SAMPLING ANALYSIS PLAN AND QUALITY ASSURANCE PROJECT PLAN FOR A PILOT STUDY TO ASSESS VOLUME OF MINE WASTE AND CONCENTRATION OF SELECTED METALS IN STREAM AND FLOODPLAIN SEDIMENTS WITHIN THE TRI-STATE MINING DISTRICT IN KANSAS, MISSOURI, AND OKLAHOMA

PREPARED FOR

U.S. Fish and Wildlife Service

Draft February 5, 2010

Revised Draft September 24, 2010

Final May 11, 2011

PREPARED BY:

U.S. GEOLOGICAL SURVEY

Missouri and Oklahoma Water Science Centers

APPROVED:

✓ **Mike Slifer** ______________ Date: 5/11/11
Director, Missouri Water Science Center, U.S. Geological Survey, Missouri

John Schumacher ______________ Date: 5-16-11
Supervisory Hydrologist, Missouri Water Science Center, U.S. Geological Survey, Missouri

✓ **Doug Mugel** ______________ Date: 5/10/11
Project Chief, Missouri Water Science Center, U.S. Geological Survey, Missouri

Mark Becker ______________ Date: 5/24/11
Project Chief, Oklahoma Water Science Center, U.S. Geological Survey, Oklahoma

✓ **Jim Dwyer** ______________ Date: 6/1/11
U.S. Fish and Wildlife Service

USGS
science for a changing world

Contents

List of Figures (at the back of the report)

Tables

Sampling Analysis Plan and Quality Assurance Project Plan for a Pilot Study to Assess the Volume of Mine Wastes and Concentration of Selected Metals in Stream and Floodplain Sediments within the Tri-State Mining District in Kansas, Missouri, and Oklahoma

1.0 Introduction

Lead and zinc mining began in the mid-1800s in the Tri-State Mining District (TSMD) leaving a legacy of mine waste distributed throughout the region. Waste products from the mining, milling and extraction of ore include chat and tailings which contain elevated concentrations of lead (Pb), zinc (Zn), and cadmium (Cd). Generally, chat is small gravel size material (0.6 – 1.6 cm) while tailings are sand sized (2 mm or less). Because of the size of tailings, they are easily mobilized into streams and waterways and transported great distances from their source. Over time, chat and tailings have been deposited into streams resulting in increased concentrations of Pb, Zn, and Cd in sediments. Because of the easily mobilized nature of tailings, during flood events, tailings may also be deposited in overbank and floodplain deposits and could be transported downstream when these sediments are re-suspended in the active stream channel. The environmental contamination caused by decades of mining activity resulted in several counties in the region being listed on the U.S. Environmental Protection Agency's (USEPA) National Priority List as Superfund hazardous waste sites.

Currently the USEPA is actively remediating mine sites (e.g. tailings and coarser "chat" piles, mine shafts and mine seeps) in the TSMD. Recent studies by the U.S. Geological Survey (USGS), in cooperation with the U.S. Fish and Wildlife Service (USFWS), Kansas Department of Health and Environment (KDHE) and USEPA (Regions 6 and 7) documented Pb, Zn, and Cd concentrations in sediment that far exceeded background levels as well as probable effects guidelines for adverse biological effects for aquatic biota (Pope, 2005; Juracek, 2006; Ingersoll and others, 2009; McDonald and others, 2000). These studies sampled deposited sediment in the Spring River and Neosho River and their tributaries, Empire Lake in Cherokee County, Kansas, and Grand Lake O' the Cherokees (Grand Lake) in Oklahoma. The adverse effect of the mining-related contamination on freshwater mussels was documented by Angelo and others (2007).

1.1 Problem

As remediation of mine waste areas continues, increased attention is focused on the extent and magnitude of metals contamination in area streams and floodplains. In particular, obtaining reliable information on the distribution and volume of mine waste and their associated metals contained within stream and floodplain sediments in the TSMD. Standard practice for determining the extent of metal contamination in streambed sediments is the collection of samples from the upper few centimeters of the streambed, either in a biased manner by targeting depositional areas of finer sediments behind rocks, etc., or collecting a composite of subsamples along one or more transects across the stream. While these methods are effective at characterizing the spatial or downstream extent of contamination, they do not provide information on the depth of contamination or variability in contamination within stream features, such as bars, riffles, pools, etc. While some mine waste deposits currently are exposed in sand or gravel bars within and adjacent to the stream, an unknown volume has been transported and redeposited, covered by native sediments or vegetation, or deposited in deep pools. The thickness of these deposits is unknown, but likely variable across and along the stream and the stream floodplain. Presently, the aerial extent of contamination is generally known, however, there is insufficient information to allow for estimates of the actual volume of contaminated sediments and mass of mining-related metals in the streams or on the adjacent floodplains.

1.2 Description of Project Objectives and Scope

The primary objective of this investigation is to characterize the lateral and vertical extent of mining-related metals contamination in streambed and adjacent floodplain sediments along selected representative reaches of streams in the TSMD. This pilot study is designed to supplement existing surficial streambed sediment data, and an ongoing USEPA floodplain study in Cherokee County, Kansas, by providing previously unknown information on the depth of mine waste contamination within the stream channel (bank to bank) and adjacent floodplain. Additionally,   the volume of contaminated sediment within the selected stream reaches will be estimated. Sediment samples will be collected from within the active stream channel (hereinafter referred to as in-channel) and from the adjacent floodplain using a variety of techniques and drilling platforms. An important result of this effort will be a determination of which methods are most appropriate to obtain sediment samples.

A traditional method to characterize subsurface contamination is to obtain depth dependent sediment samples. Sediment cores provide an intact representative sample of the sediment/soil profile at the location of the core and an appropriate density of cores is needed to adequately characterize the subsurface. However, a traditional sediment-core characterization of affected streams in the district is impracticable. This impracticality is due to the heterogeneous nature of the sediments and the broad scale of the impacted area which would necessitate a large number of cores and have a significant corresponding expense. A pilot-scale assessment of representative reaches of streams in the Ozark Plateaus and Osage Plains physiographic provinces in the TSMD is proposed. Results from this pilot assessment will provide information on the vertical and lateral extent of mine waste and metal concentrations and allow for comparison of several methods to estimate volumes of contaminated sediments along the study reaches. This information, combined with geospatial information, could then be used to extrapolate outside the study reaches within the TSMD or design a cost-efficient method for a district-wide assessment of the volume of mine tailings and mass of metal contamination in streams across the TSMD. Data density within these representative reaches will be higher than anticipated during a district-wide implementation.

Preliminary discussion with the USFWS and USEPA, have defined streams of interest for this study. Sediment samples will be collected from representative reaches on Center Creek, Turkey Creek, and Shoal Creek in Missouri, Tar Creek in Oklahoma, and along two reaches of the Spring River in Kansas. Up to 25 samples will be collected from each selected reach and the adjacent flood plain. Core samples will be logged by a field geologist and screened with X-ray fluorescence (XRF) for bulk concentrations of Pb, Zn, and Cd. A subset of the field XRF scans will be verified with laboratory split samples. A geomorphic analysis of the study reach will be done to provide: an estimate of the volume of unconsolidated sediments within the stream channel; the fraction of those sediments contaminated with mine waste utilizing a Geographic Information System (GIS); field estimates of sediment thickness using tile probe measurements; and a field Differential Global Position System (DGPS) survey of primary channel features (primarily bars).

Data will be collected at several scales, such as digitizing features using the 2009 imagery and the GIS versus field DGPS mapping of primary channel features, and the comparison of higher density sediment or composite sediment samples to lower density sampling methods. This should provide information for optimization of methods that might be used for scaling up to a larger district-wide assessment. Results of the investigation, including the evaluation of sediment collection methods, geomorphic analyses, and analytical data will be published in a USGS interpretive report.

1.3 Project organization

The following is a summary of project team members, organizational structure, and responsibilities. The project is a coordinated effort between the USGS Missouri and Oklahoma Water Science Centers (WSC). The USGS will organize two field teams to meet the two general project tasks of in-channel and floodplain core sampling (Table 1). The in-channel sampling team will be headed by the Oklahoma WSC and the floodplain coring team will be headed by the Missouri WSC. Except for Tar Creek, the Missouri WSC is primarily responsible for the reconnaissance, selection of the study reaches, obtaining landowner consent and utility clearances, conducting floodplain sampling, and maintaining the project GIS database. The Missouri WSC will also be responsible for coordination with the ongoing USEPA Spring River Floodplain study in Cherokee County, Kansas and ensuring data compatibility between the two studies. Data review and compilation, database management, and GIS support is primarily the responsibility of the Missouri WSC. The Oklahoma Center is primarily responsible for initial preparation of the Sampling Analysis Plan (SAP), in-channel coring activities, and will lead all activities at the Tar Creek study area. The Oklahoma WSC will also be responsible for coordination of XRF analytical support from the USFWS, as needed. The final report will be jointly co-authored by both the Missouri and Oklahoma WSC. Key individuals participating in the project and their specific roles and responsibilities are discussed below:

Table 1. Summary of key project team members.

Function	Team member	Project Role	Title	Office
Project Management Team	Jim Dwyer	Overall project coordinator	Environmental Protection Specialist	USFWS
	Dave Mosby (or designee)	USFWS Analytical Support	Fish and Wildlife Specialist	USFWS
	Mike Slifer	USGS Approval official	Director	Missouri WSC
	John Schumacher	USGS/USFWS project liaison	Supervisory Hydrologist	Missouri WSC

	Doug Mugel	Project principle investigator	Hydrologist	Missouri WSC
In-channel field team	Mark Becker	Team leader	Hydrologist	Oklahoma WSC
	--	Team member	Technician	Oklahoma WSC
	Jacob Morris	Team member	Technician	Missouri WSC
	Mike Kleeschulte	Team member	Hydrologist	Missouri WSC
	Doug Mugel	Team member	Hydrologist	Missouri WSC
Floodplain sampling team	Doug Mugel	Team leader	Hydrologist	Missouri WSC
	Paul Brenden	Team member	Technician	Missouri WSC
	Jacob Morris	Team member	Technician	Missouri WSC
	Mike Kleeschulte	Team member	Hydrologist	Missouri WSC
	Mark Becker	Team member	Hydrologist	Oklahoma WSC
Project GIS	Joe Richards	GIS specialist	Hydrologist	Missouri WSC
Project Reporting	Mark Becker	Project lead author	Hydrologist	Oklahoma WSC
	Doug Mugel	Project coauthor	Hydrologist	Missouri WSC
	John Schumacher	Project coauthor	Hydrologist	Missouri WSC

Jim Dwyer, USFWS, Project Manager – the primary decision maker for the project and the primary user of the data to determine if the project results meet the study objectives and if further investigation in the study area is required and to what extent. His primary duties are:

- Overall responsibility for the investigation;
- Reviewing and approving the project SAP/QAPP;
- Reviewing reports and ensuring plans are implemented according to schedule; and
- Coordinating with TSMD Case Managers related to study plans, implementation, results, and reporting.

Dave Mosby (or designee) USFWS Fish and Wildlife Biologist

- Provide XRF analytical support in the field and/or laboratory

Mike Slifer, USGS Approving Official –Director of the Missouri Water Science Center; will serve as the approving official for all USGS activities for the project. Specific project duties include:

- Reviewing and approving the project SAP/QAPP;
- Ensuring that study objectives are relevant and within the mission of the USGS;
- Reviewing reports and ensuring plans are implemented according to schedule;
- Making final project decisions with the authority to commit the necessary resources to conduct the project; and
- MOWSC approving official for the project final report.

John Schumacher, Overall USGS Project Coordinator – The USGS Project coordinator has the following specific responsibilities:

- In conjunction with project technical team, revises the SAP/QAPP as needed to define project goals and activities;
- Serve as a liaison between USGS and USFWS and coordinates overall field and laboratory activities (field XRF screening) associated with the project and prepares project updates;
- Coordinates with project team members to ensure project operates within allotted schedule and budget;
- Provides technical assistance to the project team members on matters related to geochemical processes, sampling protocols, and quality-assurance issues; and
- Coordinates with ongoing USEPA Region 7 studies and activities in the TSMD.

Doug Mugel, Principal Investigator–Missouri Project Leader. Will oversee project activities in Missouri, including Center Creek, Turkey Creek, and Shoal Creek. The Principal Investigator has the following specific responsibilities:

- Responsible for reconnaissance and selection of study area on Center, Turkey, and Shoal Creeks. This includes coordinating and obtaining access from landowners, and utility clearances;
- Serve as head of the floodplain sampling team. Coordinate overall field and laboratory activities associated with sampling of floodplain soil;
- Conducts project activities in accordance with the SAP/QAPP within the allotted time frame and document and obtains approval for deviations;
- Verify and validate field and laboratory data generated from sampling activities;
- Ensures that all relevant project data and sample sites are properly entered into the USGS National Water Information System (NWIS); and
- Assists in the preparation of the report describing the extent and magnitude of mining contaminated sediments in the representative stream reaches studied.

Mike Kleeschulte, Missouri Project team member. Serves as a field team member and provides support to the Principle Investigator and be capable of fulfilling any of the responsibilities of the Principle Investigator.

Mark Becker, Lead Author –Oklahoma Project Leader. Specific project duties include:

- Responsible for all field activities at the Tar Creek study reach (reconnaissance, access, utility clearance, and sampling);
- Serve as head of the in-channel sampling team. Coordinates overall field activities associated with in-channel sediment sampling;
- Responsible for preparation of the final study report;
- Verify and validate field and laboratory data generated from sampling activities;
- Ensures that all relevant project data for the Tar Creek area are properly entered into the NWIS;
- Ensures that field activities follow USGS safety protocols and boat operations plans; and
- Coordinates project activities with USEPA Region 6 activities in the Oklahoma part of the TSMD.

Paul Brenden, Hydrologic Technician – Missouri. Drill rig operator. Primary responsibility includes safe operation, maintenance, and cleaning of drill rigs and sampling equipment.

Jacob Morris, Hydrologic Technician – Missouri. Collection of field data and preparation of geologic logs, and compilation and review of field XRF, laboratory, and geologic data. Also assist with or operate drilling and sampling equipment.

David Detra, USGS Central Region Mineral Resource Coordinator–As the coordinator for analytical services by the USGS Central Region Mineral Resource Assessment Team (CRMR), is responsible for coordinating the analysis of sediment samples for laboratory grain-size, elemental analysis and validation of laboratory data. This coordination will include the receipt of samples at the laboratory, selection of the analytical team, verification that internal laboratory audits are conducted per standard CRMR operating procedures (SOPs). The Coordinator will oversee internal laboratory Quality Assurance (QA) procedures to include the analysis of standard reference samples (control samples) and split-replicate samples. Associated laboratory QA data and any identified laboratory problems will be reported to the project Principal Investigator as soon as they are determined.

2.0 Approach and Methods

Some stream sampling locations will present access problems and difficulties in obtaining representative samples. Initially, data collection will take place at one or two streams to determine which approach and sampling methods are best suited for achieving the objectives of this project (Phase 1). While it is understood that each stream has its unique attributes that may require a unique approach and different methods, the lessons learned from the initial sampling will be applied to the remaining streams (Phase 2).

2.1 Stream Reach Selection

2.1.1 Identification of candidate stream reaches

Based on discussions with the USFWS and other members of the Trustee Councils of Tri-State, five streams in the TSMD were selected to be included in this pilot study (1) Center Creek, (2) Turkey Creek, (3) Shoal Creek, (4) Tar Creek, and (5) Spring River. One representative study reach will be investigated along each stream except for the Spring River, where two reaches will be selected to coincide with locations of the USEPA Spring River floodplain study (fig. 1). In-channel samples will be collected from all reaches. Samples will be collected from the floodplain of all streams except Spring River, as floodplain coring of Spring River is part of the USEPA Cherokee County study. Stream reaches selected for sampling will be determined based upon the proximity to downstream tributaries, access, and evidence of extensive stream alteration since mining has occurred. Historical aerial photos will be compared with recent photos to determine anthropogenic or natural changes that may affect or bias the results. Stream segments in Missouri selected for sampling must contain several of the geomorphic channel units (GCU) such as pools, riffles, and runs. These are common characteristics in Ozark streams within the TSMD. Tar Creek is a typical prairie stream and does not naturally contain the course sediment found in Ozark streams.

2.1.2 Field Reconnaissance

After candidate reaches have been selected a field reconnaissance of the locations will be done to verify that the reaches contain the primary GCUs and that there is adequate access to the stream reach. Notes will be taken on approximate stream width, type and number of physical features within the channel (bars, riffles, manmade features, bank heights, obvious utilities, etc.) and floodplain (natural levees, terraces, old meanders, and cultural features), and a determination made if the reach is wadeable or non-wadeable. Physical conditions of the stream bank (height, slope, vegetative cover, etc.), water depth, and access will dictate the types of equipment that can be used at the site (hand operated, tractor or ATV, vehicle access). During the reconnaissance, a tentative layout of in-channel and floodplain core locations will be made to estimate the number of cores and samples to be collected at each candidate reach. A hand-held GPS will be utilized to provide estimated locations of transects and core locations and to locate noteworthy features observed such as tailings exposures, utilities, target areas of bias sampling (old cutoff meanders, etc.) It is anticipated that most access will be on or across private property and an important focus of the field reconnaissance will be contacting and securing access from property owners. Study reaches will be moved or adjusted depending on access restrictions. More than one reconnaissance may be required for each reach.

2.1.3 Study Reach Selection and Initial GIS Mapping

Based on the field reconnaissance, study reaches will be selected and a layout of proposed in-channel sample sites will be done using a GIS. Any specific points of interest noted during the field reconnaissance (old channel meanders or mine shafts, tailings exposures) that may affect the study design will be imported into the GIS. The layout will include determination of the length of the study reach, proposed locations and number of in-channel and floodplain sample locations. The base map for the study will be 2009 NAIP imagery with overlays of the 1938 Soil Conservation Service (SCS) imagery. The location of depositional features in the channel (bars and riffles) observed on the 2009 imagery will be digitized using the GIS to provide an estimate of the area of these features along each study reach for comparison to the mapping of these features during the field effort. The results of this comparison will be used to determine the validity of using GIS mapping to extrapolate beyond the selected reaches to other portions of the streams. Coordinates of the study reach and of proposed subsurface activities will be used to obtain the required utility clearances (e.g. Missouri One-Call). More than one visit to each study reach may be required to stake locations of floodplain core sites and verify locations of marked utility crossings.

2.2 Sample Site Selection and Methods

The following sections describe the theoretical approach for the collection of samples along each representative stream reach. One of two general approaches will be used at each stream reach. In addition to floodplain core sampling, the initial approach for each stream reach will be to collect in-channel samples at sites along transects. However, because of the expected heterogeneous nature of sediment distribution in some if not all in-channel streams reaches, a directed (bias) approach to sites where sediment accumulations are observed may be used instead. The directed approach may be necessary because regularly-spaced samples along a transect might not adequately represent the sediments in the reach, and other possible issues such as access at transects. The determination of sample approach will be made during sampling depending on conditions encountered. Results from initial sampling will help direct the approach in subsequent sampling. One outcome of this pilot study will be the determination of which of these approaches is most suitable for sediment sampling of the TSMD. Also, because of the uncertainty of subsurface conditions and physical limitations regarding the collection of in-channel core samples, sample methods, including modifications to methods described herein or new methods will to some extent be determined at the time of sample collection.

Sample collection along each representative stream reach will be divided into two tasks. Task 1 will involve the collection of in-channel samples (between top of banks). Task 2 will involve the collection of core samples from the floodplain adjacent to the sampled stream reach. A third, non-sample task (task 3) will be to estimate the depth of in-channel sediments along the study reach using a tile probe or maximum refusal depth from coring. The following describes the general approach to the layout of sample sites along a representative stream reach. As an example, a possible layout of in-channel and floodplain cores along a candidate study reach along Center Creek is shown in figure 2. The candidate reach shown in figures 2 and 3 is along the lower part of Center Creek about 0.7-mi (miles) upstream from the mouth. This area was identified because of a complex series of old channel meanders and channel alternations, including a low-water dam evident on the 1938 air photograph.

2.2.1 Task 1. In-channel Core Site Selection

A maximum of 20 in-channel core samples will be collected along each representative stream reach. For the transect approach, in-channel sediment samples are proposed to be collected using three strategies:

Transect sampling --by selecting transects perpendicular to the stream channel crossing the stream at a specific GCU within the study reach (9 to 15 samples),

Longitudinal sampling --by evenly dividing the length of the study reach and placing one core in the middle of the channel at each interval (3 to 5 samples),

Special sampling to target unusual features may be done, to supplement other samples (0 to 2 samples).

The number of transects in each GCU (one or two) and spacing of sample sites along each transect will be dependent on the channel complexity along the study reach and width (between top of banks) of the channel, and access from adjacent landowners. The spacing of cores along each transect will be determined by dividing the channel width (W) at that transect location by (n+1) where n is the number of cores (typically 3 or 5 depending on whether one or two transects per GCU are done) to be collected along the transect. The first core sample will be collected at W/(n+1) feet from the top of the right bank (looking downstream). Using this method, core spacing along each transect will vary depending upon the channel width at each cross section. Transects will be labeled with a letter designation beginning with "A" and increasing from upstream to downstream order. Core sites will be numbered from the right bank (looking downstream) beginning with "01". Generally cores along a transect will not be spaced closer than about 25 ft, such that only three cores are planned if the channel is less than about 100-ft wide.

As part of the transect approach and to test this approach, longitudinal sampling will be done to compare with the results from transect sampling. Generally these samples will be collected after the transect samples have been collected. Spacing of the samples will be done by dividing the length of the study reach by (n+1) where n is the number of longitudinal samples to be collected. Depending upon the complexity of the channel and number of transect samples collected, three to five longitudinal samples will be collected. The samples will be collected from the center of the channel (midpoint between banks) and thus could be from within a pool, riffle, run, or gravel bar, depending on the feature present at that location. Longitudinal cores will be given a "L" prefix and numbered in downstream order beginning with "L01" at the upstream location. It is possible that unusual features may be encountered along a study reach that were not sampled by the transect or longitudinal samples. These features may be selected for special sampling (maximum of two samples). Such unusual features may include a depositional area of fine grained material or an accumulation of visually identified mine waste immediately upstream or downstream from a pipeline crossing or low-water bridge. Special samples will be given an "S" prefix and numbered sequentially in the order collected.

The alternative approach to the transect approach is directed (bias) sampling at locations where sediments are known to occur in substantial thicknesses. This approach may be superior to the transect approach if the transect sample sites, which are determined by regular spacing along the transect, are not located where sediments are thick enough to yield samples representative of the reach, or are located where access or other issues present a problem. If this appears to be the case at the time of sampling, the decision will be made to collect samples using the bias approach. Up to 20 samples would be collected along the length of the reach, primarily in bars where sediments are thick, but also including up to 5 samples in the wetted channel (in-stream) where sediment character is likely to be different. A hypothetical layout of bias sample sites is shown in figure 3.

A variety of methods will be used to collect in-channel samples ranging from hand operated vibrating core and auger to machine driven direct push and split spoon, to hand shoveling , etc. Collection of core samples is the preferred method of in-channel sample collection. However, it is anticipated that because of the difficulties in sampling gravel with traditional coring devices, alternative sampling methodologies are likely to be employed which may or may not result in actual core samples. The target depth of in-channel samples is variable and dependent upon the method used to obtain the sample, equipment used, and grain-size range of the material. A target depth of 3-5 ft beneath the land surface or water-sediment interface is proposed because this is the maximum practical depth thought to be possible with hand operated devices. However, attempts will be made to collect samples from depths up to 8 ft or refusal.

A hierarchy of sampling methods will be used for in-channel sampling, starting with mechanical core drill rigs (truck, tractor, or ATV mounted). Locations that are accessible by these drill rigs (gravel bars and shallow riffles, if access to these locations across floodplains is possible) are areas where continuous cores to depths of 8 ft may be possible given favorable grain-size and other conditions, resulting in high-resolution vertical characterization of the sediments and their metal contents. Where larger cobbles are encountered, those zones may be bypassed or larger diameter “split spoon” type samples attempted. If grain-size is not too large, the most reliable samples can be obtained using 2-in diameter core tubes with disposable liners that can be advanced to specific depths, opened, and “pushed” to obtain core samples from saturated materials that would otherwise collapse within an unlined borehole. Larger diameter (5-in. or larger) split spoon samples can be used, however, these larger tools are limited to about 5 ft below the water table or water-sediment interface because they will be advanced in an open borehole. Remote areas not accessible by the truck, tractor, or ATV drill rigs will be limited to hand operated power equipment or manual equipment (eg., shovel). On gravel bars and in shallow riffles (less than about 2 ft of water depth) several methods ranging from vibratory and gasoline powered augers combined with vibratory techniques [limited to smaller diameter (2-in or less) core tools] can be attempted (Box and others, 2001). Hand methods likely will be limited to depths of less than 5 ft. For in-stream samples in non-wadeable conditions, a floating platform will need to be used. This may consist of a john boat, dock floats, or a pontoon boat.

2.2.2. Task 2 Flood-plain Core Site Selection

Core samples from the floodplain will be collected along each representative reach where in-channel samples are collected, with the exception of Spring River where floodplain samples have already been collected as part of the USEPA/USGS floodplain study. About 5 to 10 floodplain core samples will be collected along each representative reach. The number of floodplain core samples is dependent upon the number of in-channel samples collected (maximum of 25 in-channel plus floodplain samples per study reach), the length of the study reach, and complexity of floodplain features. Locations of floodplain core samples will be determined in a manner similar to that done for the USEPA/USGS Cherokee County, Kansas floodplain study. A transect will be established generally perpendicular to the stream. The width of the flood plain along the transect will be estimated from topographic maps and NRCS soils maps, and will include soils that are classified by NRCS as “frequently flooded”, where the probability of flooding in any year is greater than 50 percent, or “occasionally flooded” where the probability of flooding in any year is 5 to 50 percent (Natural Resources Conservation Service, 2002) and verified in the field. Core samples will be collected at equal-spaced intervals across the floodplain and samples designated with a “FP” prefix. Spacing between cores will be established by dividing the floodplain width (W) by (n+1) where n is the number of core samples to be collected (generally 5). Core samples will be numbered sequentially from the right edge of the floodplain (looking downstream) and the first core sample site will be approximately W/(n+1) ft from the right edge of the flood plain. Spacing may be adjusted depending upon access, landowner permission, and other on-site considerations. If the floodplain appears complex with obvious old channel meanders, it is possible that two transects will be done across the floodplain with 3 to 5 cores per transect. Several biased floodplain cores also may be taken in unusual features such as old channel meanders or other possible depositional areas. Biased floodplain core samples will be designated with a “FB” prefix and numbered in the order collected. The anticipated depth of floodplain cores is to refusal but not to exceed 16 ft. The 16 ft baseline is based on the maximum depth of core from the USEPA/USGS Cherokee County, Kansas Spring River floodplain study (Kyle Juracek , U.S. Geological Survey, oral communication, 2010).

2.2.3 Task 3 Determination of streambed sediment depth

Estimates of the depth of unconsolidated sediments in the stream channel will be made along each representative reach studied. For transect sampling, a tile probe will be used to probe to refusal at 5 to 10 locations along each transect, including at each transect sample site, and at longitudinal sample sites, to provide perspective on the adequacy of either the sampling method or the tile probe to characterize the depth of the sediments. In the case of bias sampling of in-channel sediments, a tile probe will be used at several locations at each bar where samples are collected, including at each sample site. Tile probes have recently been used in Missouri and Oklahoma to estimate the depths of unconsolidated sediments in streams and tailings near mine-waste piles (Pavlowsky and others, 2008; CH2MHill, 2009). A unique identification number will be assigned to each tile probe location and the horizontal and vertical coordinates will be obtained with DGPS or GPS and levels. Tile probe data will be used to make a rough estimate of in-channel sediment thickness and volume of bars within the study reach. To supplement transect and longitudinal tile probe data, the average height of bars that were identified and digitized during the initial GIS mapping will be estimated using a DGPS or GPS and levels.

2.2.4 Field GPS survey

A sub-meter-accurate DGPS or GPS and levels will be used to provide coordinates and elevations for each in-channel and floodplain sample and tile probe site. Several bars or riffles along each study reach will be mapped in greater detail (point spacing about 25 ft) using the DGPS or GPS and levels to obtain horizontal and vertical coordinates. The average height of these same bars above the water surface will be estimated for later use in estimating volumes of sediment, and for comparing the accuracy of the size of these features to values obtained from digitizing of the NAIP imagery.

2.3 Sample Handling and Field Processing

2.3.1 Sample collection

For both in-channel and floodplain sampling, the primary method for collection of core samples will be direct-push using truck, tractor, or ATV mounted Geoprobe™ type drilling system. A wide variety of sampling devices, core tube sizes, slit spoons, Shelby tubes, etc., are available for use with direct-push drilling. Saturated alluvial sediments, especially gravels and sands, are typically the most difficult sediments from which to collect continuous core samples. There are two primary concerns when coring in saturated sediments. One concern is retention of the core inside the sampling tube or device. Typically this is done using a plastic or stainless steel “sand catcher” placed behind the core bit (consisting of a circular array of curved plastic or steel “fingers” pointed upward) to hold the core inside the sample tube when the tube is removed from the subsurface. The second concern is feeding of sediments into the sampling tube. Oversized cobbles or debris larger than the opening of the sample tube will block the end of the tube resulting in refusal or prevent smaller sediments from feeding into the sample tube. This is a more common problem and source of poor core recovery. Gravel bars typically are armored at the surface with larger cobbles or contain cobble beds at depth. If core recovery is poor, larger sample tubes will be used or auger methods will be used to advance through cobble beds. When core tubes are removed from the saturated sediments, the borehole will collapse preventing collection of core from deeper depths. One solution is to use a “discrete” core tube that has a plug at the bottom that can be driven to the desired depth, after which the plug is removed, and the tube driven further.

Core diameter will be determined by the largest diameter of the sediments. Continuous core tubes suitable for discrete sampling are less than 3.0-in. diameter. If larger sized sediments are encountered then larger diameter core tubes such as split spoon or “Shelby tube” samplers may be used. A disadvantage of larger core tubes is that disposable liners may not be available (requiring considerable decontamination between samples) and they may not be suitable in remote areas where hand operated equipment is used or where coring must be done from a boat. In addition, split spoons are not discrete devices and must be advanced inside augers or an open ended casing where soft or saturated sediments would cause borehole wall to collapse. Rather than a continuous core, these methods result in a series of sampled intervals that may have gaps where samples are not available.

2.3.2 Other sediment sample collection methods

Many sample locations will not be accessible by truck, tractor, or ATV mounted drilling platforms, and hand-operated methods will be required. Hand-operated methods will employ a variety of hammer/vibratory/auger, and shovel methods; however, the available options for core sample collection and penetration depth are reduced. In these areas, the maximum target depth anticipated is about 5 ft deep.

2.3.2.1 Vibro-core methods

Hand methods will use a 35 lb (pound) hammer drill, a 5-hp gasoline powered concrete shake, or small air or hydraulic hammer to vibrate core tubes or other devices into the in-channel sediments. This method has been used by the USGS to collect shallow sediment samples from Grand Lake in Oklahoma and by the USGS to collect sandy streambed sediment samples from streams in the Coeur D’ Alene Mining District in Idaho (Box and others, 2001).

Vibro-core drilling is particularly well suited to core sampling in sandy unconsolidated sediments that are water-saturated. A vibrating drill pipe agitates the intergranular pore water, which lifts and separates sand grains, allowing downward penetration of the drill pipe. A gasoline powered concrete vibrator or hammer drill is clamped to the pipe. Eccentric rotation of the vibrator creates very strong vibrations, which are transmitted to the drill pipe. This method works well but as the pipe fills its vibration is dampened causing decreasing drill rates and refusal. Before the tube is withdrawn, a rubber plug is placed in the top to create a near vacuum as the tube is removed. Sandy sediments tend to fall out of the tube bottom resulting in loss near the bottom of the core run. Once extracted, the tubes will be transported to a work area on the bank. Samples can be removed from the tube by either tipping the tube at an angle and lightly tapping to allow the material to slump out onto a plastic sheet or tray (wallpaper tray) or plywood, or the tube can be cut lengthwise with a battery-powered saw.

2.3.2.2 Auger-Vibro core

Modifications to the vibro-core methods likely will be necessary. If refusal is encountered because the tube becomes filled with sediment, the sediment inside the tube can be sampled and removed with hand bucket augers and piston samplers, then the tube advanced further into the bottom. Typically, the overlying water must be removed with a peristaltic pump or bilge pump. A section of sediment in the tube is removed with a bucket auger, then a hand driven piston sampler can be used to collect a sample from a discrete intervals inside the tube and the process repeated. The upper one-third to one-half of material in the bucket auger or piston sampler would be discarded as waste and only the bottom part retained as the field sample.

2.3.2.3 Auger-hand core

Traditional hand cores (bucket auger with piston core samplers) cannot be used where saturated sediments collapse the borehole. However, these methods can be used inside casing. At some locations, a hollow stem auger (HSA) may be turned into the sediments to a specified depth. The HSA would have a center plug that would be removed allowing a bucket auger or piston sampler to be turned or driven in front of the auger to obtain a discrete sample. The HSA could be advanced several feet further, the internal material removed with a bucket auger to the bottom of the HSA, then a piston sample advanced again. The upper one-third to one-half of the piston samples would be discarded to waste and only the bottom section retained as actual sample. The HSA would be advanced using a gasoline-powered hydraulic two-person boring device.

Additional sampling devices, such as the discrete core tube used with the drill rigs can be advanced up to 4 ft through the HSA using either the vibrator or hammer drill. This is the preferred method as the core tube has a liner minimizing the potential for cross-contamination.

2.3.2.4 Soft sediment piston cores or dredges

In areas where the water depth is greater than about 6 ft in smaller streams that are accessible only by a small john boat, the vibro-core unit cannot be used, and a traditional drop-type piston core will be used to collect samples from the streambed. Penetration depths generally are limited to less than 4 ft, and likely will be less than 2 ft. These samplers collect a single sample from the bottom and depth of penetration is dependent upon the substrate bottom. These samplers generally do not have disposable liners and must be thoroughly decontaminated between samples. If these methods fail, then the final alternative at these locations is a Ponar or Eckman dredge to collect a limited depth (less than 0.5 ft) grab sample from the streambed.

2.3.2.5 Freeze core

If all attempts result in poor or no recovery, two less desirable methods involve freezing the sediments either inside the sample tube bit (Murphy and Herkelrath, 1996) or onto the exterior of a steel rod (Knaus and Calhoon 1990). In some cases, core recovery can be enhanced by using liquid carbon dioxide or nitrogen to freeze the core tube bit. This method is limited to within a few feet of the water table or water surface. Traditional core tubes can be advanced as described in the above sections, but a special bit and steel tubing is added to the outside of the core tube. Once the core tube is advanced to depth, liquid carbon dioxide is pumped down the tubing to freeze sediment inside the core bit. This method is applicable where the sediment can be penetrated but slumps out of the core tube when the tube is removed from the sediment.

A second method is to freeze the fine-grained material to the exterior of a tube that is then removed from the subsurface. In this method a small diameter steel rod (1-in. diameter or less) is driven into the sediment, a copper tube is inserted inside the rod, liquid carbon-dioxide or nitrogen is bubbled inside the rod to freeze sediments to the outside of the rod, and the rod is pulled. This method results in some recovery of fines (clay up to small sand-sized particles) but does not produce high quality samples from discrete depths

2.3.2.6 Trenching

If previous attempts result in little or no core recovery, sediment samples from bar or shallow riffles accessible by a tractor will be collected from a trench using a backhoe or trencher. Because of the scale of this method, only a few locations will be sampled and those will probably be restricted to accessible gravel bars or areas above the water surface. The approach will be used to excavate a trench in 1 to 2 ft depth increments. At the desired depth, material from one backhoe bucket or trencher will be dumped onto a plywood or plastic sheet. Large cobbles will be removed by hand, and a shovel used to mix the remaining material. Ten to 15 subsamples will be collected using a plastic or stainless steel scoop passed through the entire depth of the pile at each location and composited into a clean plastic tub.

2.3.2.7 Hand Shovel

Because of access difficulties or problems getting good recovery using the above methods, it may be necessary to use a hand shovel to sample the sediment. In a similar manner as using a backhoe, the bar would be excavated by hand in 1 to 2 ft depth increments, the sediment placed on plywood or a plastic sheet, and a composite sample collected from 10-15 subsamples.

2.4 Borehole Geophysics

To examine the potential for indirect methods of characterizing mine wastes in the subsurface, a downhole electrical conductivity (EC) and resistivity probe will be evaluated. The probe will be advanced with the ATV, tractor, or truck mounted direct-push drill rig. As the probe is pushed into the subsurface, a current is sent through the sediments between two probe contacts. This current is measured along with the resulting voltage. The conductivity is a ratio of current to voltage times a constant. The conductivity is different for each type of media with finer grained sediments, such as silts or clays, having higher electrical conductance values. While coarser grained sediments, sands and gravel, will have lower values. The EC tool can be calibrated to soils in an area by matching the EC values with grain-size data of sediments obtained from core samples. While the usefulness of the EC probe in mapping general characteristics of soils (grain-size of sediments) is documented, it is not known whether sediments containing mine wastes may have a unique or anomalous EC signature possibly resulting from sulfide minerals or higher conductance interstitial water associated with oxidation of sulfide minerals. If sampled core sites show evidence of obvious mine wastes (in both appearance and XRF screening data), and are in an accessible area, the EC probe will be run though the mine waste sediments and nearby non-mine waste sediments and the results compared.

2.5 Sample Handling and Processing

Procedures used for the handling and processing of sediment samples will be similar to those used for the USEPA/USGS Cherokee County Floodplain study to allow combining of the two data sets. Sediment samples will be collected using one of the methods and equipment discussed in section 2.3. Where possible, cores will be collected in 4-ft increments using disposable plastic core tubes to hold the core inside the sample tube or split spoon, as was done in the USEPA/USGS Cherokee County Floodplain study.

Because the core barrels are lined with plastic liners, potential contamination of the core generally is restricted to the core bit and from handling and storage of the core once the tubes are opened. Between each core run, the core barrel and bit will be washed with a laboratory detergent solution and a brush, rinsed in tap water, and sprayed with deionized water using a low pressure washer.

Grab samples using dredges, shovels, trenching, freeze-core scrapping, etc., will be homogenized prior to field XRF screening or sampling for laboratory analyses. At the sample site, homogenization will include removing large cobble-size rocks or debris, and placing the samples in a plastic or stainless flat bottom container for transport to a secure location where the sample will be dried and screened by XRF.

.

A field log of each core or sample (depth, core recovery, drilling conditions, date, time, method, equipment used etc.) will be made at the time of drilling. Each core tube will be capped, labeled, and shipped to an offsite storage and processing location (Missouri or Oklahoma USGS). Processing will include making a geologic log, air drying, photographing, XRF screening, and sub-sampling of selected intervals for laboratory confirmation analysis. For each core, a geologic log describing depth intervals, core recovery, description of texture, grain size, color, moisture, etc. will be completed and the core sections photographed as part of the record for each site. As part of the core processing, the core will be subdivided into 1 ft depth intervals for XRF screening by placing small plastic tabs every foot. Non-core samples will also be described in a similar manner as core samples.

One laboratory confirmation sample will also be collected from each core after XRF screening. The laboratory sample will be collected using a plastic or stainless steel spoon. The spoon will be cleaned before each reuse. Less than 25 g of sediment are required for chemical analysis, and the length of the sample interval will be varied such that no more than one-half of the core is removed. It is anticipated that the sample interval will be about 0.5 to 1.0 ft long. The sampled interval will be selected to avoid sampling across obvious lithologic breaks and avoid large cobbles. The sample for each core interval will be dried, sieved through a No. 1 sieve, and homogenized as described in section 2.6.1.

Chain-of-custody (COC) protocol will be established and followed, as described in section 2.8.

2.6 Analytical Methods

2.6.1 Metal screening by X-Ray Fluorescence (XRF)

After geologic logging, the core will be air dried and analyzed by direct XRF for target mining-related metals (Pb, Zn, and Cd) and calcium (Ca). The USFWS will supply the XRF and trained operator, or the USGS Oklahoma office may provide a XRF later in the project. The XRF screening will be done at the USGS office in Rolla, Missouri or Oklahoma City, Oklahoma. The XRF screening will be done at intervals of 3 measurements per 1 ft section of core. Each 1-ft deep interval (previously marked by the geologist) will be sub-divided into 3 equal length sections and the XRF scan done at the middle of each 1/3 foot interval (fig. 4). This protocol was used successfully in the screening of floodplain core samples collected from the USEPA/USGS Cherokee County, Kansas project.

The primary concern for in-situ screening of the intact core is error introduced because of heterogeneity of the core (both grain size effects and unequal distribution of metals within the core) and differences in moisture content. To control error from moisture differences, cores will be air dried until the surface is dry to the touch, which may require several days before screening. If on-site screening of the damp or wet core is done at the field site to guide field sampling efforts, a re-screening of dried core will be done and the re-screening values will be considered the final values. Little can be done to control error introduced by heterogeneity of the core, except to avoid scanning large cobbles and ensure a regular surface to the extent possible..

As a quality check on the reproducibility of the XRF screening results of intact core, three repetitive scans at a fixed location will be done at a rate of about once every 15 to 20 measurement intervals (each repeat measurement recorded) and the average reported for that interval. This same procedure will be done for samples that were collected by methods other than intact core (see following paragraph). As a quality check on the variability of the XRF measurements from the intact core, after the triplicate scans are done, three additional scans will be done at the same interval but the instrument rotated about 120 degrees between each scan. These three results also will be individually recorded and their average and range compared to the average and range of the triplicate scans. Instrument scan time is proposed to be 60 to 90 seconds.

For samples that cannot be obtained from intact core, bulk samples collected in plastic ziplock bags will be transported to the USGS laboratory in Rolla, Missouri or Oklahoma City, Oklahoma where they will be processed and analyzed by XRF. Processing will include verification that sample bag labeling is consistent with field notes. Samples will be dried overnight in an oven at 60 ^{o}C. After drying, large obvious cobbles, sticks, pieces of debris such as asphalt will be removed then the sample disaggregated with a mortar and pestle (if needed), and sieved through a No. 1 (25.4 mm open size) stainless steel sieve to remove large cobbles and rock fragments atypical of mining wastes. The sieved material will be collected in a plastic bowl and a 100-200 g subsample will be removed and homogenized according to USEPA Method 6200 The subsample will be analyzed using the portable XRF (three scans per sample with individual values recorded and averaged). One laboratory confirmation per sample site (one per freeze core location, vibro-core location, trench, etc) will be collected by drawing 1to2g subsamples using a plastic or stainless steel spatula (bag mixed between each subsample) to obtain a 25 g sample. The samples will then be shipped overnight to the USGS contract soil geochemistry laboratory for geochemical analyses. Any remaining homogenized material will be archived in a clean plastic bag. A second set of XRF measurements (five scans per sample) will be made on the exact sample to be shipped for fixed laboratory analyses by ICP-AES.

The XRF will be operated by USFWS or USGS personnel in accordance with standard procedures described in USEPA Method 6200. Before analyses of environmental samples, a daily energy calibration check, and operational checks will be done per USEPA Method 6200 and the manufacture operating instructions. Instrument blanks, calibration verification checks (using ASTM standard reference samples), and replicate samples, will be run every 10 to 20 samples.

The replicate samples will be analyzed a minimum of 7 times to establish the precision of the XRF.

2.6.2 Laboratory Analyses

One laboratory confirmatory sample will be collected from each core or non-core sample site (maximum of 25 samples per stream reach studied). Laboratory confirmatory samples will be selected to represent a range of metal (primarily Pb) concentrations determined by XRF screening. These samples will be dried, sieved (No. 1 slot), and homogenized as described in section 2.6.1 and discussed in USEPA Method 6200 and placed in clean sealed plastic bags. Before shipping, each sample will be placed flat on a table for an additional XRF screening. Five individual XRF scans will be made on the sample with one in the center and four in each quadrant of the sample. Each individual result will be recorded and the values averaged. After XRF screening, the samples will be submitted to the USGS Central Region Mineral Resources Geochemistry (CRMR) laboratory in Denver, Colorado for processing. The CRMR laboratory will log the samples into a Laboratory Information Management System (LIMS), and process the samples for subsequent elemental analysis. Processing will include drying, disaggregating, splitting, archiving, and grain-size determination (sand, silt, and clay-size fractions). Upon receipt the bulk samples will be dried then split with one half being archived. The remaining split will be split again. One split will be sieved to obtain a fine fraction sample (less than 63-micron). The remaining split will be weighed and sieved to determine the percent by weight of sand, silt, and clay-size fractions then recombined into a single bulk sample. Each of these splits samples (fine and bulk) will be submitted to a USGS contract laboratory for routine analysis for total (4-acid) digestion and elemental analysis by Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The ICP-AES elements analyzed and reporting limits are listed in table 2.

Table 2. List of target elements to be determined by Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) in laboratory samples.

Element and Abbreviation	Units	Concentration Range	
Aluminum, Al	Weight percent	0.005	0.5
Calcium, Ca	Weight percent	0.005	0.5
Iron, Fe	Weight percent	0.02	0.25
Potassium, K	Weight percent	0.01	0.5

Element and Abbreviation	Units	Concentration Range	
Magnesium, Mg	Weight percent	0.005	0.05
Sodium, Na	Weight percent	0.005	0.5
Phosphorous, P	Weight percent	0.005	0.5
Titanium, Ti	Weight percent	0.005	0.25
Arsenic, As	mg/kg	10	50,000
Barium, Ba	mg/kg	1	35,000
Beryllium, Be	mg/kg	1	5,000
Bismuth, Bi	mg/kg	50	50,000
Cadmium, Cd	mg/kg	2	25,000
Cerium, Ce	mg/kg	5	50,000
Chromium, Cr	mg/kg	2	25,000
Cobalt, Co	mg/kg	2	25,000
Copper, Cu	mg/kg	2	15,000
Europium, Eu	mg/kg	2	5,000
Gallium, Ga	mg/kg	4	50,000
Gold, Au	mg/kg	8	50,000
Holmium, Ho	mg/kg	4	5,000
Lanthanum, La	mg/kg	2	50,000
Lead, Pb	mg/kg	4	50,000
Lithium, Li	mg/kg	2	50,000
Manganese, Mn	mg/kg	4	50,000
Molybdenum, Mo	mg/kg	2	50,000
Neodymium, Nd	mg/kg	9	50,000
Nickel, Ni	mg/kg	3	50,000
Niobium, Nb	mg/kg	4	50,000
Scandium, Sc	mg/kg	2	50,000
Silver, Ag	mg/kg	2	10,000
Strontium, Sr	mg/kg	2	15,000
Tantalum, Ta	mg/kg	40	50,000
Thorium, Th	mg/kg	6	50,000
Tin, Sn	mg/kg	50	50,000
Uranium, U	mg/kg	100	100,000
Vanadium, V	mg/kg	2	30,000
Ytterbium, Yb	mg/kg	1	5,000
Yttrium, Y	mg/kg	2	25,000
Zinc, Zn	mg/kg	2	15,000

All sediment samples not consumed during analysis (core, grab, or otherwise) will be archived for the duration of the project at either the USGS office in Oklahoma City, Oklahoma or Rolla, Missouri. The final disposition of the samples beyond the project duration has not been determined.

2.7 Quality Issues

2.7.1 Quality Control

Quality control of sampling site variability and analytical determinations of trace metals in soil will be maintained through the use of replicate samples and standard reference samples. Within site variability in trace metal concentrations will be evaluated through the collection of sequential-replicate samples or measurements. Relative percent differences will be calculated for each replicate pair and evaluated against acceptance criteria discussed below. 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 10 percent of the number of environmental samples.

2.7.2 Data Quality Objectives for Measurement Data

Valid data of known and documented quality are needed to meet the objectives of the project. The majority of concentrations of selected metals sediment samples collected for this study will be determined by portable XRF screening and compared to concentrations in sediment from non-mined areas to assess the depth and extent of metal contamination from mining activities along the study reaches. Background concentrations of metals will be values reported in Pope (2005) and Juracek (2006). In addition, concentrations of selected metals in samples collected and analyzed by laboratory methods used during this study may be compared to sediment-quality guidelines to determine potential environmental effects of metals in these sediments. 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, precision of the XRF screening data will be evaluated by making a minimum of seven replicate XRF measurements made at a single point on the core or sample without moving the instrument as described in USEPA Method 6200. One precision measurement will be made each day of XRF operation. Split-replicate samples will be analyzed for 10 percent of the field XRF screening samples and laboratory samples submitted. Replicate field XRF screening will be done by making three repetitive scans as described in section 2.6.1. Precision of laboratory data will be evaluated by the preparation of blind split samples routinely prepared by the CRMR Geochemistry laboratory and submitted blindly to the contract analytical laboratory. 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 the XRF screening will be measured by analysis of standard reference samples. Confirmation of XRF accuracy and overall XRF analyses of sample handling methods will be evaluated by analysis of split samples between the XRF and the analytical laboratory, where the laboratory value is assumed to be the “true” value. Before a laboratory sample is shipped, five individual XRF scans will be done as described in section 2.6.2.

Accuracy of laboratory analyses will be determined by the analysis of standard reference samples of sediment with known concentrations of selected trace metals. Acceptable variability among analyses of standard reference samples will be within the published limits for each constituent for each standard or plus or minus 20 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 represents a characteristic of a population parameter at a sampling location. The representativeness of the XRF data will be evaluated by rotating the instrument about a fixed point and making three replicate measurements at the same depth interval as described in section 2.6.1. Comparison of the average, range, and standard deviation of these three measurements will provide an assessment of the ability of the sample collection to adequately describe the average concentrations of selected trace metals in the sample. Because of the variable nature of metals in sediment (typically associated with small metal-rich mineral grains such as galena) the acceptable variability among analyses of sequential-replicate samples will be a percent relative standard deviation (RSD) of plus or minus 40 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. This includes the collection, proper handling and labeling, shipping, and analysis of the samples. To generate data of the quantity necessary to meet the objectives stated for this project, 70 percent of the data in the designed assessment system should be collected and analyzed. This unusually low percentage is because of the high density of data proposed to be collected and because of the unknown nature of the sediments and difficulty in obtaining sediment samples from a river environment. In addition, the desired completeness ratio may be modified because of the variable physical or environmental characteristics at the time of sample collection. Any deviation from a 70 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. The preparation, splitting, and analysis of laboratory samples for this project will be done as part of the routine USGS geochemistry surveys done by the CMRA team and compatible with thousands of samples analyzed from across North America. In addition, the comparison (regression analysis) between the XRF screening of laboratory samples prior to submittal with the bulk laboratory data will enable comparison between the XRF and total digestion and ICP-AES analytical data.

2.8 Documentation

The records for this project will include miscellaneous correspondence, field logs or notebooks and field data work sheets, laboratory analytical reports, field activity documents, quarterly progress reports, and the final report prepared at the conclusion of this project. Field bound notebooks will be kept that will document the general daily field activities. Field logs will include observations about weather and physical conditions of the study reach, descriptions of specific sampling sites, descriptions of field visits (reconnaissance, utility clearances, sampling activities), personnel involved, and contacts with landowners or other officials. Geologic logs will be kept for each core or sampling site describing the equipment used, drilling methods, field personnel, general lithology, recovery, sample depths, etc. Sampling site folders (for each representative stream reach investigated) 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 Rolla, Missouri.

Reports, geologic logs, and results of field XRF screening and laboratory analyses will be submitted to the USFWS Project Manager upon publication or completion. Any other pertinent observations or deviations from the general SAP procedures also will be recorded on the field sheets. Field books and field sheets will be signed and dated by the person making the entries.

In accordance with USGS policy, all data collected as part of routine data collection by the USGS are stored in the National Water Information System (NWIS) computer database. Sample sites are assigned a unique 15 digit station number that generally is a combination of the latitude and longitude of the site to the nearest second plus a 2-digit suffix that is a sequence number from 01 to 99. The field XRF screening data will not be entered into the NWIS, but will be tied to the NWIS station number in the internal project database.

The NWIS is organized by state where the sample site is located, such that the responsibility for uploading and maintaining backups of data stored electronically in NWIS is the responsibility of the USGS state office. The USGS principle investigator (Doug Mugel) will ensure that all sample sites are entered into the NWIS.

The Principal Investigator also 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 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*.

Data from the USGS contract geochemistry laboratory are transmitted electronically to the Principal Investigator and entered into the NWIS. Environmental sample data are entered into the NWIS QWDATA database 01 (DB1); QC data are entered into the NWIS QWDATA database 02 (DB02). Data entry is the responsibility of the Principal Investigator or designee. The NWIS QWDATA database receives daily incremental backup and weekly full backup.

2.9 Geospatial Analysis

A GIS will be used to organize all data collected in this study. All sample sites will have GPS coordinates and a unique ID number to allow spatial analysis of the data. In addition to its use for organizing and simple mapping and overlaying of sample sites on current and historical images, soils maps, etc., the GIS will be used to estimate sediment thickness stored within the current stream channel along each study reach. Two methods for estimating these thicknesses will be compared. First, streambed and gravel bar areas along the study reach will be estimated by digitizing from the NAIP imagery and combined with tile probe depths and depths of contamination to provide thickness estimates of contaminated streambed or bar sediments. Generally, the elevation of the maximum depth of the tile probe along the reach (adjusted for channel slope) will be used to establish a base plane that will be assumed to be the base of the channel sediments. Second, the thickness of selected bars will be estimated using the base plane as above and the footprint and elevations from the DGPS or GSP and level survey. Direct comparison of these two methods will determine if methods can be extrapolated to estimate sediment thickness and volume of contaminated sediment outside the study reaches within the TSMD, or what additional low-density data might be needed along the streams.

3.0 Deliverables and Schedule

3.1 Deliverables

The USGS will prepare a progress report to the USFWS project manager each calendar quarter. The reports will describe general project activities and scheduling. Reports will be submitted monthly during periods of intense field activity.

A final report such as a USGS Scientific Investigations Report will be produced describing the methods used, and the spatial and vertical distribution of target metals within sampled reaches of streams in the TSMD. Concentrations of metals will be illustrated in cross sections showing depth and general lithology. The total volume of contaminated sediment and mass of target metals (Pb, Zn, and Cd) will be estimated by different GIS methods along each sampled study reach. Comparison of the in-channel longitudinal and special sample sites to the transect sites, and the use of bias sampling instead of transect sampling will be presented and discussed in the context of optimization of a sample design for wider-scale implementation across the TSMD. The various sampling methods will be discussed and compared to benefit any future study.

3.2 Project Schedule

The project funding was secured during fiscal year 2009. The project is anticipated to require two and one half years to complete beginning with finalization of the SAP. Initial field reconnaissance and selection of representative study reaches of Tarr Creek and Center Creek (Phase 1) was completed in June 2010. Initial (Phase 1) field sample collection is expected to take place in late spring/summer 2011. Subsequent (Phase 2) field work will take place in fall 2011 and spring/summer 2012. Data compilation and analysis will be conducted from fall 2012 through winter 2013. A final interpretive report will be written during 2013 and will be published by November 2013. A summary of the project timeline is shown in table 3

Table 3. Generalized project timeline.

Task	Estimated begin date	Estimated completion date
Prepare SAP	Feb 2010	April 2010
Draft SAP review by USFWS	April 2010	May 2010
Revise and prepare final draft SAP	June 2010	September 2010
Final draft SAP to USFWS	September 2010	September 2010
Finalize SAP	Mar 2011	May 2011
Begin field reconnaissance (phase 1)	June-2010	July 2011
Select study reaches and obtain	June 2010	June 2012

access/clearances		
Phase 1 field sampling effort	June 2011	August 2011
Laboratory analyses (phase 1 and 2)	August 2011	October 2012
Phase 2 field sampling	October 2011	August 2012
Data compilation and analyses	September 2012	February 2013
Draft report preparation	February 2013	May 2013
USFWS review of draft report	May 2013	June 2013
Final Report preparation and publication	July 2013	November 2013

4.0 References

Angelo, R.T., Cringan, M.S., Chamberlain, D.L., Stahl, A.J., Haslouer, S.G., and Goodrich, C.A., 2007, Residual effects of lead and zinc mining on freshwater mussels in the Spring River Basin (Kansas, Missouri, and Oklahoma, USA): Science of the Total Environment, v. 384, p. 467-496

Box, Stephen, E., Brookstrom, A.A., Ikramuddin, M., and Linday, J., 2001, Geochemical analyses of soils and sediments, Coeur ’Alene drainage basin, Idaho: Sampling, analytical methods, and results: U.S. Geological Survey Open-File Report 01-139, 206 p.

CH2MHill, 2009, Field sampling plan for the integrated site assessment/investigation of the Tar Creek superfund site, Ottawa County, Oklahoma: U.S. Environmental Protection Agency, Region 6 Contract No. EP-W-6-01, March 2009:

Fitzpatrick, F.A., Waite, I.R., D’Arconte, P.J., Meador, M.R., Maupin, M.A., and Gurtz, M.E., 1998, Revised methods for characterizing stream habitat in the National Water-Quality Assessment Program: U.S. Geological Survey Water-Resources Investigations Report 98-4052, 67 p.Knaus, R.M. and Cahoon, 1990, Improved cryogenic coring device for measuring soil accretion and bulk density: Journal of Sedimentary Petrology v. 60, no. 4, pp 622-623.

Ingersoll, C.G., Ivey, C.D., Brumbaugh, W.G., Besser, J.M., and Kemble, N.E., 2009, Toxicity assessment of sediments from the Grand Lake O’ the Cherokees with the amphipod *Hyalella azteca*: U.S. Geological Survey Administrative Report CERC-8335-FY09-20-01, various pagination.

Juracek, K.E. 2006. Sedimentation and occurrence and trends of selected chemical constituents in bottom sediment, Empire Lake, Cherokee County, Kansas, 1905-2005. U.S. Geological Survey Scientific Investigations Report 2006-5307, 79 p

Knaus, R.M., and Cahoon, D.R., 1990, Improved cryogenic coring device for measuring soil accretion and bulk density: Journal of Sedimentary Research, Vol 60, No. 4, pp 622-623

MacDonald, D.D., Ingersoll, C.G., and Berger, T.A., 2000, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems: Archives of Environmental Contamination and Toxicology, v. 39, p. 20-31.

Murphy, F., and Herkelrath, W.N., 1996, A sample-freezing drive shoe for a wire-line piston core sampler: Groundwater Monitoring and Remediation, Vol. 86, pp 86-90.

Natural Resources Conservation Service, 2002, Soil Survey of Jasper County Missouri, accessed August 2010, at *http://soildatamart.nrcs.usda.gov/Manuscripts/MO097/0/Jasper_MO.pdf*.

Pavlowsky, R.T., Lecce, S., and Mickus, K., 2008, Big River Mine Sediment Assessment Project (2008-2009), prepared for the Missouri Department of Natural Resources: 14p, accessed at URL *http://www.dnr.mo.gov/ENV/hwp/docs/081125bigriversedimentassessment.pdf*.

Pope, L.M. 2005. Assessment of contaminated streambed sediment in the Kansas part of the historic Tri-State Lead and Zinc Mining District, Cherokee County, 2004. U.S. Geological Survey Scientific Investigations Report 2005-5251, 61 p.

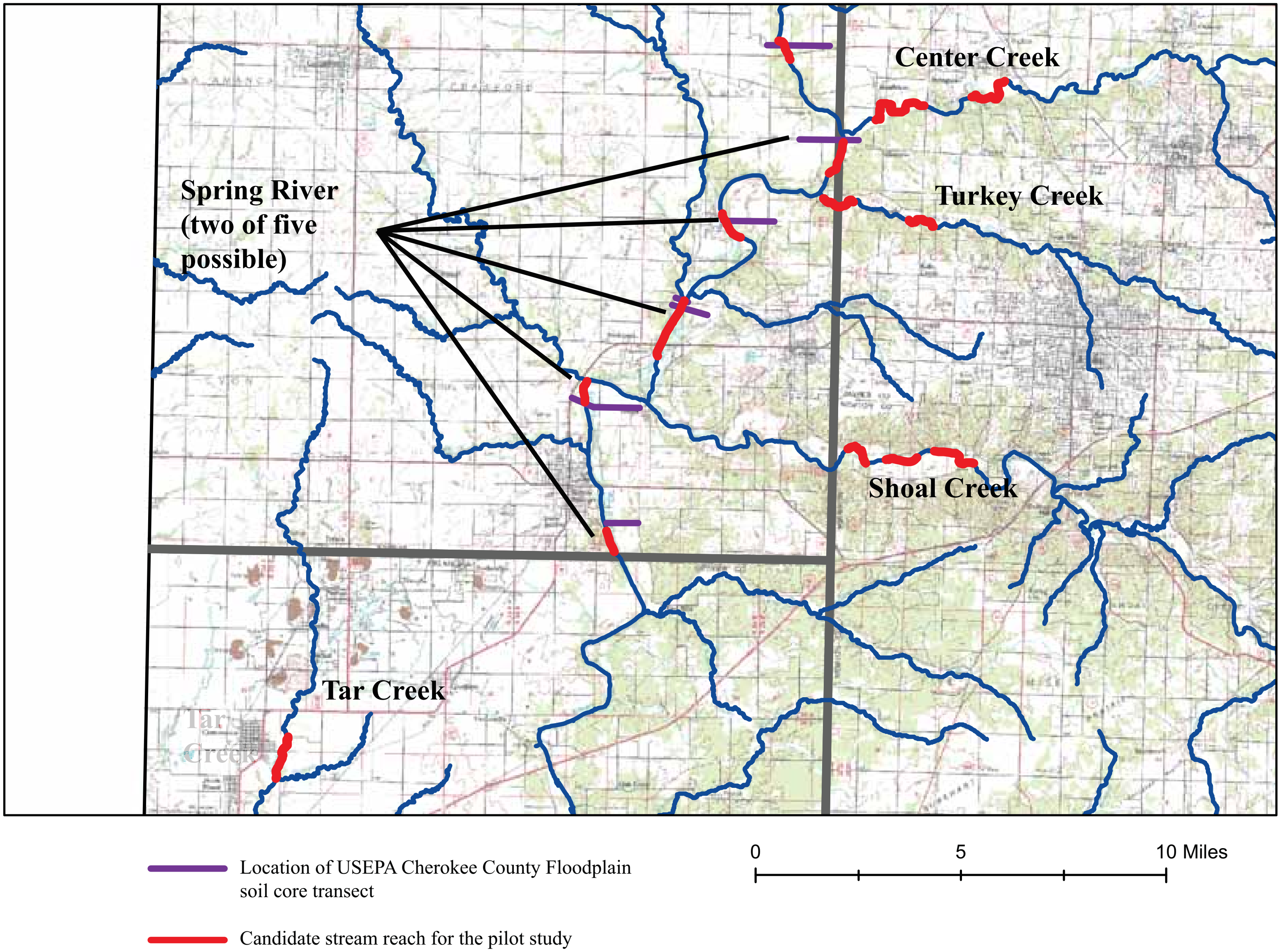
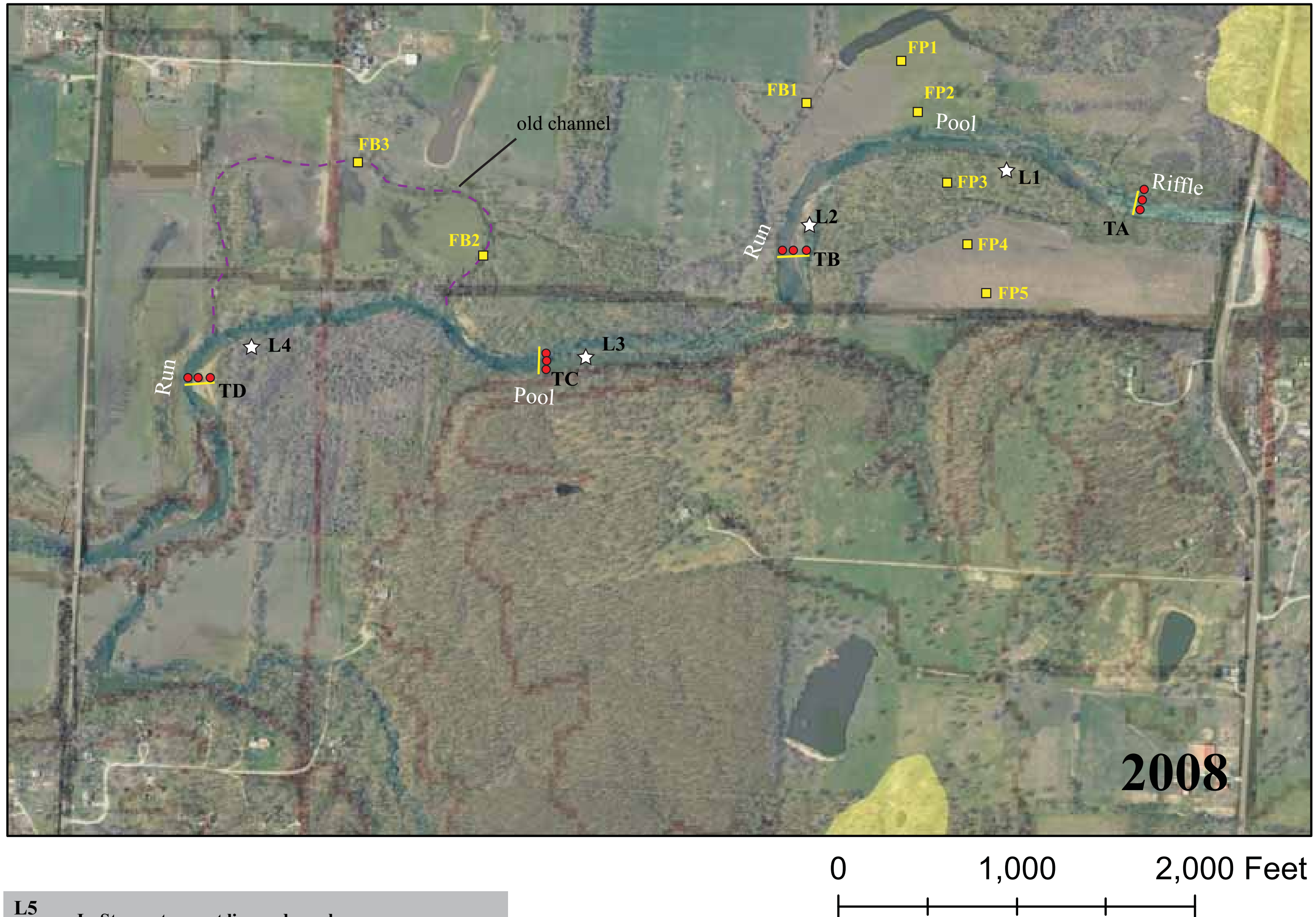


Figure 1. Location of candidate stream reaches to be investigated in the Tri-state Mining District (TSMD)



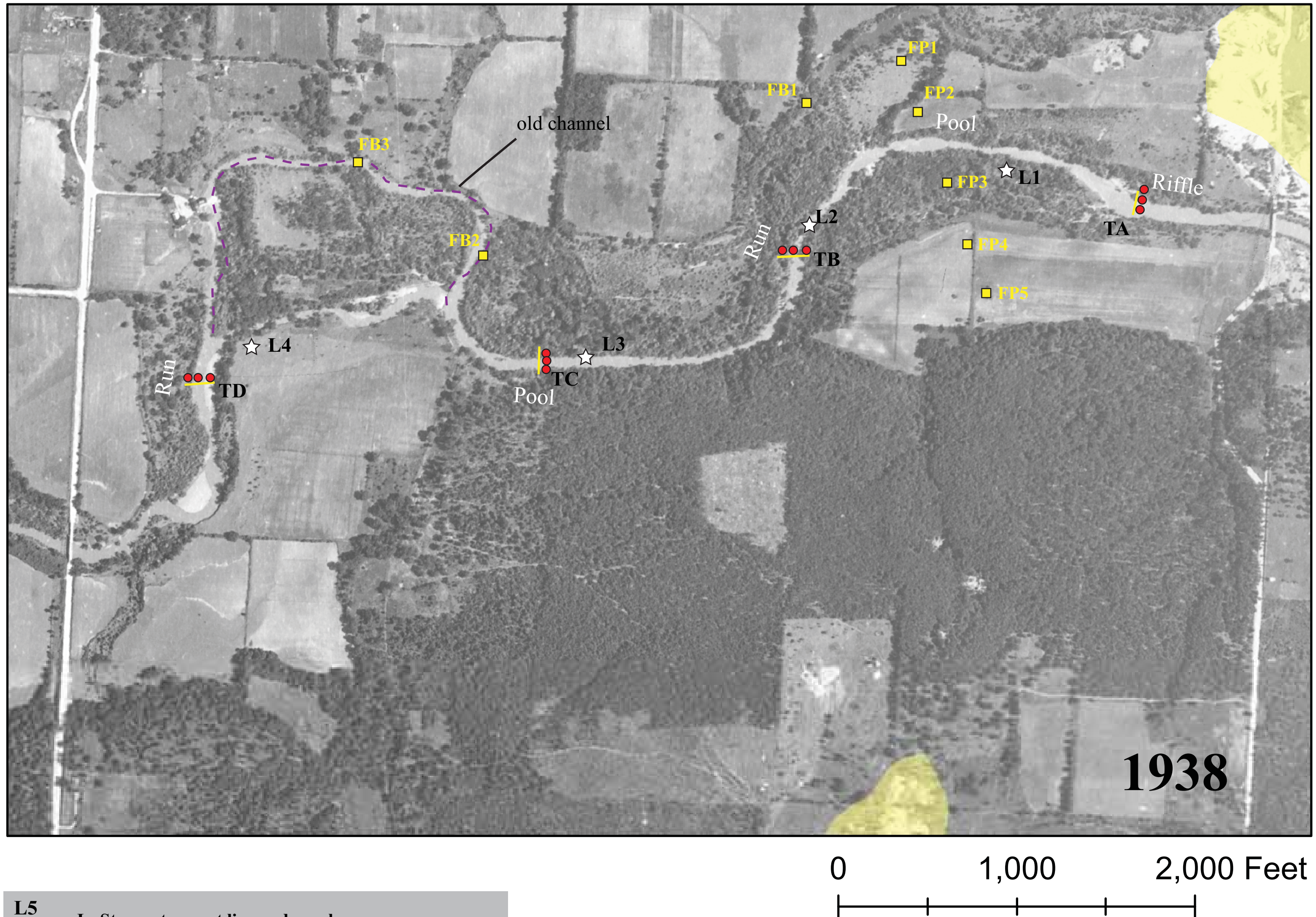
L5 — **In-Stream transect line and number**

● **In-stream sample site**

L5 ☆ **Longitudinal stream sample site and number**

FP1 ■ **Floodplain core site and number (FP= regular sample, FB=bias sample)**

Figure 2. Theoretical layout of in-channel transect and floodplain core sample sites along a candidate representative study reach along Center Creek. Imagery from the 2008 U.S. Department of Agriculture National Agriculture Imagery Program (NAIP).



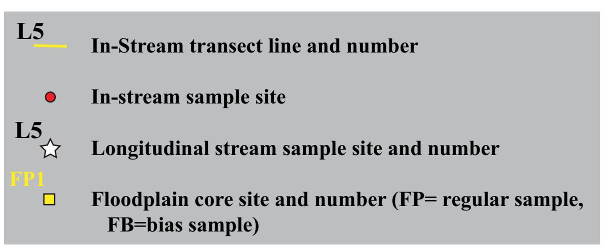
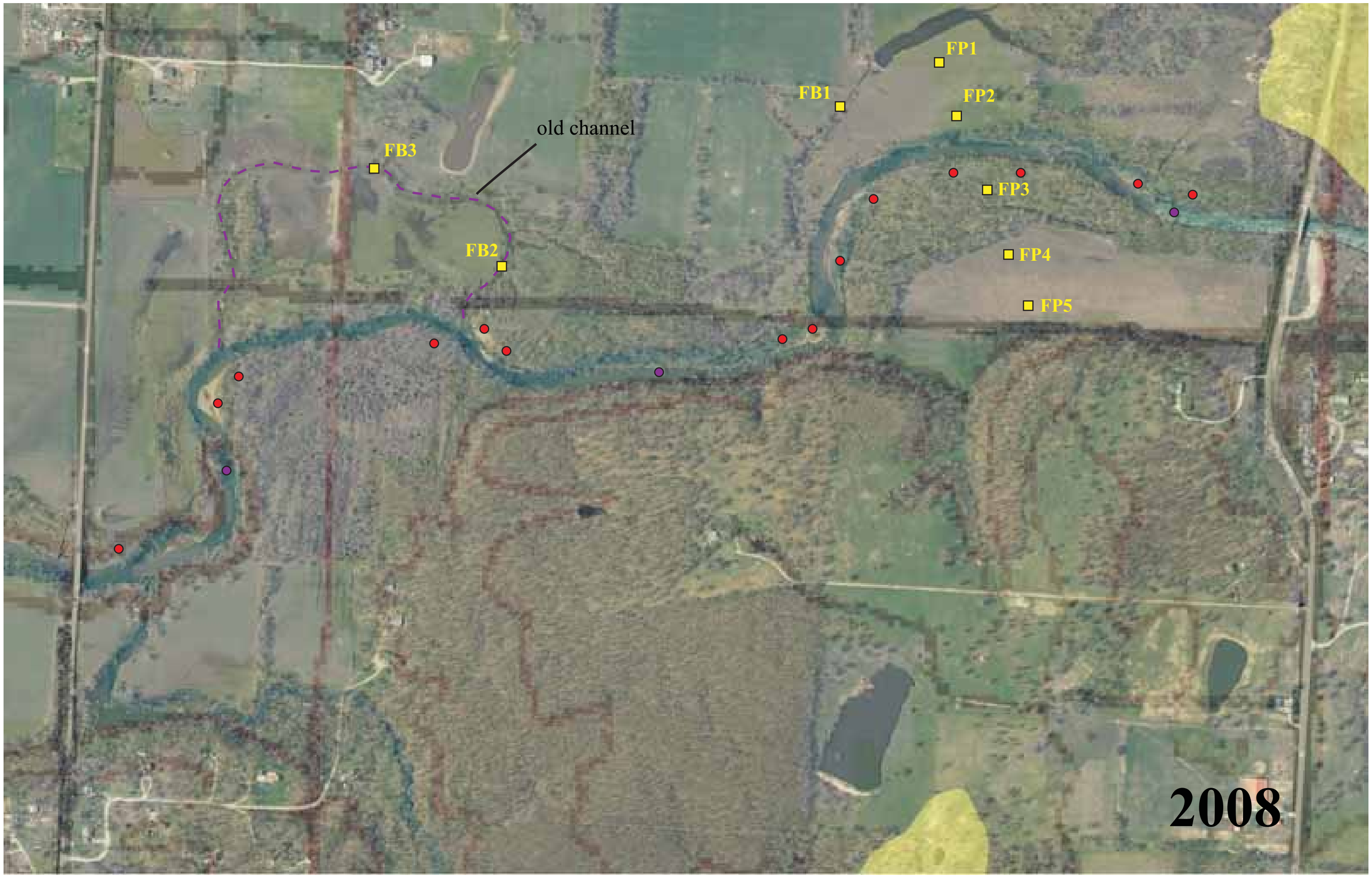


Figure 2--Continued. Theoretical layout of in-channel transect and floodplain core sample sites along a candidate representative study reach along Center Creek. Imagery from the U.S. Soil Conservation Service (1938).



In-channel bias sample site

In-stream bias sample site

Floodplain core site and number (FP= regular sample, FB=bias sample)

Figure 3. Theoretical layout of in-channel bias and floodplain core sample sites along a candidate representative study reach along Center Creek. Imagery from the 2008 U.S. Department of Agriculture National Agriculture Imagery Program (NAIP).

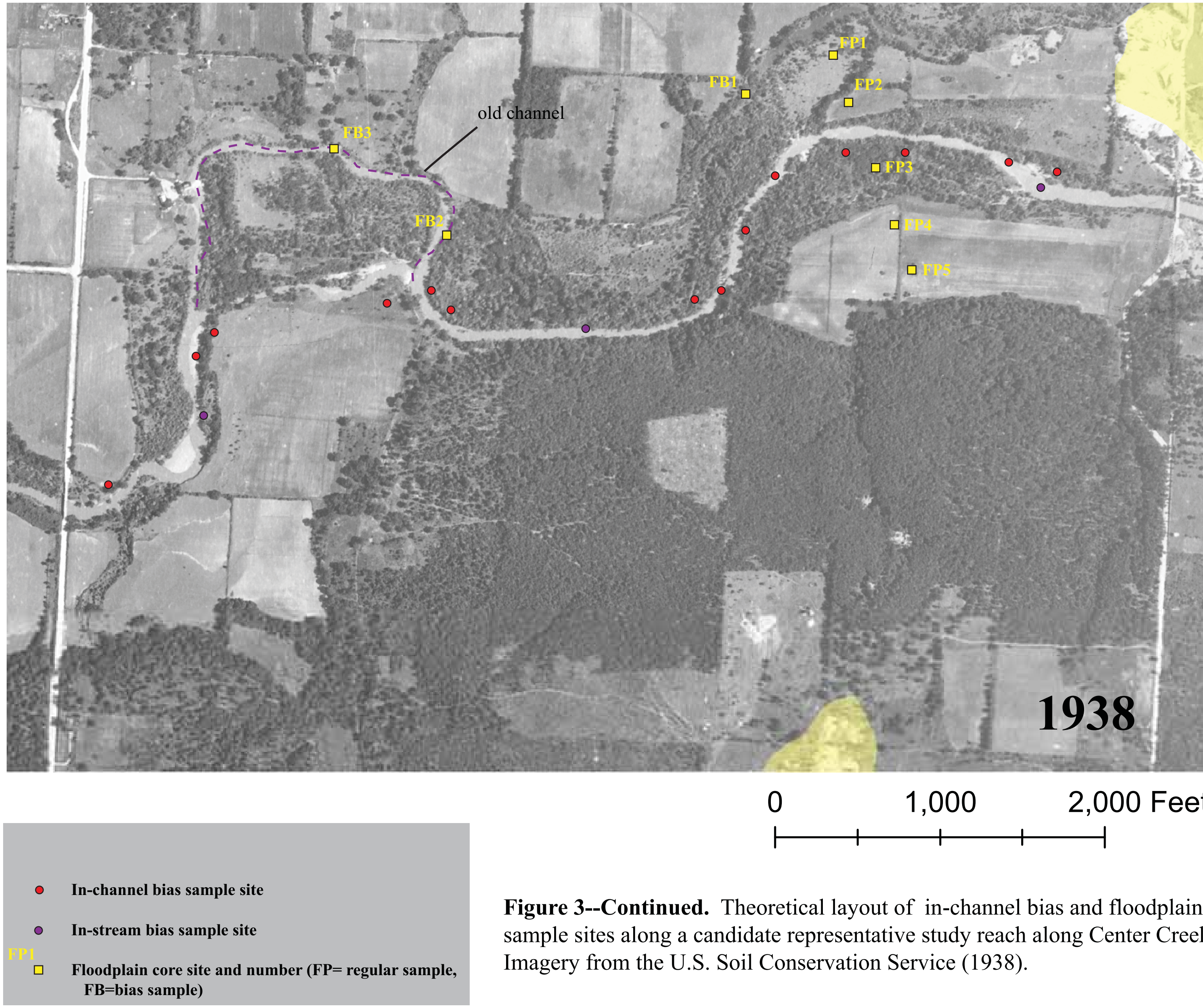


Figure 3--Continued. Theoretical layout of in-channel bias and floodplain core sample sites along a candidate representative study reach along Center Creek. Imagery from the U.S. Soil Conservation Service (1938).

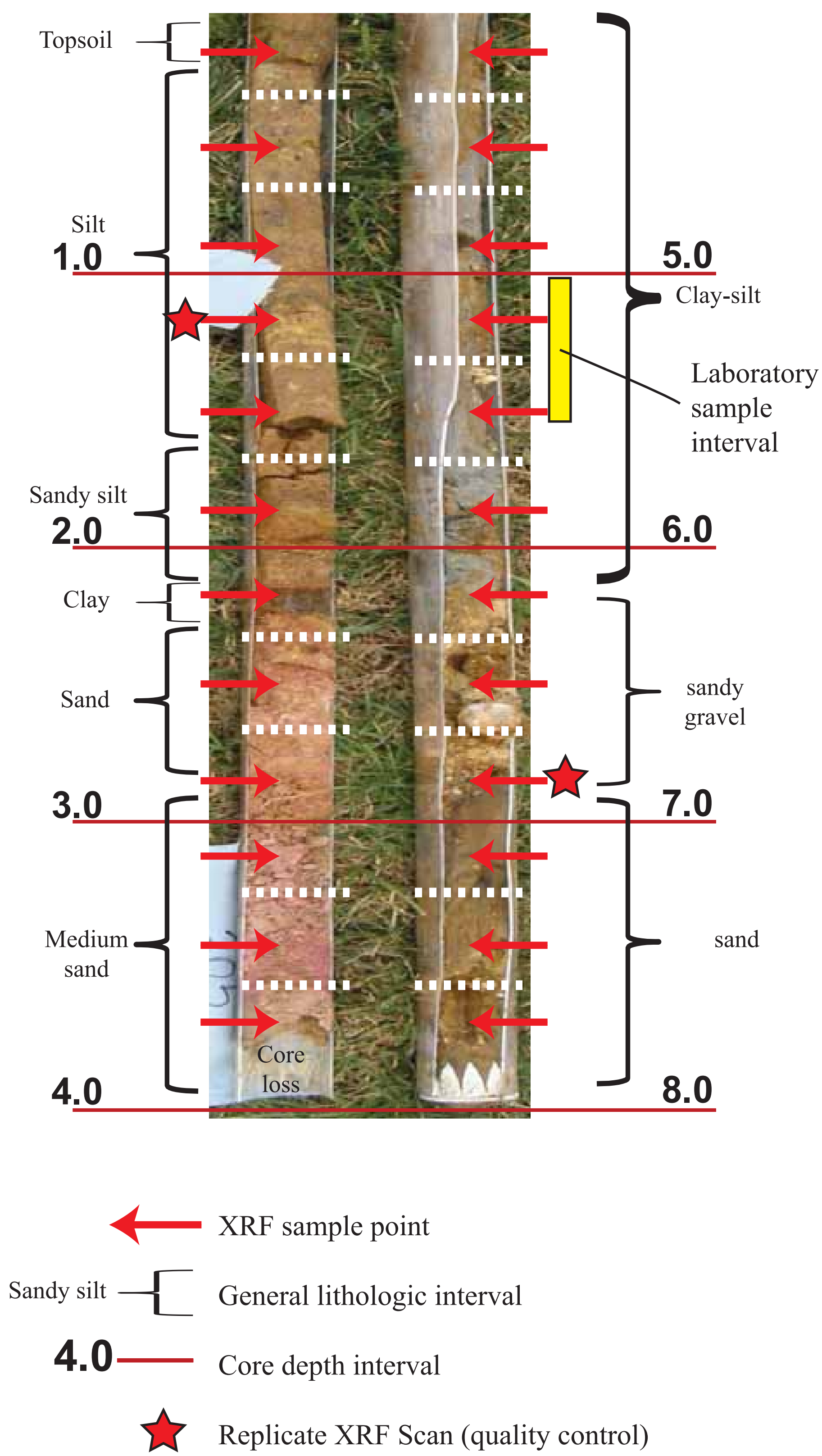


Figure 4. Generalized X-Ray fluoroscence (XRF) screening approach for a sediment core.