area.

dominated by mine waste. While the mining ended by 1970 and some remediation has occurred, potentially contaminated sediments in the Spring River and Tar Creek systems, including Empire Lake, remains. The environmental contamination caused by 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. In order to address sediment and water-quality issues due to metals contamination in the Spring River, the State of Kansas, in 2004, established total maximum daily loads (Kansas Department of Health and Environment, 2004).

The Spring River system is home to the Neosho madtom (*Noturus placidus*), a species of catfish listed as threatened under the Endangered Species Act of 1972, as amended. While still found in the Spring River downstream from Empire Lake and upstream in Missouri, the madtom has apparently been eliminated from the Spring River immediately upstream from Empire Lake (John Miesner, U.S. Fish and Wildlife Service, oral commun., 2003). The absence of the madtom may be attributable to habitat degradation resulting from the accumulation of potentially contaminated sediment resulting from the historical mining activities. Other species (e.g., mussels) also may be at risk (John Miesner, U.S. Fish and Wildlife Service, oral commun., 2003). Additionally, information on the transport of metals from Missouri to Kansas and from Kansas to Oklahoma will need to be addressed in the future after the completion of this proposed study. This information will be important for the prioritization, planning, and undertaking of restoration projects designed to improve the ecological health of Empire Lake and the Spring River and Tar Creek systems.

A6. Project Description and Schedule

The specific objectives of this proposed study are to:

(1) determine the metals concentrations in sediment in Empire Lake and the Spring River and Tar Creek systems;

(2) estimate naturally occurring metals concentrations in sediment in the Spring River system;

(3) determine the thickness, total volume, and total mass of potentially contaminated sediment in Empire Lake;

(4) assess the spatial variability of metals concentrations in sediment in Empire Lake and the Spring River and Tar Creek systems; and

(5) assess the temporal variability of metals concentrations in the deposited sediment in Empire Lake.

Geographically, this proposed study is limited to the Spring River and Tar Creek systems in southeast Cherokee County as bounded by the Kansas state line and the boundary of the Cherokee County Superfund site (fig. 1). In addition to Empire Lake, the water bodies of interest include the following: Spring River (from the Missouri state line downstream to Empire Lake), Spring River (from Empire Lake downstream to the Oklahoma state line), Turkey Creek (from its confluence with the Spring River upstream to the Missouri state line), Short Creek (from its confluence with the Spring River upstream to the Missouri state line), Shoal Creek (from Empire Lake upstream to the Missouri state line), Willow Creek (from its confluence with the Spring River upstream to the boundary of the Cherokee County Superfund site), Brush Creek (from its confluence with the Spring River upstream to the boundary of the Cherokee County Superfund site), Shawnee Creek (from its confluence with the Spring River upstream to the boundary of the Cherokee County Superfund site), Tar Creek (from the Oklahoma state line upstream to the boundary of the Cherokee County Superfund site), and Spring Branch (from its confluence with the Spring River upstream to its headwaters west of Baxter Springs).

This proposed study will provide a determination of the spatial distribution of, and metals concentrations in, sediment in Empire Lake and the Spring River and Tar Creek systems. These data will be used to evaluate the effects of the historical mining activity on habitat quality for threatened and endangered species. Furthermore, an analysis of changes in metals concentrations in sediment over time may provide an indication of the efficacy of remedial or future efforts. After these studies are complete, sites can be selected to evaluate the transport of metals from Missouri and to Oklahoma. In sum, this proposed study would provide fundamental information for remediation prioritization, planning, and implementation as well as a snap shot in time for future monitoring.

The project will be split into two phases. The first phase will evaluate the extent and magnitude of trace metal contamination of streambed sediments in the Spring River, tributaries to the Spring River, and Tar Creek. Data collection for this phase of the project will begin in mid-summer (July-August) 2004. Approximately 75 stream sites will be sampled in about one month. The second phase of the project will evaluate sediment (distribution, volume, mass) and trace metals (concentration, mass, depositional trends) in Empire Lake. Data collection for this phase will begin in Federal Fiscal Year 2005 and take about one month to complete.

Progress on this project will be monitored on a quarterly basis by the WQ/QC Specialist. Findings and recommendations resulting from these reviews will be communicated to the principal investigators and appropriate adjustments to the design or work plan will be made to ensure that project objectives are met and schedules completed in the established time frame. The Project Manager will be provided quarterly project updates and status reports.

Required QA samples and records are described in sections A7 and A9 of this QAPP. Reports will be prepared for each phase of this project. These reports will summarize project results, QC data, and document the extent of contaminated sediments in the Spring River and Tar Creek systems and Empire Lake. Section C2 of this QAPP provides additional details regarding these reports. These reports will receive technical peer review and be published and made available to the public.

Operating procedures for activities associated with this project can be found in the USGS National Field Manual for the Collection of Water-Quality Data (bottom sediment collection) (Wilde and Radtke, variously dated); Guidelines for collecting and processing samples of stream bed sediment (Shelton and Capel, 1994); Field methods for collecting fluvial sediment (Edwards and Glysson, 1999); Laboratory theory and methods for sediment analysis (Guy, 1964); Methods for determination of inorganic substances in water and fluvial sediment (Fishman, 1993); and other stream and lake bottom sampling projects conducted by the USGS such as Christensen and Juracek (2001), Juracek and Mau (2002), and Juracek (2003). Field safety protocols are described in the USGS National Field Manual (Wilde and Radtke, variously dated). General quality-assurance protocols are discussed in the quality-assurance plan for water-quality activities by the USGS in Kansas, accessible on the World Wide Web at URL http://wwwdkslwr.cr.usgs.gov/hydrologic/QAWQ.pdf

Environmental measurements of trace metal concentrations will be compared to sediment-quality guidelines as presented in USEPA (1997) and MacDonald (1994). These guidelines establish concentration threshold limits for selected trace elements above which detrimental effects on aquatic benthic organisms may occur.

A7. Data Quality Objectives for Measurement Data

Valid data of known and documented quality are needed to meet the objectives of the project as outlined in section A6 of this QAPP. Concentrations of selected trace elements in stream and lake-bed sediments will be compared to sediment quality guidelines and to concentrations in sediment from non-mined areas. This comparison will be used to determine the extent and magnitude of contamination and the potential extent of needed remediation efforts.

Data Quality Indicators:

Data quality indicators include precision, accuracy, representativeness, comparability, and completeness. Measures of these indicators will be used to validate the data collected for this project.

Precision. Precision is the measure of agreement among replicate measurements of the same property. In this project, it is the ability of laboratories to reproduce the same or nearly the same concentration of selected constituents in homogeneous split-replicate sediment samples. Acceptable variability among analyses of split replicate samples for this project will be a relative percent difference ([(A-B)/(A+B/2)]*100) between replicate pairs (A and B) of plus or minus 20 percent.

Accuracy. Accuracy is the measure of an individual measurement or the average of a number of measurements to the true value of that being measured. Accuracy includes the combination of random error (precision) and systematic error (bias) components that may result from the sampling and analytical operations. Accuracy of laboratory analyses will be determined by the analysis of standard reference samples of sediment with known concentrations of selected trace elements. Acceptable variability among analyses of standard reference samples will be within the published limits for each constituent for each standard or plus or minus 10 percent whichever is greater, except when constituent concentrations are at or near analytical detection limits.

Representativeness. Representativeness is the degree to which data accurately and precisely represent a characteristic of a population parameter at a sampling site. Sequential replicate samples of stream and lake bottom sediments will determine the ability of sample collection to adequately describe the average concentrations of selected trace elements at sampling locations. Acceptable variability among analyses of sequential replicate samples will be a relative percentage difference of plus or minus 20 percent.

Completeness. Completeness is the measure of the amount of valid data obtained from a measurement system as expressed as a percentage of the number of valid measurements that should have been collected. To generate data of the quantity necessary to meet the objectives stated for this project, 95 percent of the data in the designed assessment system should be collected and analyzed. However, operational or environmental characteristics in place at the time of sample collection and (or) analysis may modify the desired completeness ratio. Any deviation from a 95 percent completeness ratio will be evaluated in context of all other available data before the decision is made that missing data have irreparably affected the potential for the project to meet the stated objectives.

Comparability. Comparability is a measure of the confidence with which one data set or method can be compared to another. For this project, comparability will be addressed through the use of common and accepted practices in sample collection and analysis and by reporting data in standard units.

A8. Special Training and Certification

Specialized training necessary for the collection of samples required for this project will be conducted prior to actual data-collection activities. This training will include procedures for the identification and collection of silt/clay-size stream-bed sediment, coring of lake-bed sediments, and the proper processing, handling, and disposition of collected samples. Personnel will be instructed as to the proper shipping procedures for the transport of samples to the laboratory. Shipping procedures will be in compliance with the Department of Transportation regulations.

All study participants will be reminded of proper safety procedures for field and laboratory activities. These procedures are outlined in USGS National Field Manual for the Collection of Water-Quality Data (Wilde and Radtke, variously dated). These safety procedures will include proper boat operation. Only USGS/USCG certified personnel will be allowed to operate boats used in lake-bed sediment sampling.

A9. Documents and Records

The records for this project will include miscellaneous correspondence, field logs and field data work sheets, laboratory analytical reports, field activity documents, and reports prepared at the conclusion of both phases of this project. Sampling site folders will be maintained by the USGS for the duration of the project. These folders will contain all of the aforementioned documents and will be kept at the USGS office in Lawrence, Kansas.

Reports, field logs, and results of analytical analyses will be submitted to the Project Manager upon publication or completion. Field logs will include site locations and observations about weather and physical conditions at the site when samples are collected. Any other pertinent observations or deviations from the procedures in this QAPP also will be recorded on the field sheets. Field sheets will be signed and dated by the person making the entries. Examples of field sheets used for the recording of water- and sediment-quality data can be viewed at URL http://water.usgs.gov/usgs/owq/Forms.html

In accordance with USGS policy, all water data collected as part of routine data collection by the USGS are stored in the National Water Information System (NWIS) computer database. Data collected by others, such as cooperators, universities, or consultants, which are used to support published USGS documents and are not published or archived elsewhere, also will be entered into NWIS and identified according to analytical laboratory and collection organization; however, these data must be flagged with the appropriate data quality indicator code to restrict access by the public and identified according to analytical laboratory and collection organization. Electronically stored data that cannot be entered into NWIS are stored in project databases online or offline. The Kansas Water-Quality Database Manager has responsibility for maintaining backups of data stored electronically in NWIS or online. Data stored electronically offline are maintained by the Principal Investigator.

The Principal Investigator will establish, maintain, and document a chain-of-custody (COC) system for field samples that is commensurate with the intended use of the data. A sample is in custody if it is in actual physical possession or in a secured area that is restricted to authorized personnel. Every exchange of a sample between people or places that involves a transfer of custody will be recorded on appropriate forms that document the release and acceptance of the sample. Each person involved in the release or acceptance of a sample will keep a copy of the transfer paperwork. The Principal Investigator or designee, is responsible for ensuring that custody transfers of samples are performed and documented according to the requirements listed below.

- The means for identifying custody should be clearly understood (use of forms, stickers, etc.);
- Instructions for documenting the transfer of samples and the person responsible for this documentation must be clearly defined; and
- A plan must be in place for maintaining records in a specific location for a specific period of time (for example, in the site folder).

Detailed guidance on chain-of-custody procedures is provided by the USGS National Water-Quality Laboratory (NWQL) at URL http://rstalcoarv.cr.usgs.gov/USGS/ASRs/asr_instructions.html

Analytical data are results of field and laboratory chemical, physical, or biological determinations. Sediment-quality samples are analyzed at the NWQL or Georgia trace metal laboratory.

Field measurements are entered into the NWIS database by water-quality database manager as soon as possible after returning from the sampling field trip, with the goal being within 7 days after data collection. A record number is assigned by the system and is recorded on the field form and on a sample tracking log.

All data from the NWQL are electronically transferred to the appropriate District database by the Water-Quality Database Manager twice per week. The Database Manager, Principal Investigator, or designee is notified in email of the data availability. It is the responsibility of the Principal Investigator to ensure that the files are retrieved and reviewed in a timely manner.

Data analyzed by laboratories other than the NWQL must be entered into NWIS and identified according to the analyzing laboratory. Data from the Georgia trace metal laboratory are transmitted electronically to the Principal Investigators and entered into the NWIS by the database manager.

Environmental sample data are entered into the District NWIS QWDATA database 01 (DB1); QC data are entered into the District NWIS QWDATA database 20 (DB20). Data entry is the responsibility of the Project Database Manager. The NWIS QWDATA database receives daily incremental backup and weekly full backup.

The Project Manager will disseminate copies of this QAPP to the people listed in the distribution list (section A3) once it is approved. Any revisions to the QAPP will be numbered sequentially. It will be the responsibility of the Project Manager to see to it that each person on the distribution list receives copies of any revisions.

MEASUREMENT/DATA ACQUISITION

B1. Sampling Design

The purpose of this project is to document the extent and magnitude of trace metal concentrations in bottom sediments of streams in the Spring River and Tar Creek watersheds and in Empire Lake. This project will proceed in phases as described in the following sections.

Phase I

Phase I will include the following: (1) a determination of the spatial variability of metals concentrations in the sediment of the Spring River (upstream and downstream of Empire Lake), seven tributaries to the Spring River, and Tar Creek; and (2) a determination of background metals concentrations in sediment in the Spring River system. A total of 10 river/stream channels will be sampled for this phase of the project.

The extent and magnitude of concentrations of selected metals and trace elements (table 1) in bed sediments of the stream channels listed in the “Objectives and Scope” section of this proposal will be determined through sampling of these sediments at a minimum of one sampling location in Turkey Creek to a maximum of 10-11 locations in Willow Creek (total of about 75 locations). This study will focus on the collection and analysis of silt/clay size (<0.063 millimeters in diameter) sediment particles. These fine-grained particles are natural accumulators of metals and trace elements, the majority of which are highly sorptive and associated with particulate matter in almost all natural surface-water regimes. A large fraction of the total mass of these chemical constituents transported in streamflow is usually associated with fine-grained material, and bed sediments in depositional environments of streams provide a time-integrated sample of particulate matter transported by a stream. Bed sediment concentrations provide a useful measure of the potential bioaccumulation or toxicological effects of metals and trace elements on bottom-dwelling aquatic organisms.

The concentration of metals and trace elements on stream-bed materials is strongly affected by the particle-size distribution of the sample (Rickert and others, 1977; Wilber and Hunter, 1979; Horowitz and Elrick, 1987). Generally, the concentration of metals and trace elements on streambed materials increases as particle size decreases. Therefore, to increase the probability of detecting these constituents and to enhance the comparability of data among sites and streams, bed-sediment samples will be sieved and the silt/clay fraction analyzed.

Naturally occurring concentrations of metals in stream sediment will be estimated by sampling the Spring River and (or) a tributary at a location upstream from the mining-disturbed lands. For example, possible locations would include the Spring River upstream from its confluence with Center Creek or the upstream reaches of streams such as Willow and Brush Creeks that have had little or no mining activities.

Based on the results of the chemical analyses of sediments collected in the stream surveys, the extent of contaminated sediments will be determined and mapped. Concentrations of metals and trace elements in contaminated sediments will be compared to guidelines established by USEPA (1997) and MacDonald (1994) for protection of aquatic biological organisms.

A report will be prepared detailing the activities and results of Phase I. A draft of this report will be submitted for Project Manager and peer review by April 1, 2005. Anticipated publication will be about September 30, 2005, if all data collection activities associated with Phase I are completed by the end of summer 2004. This report will be colleague reviewed by technical reviewers and the U.S Fish and Wildlife Service.

Phase II

Phase II is anticipated to begin by April 2005 and will include the following: (1) a determination of the thickness, total volume, and total mass of potentially contaminated sediment in Empire Lake; (2) a determination of metals concentrations in sediment in Empire Lake; (3) an assessment of the spatial and temporal variability in metals concentrations in sediment in Empire Lake; and (4) a determination of naturally occurring metals concentrations and temporal variability in sediment for a small reservoir in the Spring River Basin not affected by historical mining activities.

The estimation of sediment thickness in Empire Lake will involve the use of transects. The transects will be established near the dams and progress at regular intervals upstream in the Spring River and Shoal Creek arms of the reservoir until the point at which sediment deposition indicates the transition from a lacustrine to a riverine condition. Along each transect sediment thickness will be determined by boat or wading using a spud (i.e., a sediment probe that is pushed through the deposited sediment until refusal). Sediment thickness determinations along each transect will be made at a spacing sufficient to provide representative information. The latitude and longitude coordinates for each measurement point along each transect will be determined by GPS to a potential accuracy of plus or minus 2 centimeters.

The total volume of sediment in Empire Lake will be estimated using a partitioning approach in which the reservoir is segmented based on the locations of the transects. For each partition (defined as the area between two successive transects), the volume of sediment will be computed as the total surface area of the partition multiplied by the mean sediment thickness within the partition. Total sediment volume for Empire Lake will be computed as the sum of the volumes estimated for the individual partitions. The total mass of sediment in Empire Lake will be estimated using the same partitions as previously described. For each partition, the mass of sediment will be computed as the sediment volume multiplied by the representative bulk density. Sediment cores will be collected for bulk-density determinations. Total sediment mass for Empire Lake will be computed as the sum of the masses estimated for the individual partitions.

The total mass of cadmium, lead, zinc and other selected metals and trace elements in Empire Lake will be estimated as the total sediment mass multiplied by the mean concentration of the metals and trace elements.

The list of constituents to be included in Phase I and II is provided in table 1. All determinations indicated in table 1 are considered critical determinations.

As part of the assessment of temporal change in metals concentrations, the Empire Lake cores analyzed for chemical constituents will be used for trend analyses. Trends in constituent concentration will be examined by computing a nonparametric Spearman’s rho correlation coefficient (Helsel and Hirsch, 1992).

Table 1. Chemical analyses to be performed on bottom-sediment samples from Empire Lake and the Spring River system.

Nutrients			
Total nitrogen	Total phosphorus		
Carbon			
Carbon, total organic	Carbon, total		
Metals and trace elements			
Aluminum	Cobalt	Molybdenum	Tin
Antimony	Copper	Nickel	Titanium
Arsenic	Iron	Selenium	Uranium
Barium	Lead	Silver	Vanadium
Beryllium	Lithium	Strontium	Zinc
Cadmium	Manganese	Sulfur	
Chromium	Mercury	Thallium	
Radionuclides			
Cesium-137	Lead-210		

Results of chemical analyses will be compared to sediment-quality guidelines established by the USEPA (1997) and MacDonald (1994). The guidelines provide level-of-concern concentrations that 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 are referred to as the threshold-effects level (TEL) and the probable-effects level (PEL). The TEL is assumed to represent 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 (U.S. Environmental Protection Agency, 1997). Sediment-quality guidelines are available for arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc. A USGS report will be prepared to describe the results of phase II of this project.

Subsequent phases of the study may include (1) a description of the transport of lead, cadmium, and zinc from Missouri to Kansas and Kansas to Oklahoma; (2) determination of volume of sediment in segments of study streams contaminated by metals and trace elements; and (3) a study of ground-water and surface-water quality and interaction, which may be warranted depending on the results of this study.

Sampling for phase I of the project will begin in the summer of 2004. Phase II sampling will be conducted in Federal Fiscal Year 2005.

B2. Sampling Methods

The project Principal Investigators are responsible for ensuring that the following preparations have been completed prior to field activities associated with sample collection:

- Prepare a field folder for the project
- Ensure that the NWIS site file is current.
- Use a checklist in preparing for a trip to ensure field preparedness. Back-up instrumentation and sensors should be included on the checklist.
- Review the sampling instructions for each site and the list of sample types required.
- Prepare bottle labels for samples.
- Obtain field sheets, analytical services request forms (ASRs) if required, or other paperwork as required by specific laboratories.
- Ensure that necessary supplies are available, such as bottles, standards, filters, preservatives, meter batteries, waterproof markers, shipping containers, etc.
- Ensure that all sampling equipment is thoroughly cleaned and prepared.
- Check meters and sensors for proper performance.

The USGS National Field Manual (chapter A1) provides additional detail on preparations for sediment sampling (Wilde and Radtke, chapters variously dated).

Streambed Sediments

Procedures used for the collection of fine-grained material in this project will vary dependent upon local sampling site conditions. At sites where substantial deposition of fine material occurs, core samples (up to 1-foot in depth) of these deposits will be collected, composited, homogenized, and wet sieved to separate the silt/clay fraction (<0.063 mm diameter) from the sands and gravels. At sites where the depth of fine material is small, surficial deposits of fine material will be collected using protocols for bed-material sampling established by the USGS for its National Water Quality Assessment (NAWQA) program (Shelton and Capel, 1994). The volume of collected sediment will be estimated and possibly used in mass computations through the use of bulk densities and percent particle-size analysis.

Composite samples will be wet sieved to separate the silt/clay fraction of the bed material sample. Chemical analyses will be conducted on this fraction. A subsample (sieved through a 2.0 millimeter diameter screen) of the composite sample also will be collected and analyzed for percentages of sand and silt-clay fractions. An estimate of the in-situ volume of sampled sediments will be made for each sample collected.

Lake-Bed Sediments

Determination of metals concentrations in bottom sediment of Empire Lake will involve the collection of sediment cores to provide spatially and temporally representative information. Previous studies by the USGS have demonstrated the efficacy of using sediment cores for determining metals concentrations in sediment as well as spatial variability and temporal trends (e.g., Callender and Robbins, 1993; Christensen and Juracek, 2001; Juracek and Mau, 2002; Juracek, 2003). For Empire Lake, sediment cores will be collected within each reservoir partition (as previously described). At two sites in the main body of the reservoir, a set of three cores will be collected. One core will be subdivided into 15 intervals for chemical, particle-size, and age-dating (using cesium-137 and lead-210) analyses. The second core will be used for bulk-density and percent-moisture determinations. The third core will be archived for possible future use. The archived cores will be refrigerated (at 4^{o} C) and retained until after the study report is finalized. Throughout the rest of the reservoir, sediment cores will be collected from each partition and used for chemical, particle-size, bulk-density, and percent-moisture determinations.

The natural occurrence and temporal trends of metals in lake bottom sediments will be assessed by coring a small reservoir in an area of the Spring River Basin that was not affected by historical mining activity. The sediment core collected from this small reservoir will be subdivided into 15 intervals for chemical, particle-size, and age-dating (using cesium-137 and lead-210) analyses.

Bottom-sediment cores will be collected with a gravity corer and (or) a vibracorer using round transparent plastic liners of cellulose acetate butyrate construction with a 2.625-inch inside diameter. It is expected that all bottom sediment cores will penetrate into pre-reservoir material. This will be determined by a change in physical appearance of the sediment, change in particle-size composition, and the presence of pre-reservoir soil-surface organic matter such as small sticks, plant material, or root hairs. The presence of pre-reservoir material will ensure that a complete sedimentation record will be represented by each core.

Processing of core samples will be conducted at the USGS laboratory in Lawrence, Kansas. The plastic liner will be cut longitudinally in two places 180 degrees apart and the sediment core split in half by pulling a tightly-held nylon string through the length of the core and allowing the halves to separate. Each core will be segmented into an appropriate number of intervals for chemical and physical analyses. Core segments will be analyzed for the constituents listed in table 1. These procedures are similar to those used in other studies of reservoir bottom sediments in Kansas (Juracek, 1997; Pope, 1998; Christensen and Juracek, 2001; Mau, 2001; Juracek and Mau, 2002; and Juracek, 2003).

B3. Sample Handling and Custody

During a sampling trip, it is imperative that accurate notes be taken and that sample bottles be labeled and handled appropriately for the intended analysis. Otherwise, bottle mix-ups or other errors may occur, and the samples may be wasted. Field personnel are responsible for ensuring that the following sampling requirements are implemented:

. • Label each bottle with the site identification, date and time of sample collection, bottle type, and laboratory codes, using a permanent, waterproof marker or preprinted labels that will remain securely adhered to the bottle, even when wet.

. • Field sheets are completed before leaving each site, including documenting all sampling circumstances and any deviation from standard protocol.

Specific guidance on sample packaging, shipment, and documentation is provided in USGS NWQL Technical Memorandum 02.04 (*http://nwql.usgs.gov/Public/tech_memos/nwql.02.04.html*) and in chapter 5 of the USGS National Field Manual (Wilde and Radtke, chapters variously dated)

Some of the more important points of the aforementioned memorandum include the following steps, which should be followed prior to shipping any samples to a laboratory:

- Check that sample sets are complete and that sample bottles are labeled correctly, with all required information.
- Complete the ASRs for all samples being sent to the NWQL. If samples are being sent to a different, approved laboratory, information similar to that required on the ASRs should be provided to the laboratory. See USGS OWQ Technical Memorandum 00.09 for ASR policies and guidelines (*http://water.usgs.gov/admin/memo/QW/qw00.09.html*).
- Line all shipping containers, including those without ice, with double heavy-duty clear plastic bags.
- Pack samples carefully in shipping containers to avoid bottle breakage, shipping container leakage, and sample degradation. Check that bottle caps are securely sealed.
- Upon completion of a sampling trip, samples will be packaged and shipped to the laboratory for analysis as soon as possible.

The Principal Investigators or designee will maintain a record of all samples collected and shipped to a laboratory for analysis to ensure the complete and timely receipt of analytical results. Field personnel are responsible for recording the required information, reviewing the tracking log to determine if analyses are missing and for taking corrective action(s) if necessary. The following is a summary of USGS tracking procedures:

- The Principal Investigators or designee are responsible for ensuring that samples are logged into NWIS in a timely and efficient manner to facilitate the timely and error-free entry of analytical data received from the NWQL into the water-quality database. Samples submitted to the NWQL or Georgia trace metals laboratory must be logged into QWDATA before data are released from the laboratories. The goal should be to login samples within 7 days of shipping the samples to the laboratories.
- The Principal Investigators or designee are responsible for ensuring that sample status is tracked so that sample holding times are not exceeded. Sample tracking should also facilitate timely data review such that reruns of any questionable analytical data can be requested and completed prior to sample holding times elapsing. The NWQL provides an online sample status reporting service that can be accessed on the Web (*http://nwql.cr.usgs.gov/usgs/sampstatus/index.cfm*).
- The Principal Investigators are responsible for ensuring that all analytical data are reviewed as soon as possible after release from the laboratory to allow for any reruns prior to sample holding times elapsing. Data that are rejected from NWIS will be corrected immediately and reloaded into NWIS.

The Water-Quality Database Manager will regularly perform the following:

- Ensure that the biweekly automatic retrieval of the analytical data from the NWQL has run successfully, retrieve analytical data, and enter results into NWIS. Separate data into WATLIST files for the primary and quality-control database as well as corresponding BADQW files for data that could not be entered into NWIS.
- Notifiy Principal Investigators or designee of data availability.
- Assist personnel with problems related to sample tracking, data delivery, and NWIS.
- Enter data into the NWIS project database that originate from laboratories other than the NWQL.

Because this is a site investigation that will help to determine the need for and extent of restoration, chain-of-custody procedures will be followed. The Principal Investigators will establish, maintain, and document a COC system for field samples that is commensurate with the intended use of the data. A sample is in custody if it is in actual physical possession or in a secured area that is restricted to authorized personnel. Every exchange of a sample between people or places that involves a transfer of custody will be recorded on appropriate forms that document the release and acceptance of the sample. Each person involved in the release or acceptance of a sample will keep a copy of the transfer paperwork. The Principal Investigators or designee are responsible for ensuring that custody transfers of samples are performed and documented according to the requirements listed below. The means for identifying custody will be clearly understood (use of forms, stickers, etc.). The COC description and example COC form to be used for this project may be accessed at URL http://wwwnwql.cr.usgs.gov/USGS/COC/coc.html

B4. Analytical Methods

Samples of streambed sediments and lake-bed sediments will be analyzed for the constituents listed in table 1. Analyses used in these determinations have been approved by the USGS and (or) the USEPA and will be conducted at the USGS National Water-Quality Laboratory in Denver, Colorado, and the USGS Sediment Trace Element Partitioning Laboratory in Atlanta, Georgia. Analyses of sediment samples for total nitrogen and carbon concentrations will be preformed using methods described by Horowitz and others (2001). Analyses for total phosphorus, metals, and trace elements will be performed using the methods described by Fishman (1993), Arbogast (1996), and Briggs and Meier (1999). Age dating of bottom sediments will be accomplished by the analysis of Cesium-137 and Lead-210 using gamma-ray spectrometry (American Society for Testing and Materials, 2000).

B5. Quality Control

Quality control of sampling site variability (representativeness of collected samples) and analytical determinations of trace elements in streambed and lake-bed sediments will be maintained through the use of replicate samples and standard reference samples. The “within site” variability in trace element concentrations will be evaluated through the collection of sequential replicate samples of deposited sediment. Relative percent differences will be calculated for each replicate pair and evaluated against acceptance criteria (see section A7 of this QAPP). Split replicate samples will be used to evaluate the precision of analytical procedures. Standard reference samples will be used to evaluate the accuracy and bias of analytical procedures. The number of quality control samples submitted for analysis will equal about 20 percent of the number of environmental samples. Quality control plans and laboratory procedures at the USGS NWQL may be viewed at URL http://nwql.usgs.gov/Public/pubs/QC_Fact/text.html

Instrumentation used in the lake sampling phase (Phase II) of this project will be quality controlled daily. The reliability of the GPS and fathometer instrumentation used in bathymetric surveys will be verified at the beginning and end of each day's use. No data will be collected from these instruments unless accuracy has been previously verified. Accuracy will be determined against a location of known coordinates.

B6. Instrument/Equipment Testing, Inspection, and Maintenance

The only field equipment requiring testing, inspection, and maintenance are those used for bathymetric surveys. These instruments will be checked daily and maintained as per manufacture's instructions.

Laboratory instruments will be verified and maintained as per laboratory QA procedures (see URL, section B5 of this QAPP). All instruments will be maintained as per manufacture's instructions.

B7. Instrument Calibration and Frequency

Field instruments for global positioning (GPS) and bathymetric measurement (fathometer) will be calibrated and (or) checked for reliable performance at least twice daily. These checks will be done before and after each day's work. Adjustments, recalculations, or recollection of data will be performed as appropriate based on the results of instrument calibration checks. Laboratory instruments will be calibrated as per manufacture's instructions and at frequencies specified in laboratory QA plans (see URL, section B5 of this QAPP).

B8. Inspection/Acceptance for Supplies and Consumables

The Principal Investigator or Field Specialist will be responsible for inspecting sample containers before leaving for the field. Only containers compatible with trace element sample collection will be used during this project. Compatible materials would not be made from metal or metal products. Compatible materials include glass, plastic, nylon, and Teflon. Sample containers will be inspected for cracks, ill-fitting lids, and other obvious defects before use and will be discarded if defects are found to be present.

Analysts at the USGS NWQL and Sediment Trace Element Laboratories will be responsible for inspecting equipment and supplies upon receipt. The manufacture’s specifications for product performance and purity will be used as the acceptance criteria.

B9. Data Acquisition Requirements for Indirect Measurements

A sampling site reconnaissance will be conducted in July or August 2004 for selection of streambed sampling sites in the Spring River and Tar Creek watersheds. This reconnaissance will examine potential sampling sites for deposits of fine sediment (<0.063 mm) for trace element analysis. Other characteristics to be examined include (1) uniformity in cross-sectional and vertical distribution of deposited sediment; (2) access to site; (3) location of site relative to other geographical features such as point-source discharges and stream confluences, and (4) potential effects of nearby cultural features such as smelters and mines. Field notes will be made at each site to document site characteristics. Photographs will be taken of each site visited and kept with the site folder. From the visited stream sites, about 75 will be chosen for subsequent sampling of deposited sediments.

A reconnaissance of Empire Lake will be conducted in the summer of 2004. This initial reconnaissance will include a preliminary bathymetric survey and sediment core collection to document thickness of deposited material. This information will assist in the selection of survey range lines for sediment-thickness mapping and identify potential sampling conditions and requirements for subsequent detailed sampling of bottom sediments. Collection of sediment cores for this reconnaissance will be conducted using the same equipment and protocols as the detailed examination to be conducted in 2005. Samples collected from this lake reconnaissance will be analyzed for constituents listed in table 1. Results from these analyses will be used in planning the detailed bottom sediment collection effort.

B10. Data Management

Data for this project will be generated in four locations: onsite, at the USGS NWQL (Denver, Colorado), at the USGS Sediment Trace Element Laboratory (Atlanta, Georgia), and at the USGS Iowa Sediment Analysis Laboratory (Iowa City, Iowa). Field data sheets, laboratory analytical request forms, and all site evaluation and inventory information will be kept by site file at the USGS office in Lawrence, Kansas. Laboratory data will be submitted by the three USGS laboratories to the USGS project office in Lawrence, Kansas. These data will be either electronically transferred into the NWIS database or manually entered from paper copies of analytical results (Atlanta and Iowa City Laboratories). The Principal Investigators will be responsible for ensuring that all data meet the requirements set forth in section A9 of this QAPP. Data will be retrieved from NWIS for input into a spreadsheet computer program for statistical evaluation and graphical presentations. No other special data handling equipment or software will be needed for data management. This information will be available to the Project Manager upon request. Copies of all field records and analytical reports also will be made available to the Project Manager upon request.

ASSESSMENT/OVERSIGHT

C1. Assessment and Response Actions

Status and activities of this project will be assessed on a quarterly basis by the WQ/QC Specialist and other senior staff members of the USGS Kansas District Office. These quarterly reviews will include the overall project plan, timeframes associated with these plans, planned and ongoing field activities, status of data review and evaluation, plans and progress on interpretative project reports, and status of project finances. Summaries of these quarterly reviews will be provided to the Project Manager. The WQ/QC Specialist also will review plans for and actual data collection activities to ensure adherence to data collection protocols previously described in this QAPP. The WQ/QC Specialist will have the authority to stop on-site work if the findings of the review justify such actions. Activities of this project also will be reviewed by the Project Manager.

C2. Reports

In addition to the quarterly review reports prepared by the Principal Investigators and submitted to the WQ/QC Specialist, two formal USGS series reports will be prepared and published for this project. The first of these formal reports will detail and evaluate Phase I activities (streambed sampling) of this project. This Phase I report will discuss the extent and magnitude of trace element concentrations in stream sediments. This will provide information on the extent of contaminated sediments in stream channels and the magnitude of efforts needed for restoration. This draft report will be peer reviewed, revised, published, submitted to the Project Manager by September 2005, and made available to the public by October 2005, if data collection efforts are completed by summer 2004.

The second report will detail and evaluate Phase II activities (lake-bed sampling) of this project. The Phase II report will discuss and evaluate the magnitude of trace-element concentrations in bed sediments of Empire Lake and compare these concentrations to sediment quality guidelines and to concentrations in sediments from a lake located in a non-mined part of the Spring River watershed. The phase II report also will include calculations of total trace-element mass within Empire Lake and a discussion of the depositional trends (historical transport) of the trace elements. A draft report will be published and submitted to the Project Manager in Federal Fiscal Year 2006. The finalized report will be published and made available to the public.

Problems with samples submitted to the various laboratories will be brought to the attention of the Principal Investigators immediately upon discovery. Laboratory Directors will generate quality-control reports in the event of problems with analytical data. These reports will detail the nature of the problem and proposed solutions and will be submitted to the Project Manager along with proposed corrective actions. Corrective actions will be agreed upon between the Principal Investigators, the Project Manager, and the Laboratory Director.

Final

DATA VALIDATION AND USABILITY

D1. Data Validation and Usability

Data will be accepted if they meet the following criteria:

1. Field data sheets are complete.
2. Field data and laboratory data were validated.
3. Actual sample locations and collection procedures match proposed sample locations and collection procedures identified in sections B1 and B2, respectively.
4. Sample handling procedures documented on COC forms, field sheets, and site specific narratives match the proposed sample handling procedures identified in sections B2 and B3 (for example: preservation, shipping, and holding times).
5. Field QC was conducted as planned and meets the acceptance criteria in section B5.

Any deviations from the QAPP are to be reported on field sheets, analytical services request forms, and included as a narrative report in the site file maintained by the Principal Investigators.

If data fails to meet the above criteria, they will be flagged by the Principal Investigators as estimated. Any flagged data will be discussed with the project team and Project Manager and identified as estimated in subsequent project reports.

D2. Data Validation and Verification

The Principal Investigators will validate the field data according to standard procedures typically employed by the USGS in examining such data. Any problems identified during this process will be reported to the project team immediately and subsequently to the Project Manager in the form of data or site evaluation reports. Problems identified by laboratory directors in the QC of analytical data, likewise, will be reported to the Principal Investigators and subsequently to the Project Manager. The Project Manager will have the option of reviewing any and all data generated by this project to include field sheets, site files, and analytical data. Any problems or deviations identified by the Project Manager will be discussed with the project team.

D3. Reconciliation with Data-Quality Objectives

All data generated by this project will be examined in relation to data-quality objectives previously identified in this QAPP. Statistical summaries will be produced and the data examined for “outliers”. Unusually large or small values will be identified and evaluated as to their representativeness or analytical precision and accuracy. Request for analytical reruns may be made if samples have not exceeded holding times. Data will not be deleted because of an outlier status unless analytical or contamination problems are identified.

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