

Advanced Screening-Level Ecological Risk Assessment (SLERA) for Aquatic Habitats within the Tri-State Mining District, Oklahoma, Kansas, and Missouri

Draft Final Technical Report

Submitted To:

Gary Baumgarten
U.S. Environmental Protection Agency
Region 6, 1445 Ross Avenue
Dallas, Texas 75202

Mark Doolan
U.S. Environmental Protection Agency
Region 7, 901 North 5th Street
Kansas City, Kansas 66101

David Drake
U.S. Environmental Protection Agency
Region 7, 901 North 5th Street
Kansas City, Kansas 66101

Jim Dwyer
U.S. Fish and Wildlife Service
101 Park DeVille Drive, Suite A
Columbia, Missouri 65203-0057

Submitted – October, 2009 (Revised May, 2010) – by:

Donald D. MacDonald¹, Christopher G. Ingersoll², Meara Crawford¹, Heather Prencipe¹, John M. Besser², William G. Brumbaugh², Nile Kemble², Thomas W. May², Christopher D. Ivey², Melissa Meneghetti¹, Jesse Sinclair¹, and Margaret O’Hare³

¹**MacDonald Environmental Sciences Ltd.**
#24 - 4800 Island Highway North
Nanaimo, British Columbia V9T 1W6

²**United States Geological Survey**
4200 New Haven Road
Columbia, Missouri 65201

³**CH2M Hill**
Suite 10 - 12377 Merit Drive
Dallas, Texas 75251

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List of Acronyms

$\mu\text{g/L}$	micrograms per liter
$\mu\text{g/kg}$	micrograms per kilogram
AE	assessment endpoint
Ag	silver
Al	aluminum
AoI	area of interest
As	arsenic
ASTM	American Society for Testing and Materials
AVS	acid volatile sulfide
BEHP	bis(2-ethylhexy) phthalate
BERA	baseline ecological risk assessment
CBR	critical body residue
CCC	criterion continuous concentration
Cd	cadmium
CERC	Columbia Environmental Research Center
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	contaminant of concern
COI	chemical of interest
COPC	chemical of potential concern
Cr	chromium
CSM	conceptual site model
Cu	copper
-d	-day
DERA	detailed ecological risk assessment
DDT	dichlorodiphenyl-trichloroethane
DOC	dissolved organic carbon
DW	dry weight
ESB-TU _{FCV}	equilibrium partitioning-based sediment benchmarks toxic unit (final chronic value)
ESB-TU	equilibrium partitioning-based sediment benchmarks toxic unit
EPC	exposure point concentration
ERA	ecological risk assessment
ESRI	Environmental Systems Research Institute
Fe	iron
f_{OC}	fraction total organic carbon
FS	feasibility study
GIS	geographic information system
HaLs	<i>Hyalella azteca</i> <i>Lampsilis siliquoidea</i>
HCH	hexachlorocyclohexane
Hg	mercury
HN-D	high non-detect
HMW-PAH	high molecular weight-polycyclic aromatic hydrocarbon

HQ	hazard quotient
ICAP	inductively-coupled argon plasma
ICP-MS	inductively-coupled plasma - mass spectrometry
IT	invertebrate tissue
km	kilometer
k_{ow}	octanol water partition coefficient
KS	Kansas
LMT	live mussel taxa
LOEL	lowest observed effect level
LSR	Lower Spring River Sub-Basin
max	maximum
ME	measurement endpoint
MESL	MacDonald Environmental Sciences Ltd.
min	minimum
mg/L	milligrams per liter
MO	Missouri
n	number of samples
NB	no benchmark
N-D	non detect
ND	no data
Ni	nickel
NOAEL	no observed adverse effect level
NOEL	no observed effect level
NPL	National Priority List
NRDAR	natural resource damage assessment and restoration
NR	Neosho River Sub-Basin
OC	organic carbon
OK	Oklahoma
OU	operational unit
PAH	polycyclic aromatic hydrocarbon
Pb	lead
PCB	polychlorinated biphenyl
PEC	probable effect concentration
PEC-Q	probable effect concentration-quotient
PIoT	predicted incidence of toxicity
PRGs	preliminary remediation goal
PW	pore water
PWTT	pore-water toxicity threshold
r^2	coefficients of determination
RAO	remedial action objective
RCRA	Resource Conservation and Recovery Act
RI	remedial investigation
RI/FS	remedial investigation/feasibility study
RQ	risk question
SD	standard deviation

SEM	simultaneously extracted metal
SEM-AVS	simultaneously extracted metal minus acid volatile sulfide
SEV	screening ecotoxicity value
SLERA	screening-level ecological risk assessment
SMDP	scientific management decision point
SQG	sediment quality guideline
SSTT	site-specific toxicity threshold
STT	sediment toxicity threshold
STT-Q	sediment toxicity threshold-quotient
SVOC	semi-volatile organic compound
SW	surface water
TEC	threshold effect concentration
TEMT	threatened and endangered mussel taxa
TMT	total number of mussel taxa
TSMD	Tri-State Mining District
TSV	toxicity screening value
TU	toxic unit
UMSR	Upper and Middle Spring River Sub-Basin
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VOC	volatile organic compound
WQC	water quality criteria
WW	wet weight
XRF	x-ray fluorescence
Zn	zinc

Glossary of Terms

a priori – Designated in advance.

Adverse effects – Any injury (i.e., loss of chemical or physical quality or viability) to any ecological or ecosystem component, up to and including at the regional level, over both long and short terms.

Anthropogenic – Effects, processes, objects, or materials derived from human activities, as opposed to those occurring in natural environments without human influences.

Aquatic-dependent wildlife – Wildlife species that are dependent on aquatic organisms and/or aquatic habitats for survival, including fish, amphibians, reptiles, birds, and mammals (e.g., egrets, herons, kingfishers, osprey, racoons, mink, otter).

Aquatic ecosystem – All the living and nonliving material interacting within an aquatic system (e.g., pond, lake, river, ocean).

Aquatic invertebrates – Animals without backbones that utilize habitats in freshwater, estuarine, or marine systems.

Aquatic organisms – The species that utilize habitats within aquatic ecosystems (e.g., microorganisms, aquatic plants, invertebrates, fish, amphibians, and reptiles).

Area of Interest – A portion of the study area that is targeted for investigation in a screening-level or baseline ecological risk assessment.

Autotrophic (self nourishing) – Organisms that are able to synthesize food from simple inorganic substances (e.g., carbon dioxide, nitrogen, and phosphorus) and the sun's energy. pond, lake, river, ocean).

Benthic – The lowest level of a body of water, such as an ocean or a lake inhabited by organisms that live in close relationship with (if not physically attached to) the ground, called benthos or benthic organisms.

Benthic invertebrate community – The assemblage of aquatic invertebrates that utilize the bottom substrate (e.g., sediment) within an aquatic ecosystem.

Bioaccumulation – The net accumulation of a substance by an organism as a result of uptake from all environmental sources.

Bioaccumulative substances – The chemicals that tend to accumulate in the tissues of aquatic or terrestrial organisms.

Biomass – The total mass of living biological material in a given area or of a biological community or group.

Chemicals of potential concern – The toxic or bioaccumulative substances that occur in environmental media at levels that could adversely affect ecological receptors.

Chronic toxicity – The response of an organism to long-term exposure to a chemical substance. Among others, the responses that are typically measured in chronic toxicity tests include lethality, decreased growth, and impaired reproduction.

Chronic toxicity threshold – The concentration of a substance above which adverse effects on sediment-dwelling organisms are likely to occur in longer-term toxicity tests.

Contaminants of concern – The toxic or bioaccumulative substances that occur at concentrations that are sufficient to cause or substantially contribute to adverse effects on sediment-dwelling organisms.

Contaminated sediment – Sediment that contains chemical substances at concentrations that could harm microbial, benthic invertebrate, plant, fish, avian or mammalian communities.

Detection limit – The lowest concentration of a substance that can be differentiated from zero with a 99% certainty.

Dissolved organic carbon – The organic matter in a solution that is able to pass through a filter (filters generally range in size between 0.7 and 0.22 μm).

Divalent metals – A metal whose atoms are each capable of chemically combining with two atoms of hydrogen (i.e., cadmium, copper, lead, nickel, zinc).

Ecosystem – All the living (e.g., plants, animals, and humans) and nonliving (rocks, sediments, soil, water, and air) material interacting within a specified location in time and space.

Endpoint – A measured response of a receptor to a stressor. An endpoint can be measured in a toxicity test or a field survey.

Epibenthic species – The species that live on the surface of bottom sediments.

Exposure – Co-occurrence of or contact between a stressor (e.g., chemical substance) and an ecological component a receptor (e.g., aquatic organism).

Final Chronic Value – An estimation of the concentration of the toxicant corresponding to geometric means of a No Observed Effects Concentration (NOEC) and the Lowest Observed Effects Concentration (LOEC).

Heterotrophic (other nourishing) – Organisms that utilize, transform, and decompose the materials that are synthesized by autotrophic organisms (i.e., by consuming or decomposing autotrophic and other heterotrophic organisms).

Injury – A measurable adverse change, either long or short-term, in the chemical or physical quality or the viability of a natural resource resulting either directly or indirectly from exposure to a discharge of oil or release of a hazardous substance, or exposure to a product of reactions resulting from the discharge to oil or release of a hazardous substance.

Macrophyte – An individual alga large enough to be seen easily with the unaided eye.

Mean PEC-Q – Mean Probable Effects Concentration Quotient, which was calculated using the procedure that was established by USEPA (2000a). Using this method, a PEC-Q was first determined for each metal for which a reliable PEC was available. Then, an average PEC-Q for metals was calculated by summing the PEC-Qs of each metal and dividing by the number of metals that were included in the calculation. PEC-Qs were also calculated for total PAHs and total PCBs. Finally, the mean of the average PEC-Q for metals, the PEC-Q for PAHs, and the PEC-Q for PCBs was determined for each sediment sample (termed the mean PEC-Q).

Metric – A variable that is measured to provide information on the status of an indicator of environmental quality conditions (e.g., the concentration of cadmium in sediment).

Organic matter – Matter which has come from a recently living organism; is capable of decay, or the product of decay; or is composed of organic compounds.

Periphyton – A complex matrix of algae, cyanobacteria, heterotrophic microbes, and detritus that is attached to submerged surfaces in most aquatic ecosystems.

Pore water – The water that occupies the spaces between sediment particles.

Predictive ability – A measure of the ability of a toxicity threshold to correctly classify a sediment sample as toxic or not toxic, based on data independent of those used to derive the toxicity threshold. High predictive ability occurs if the incidence of toxicity was < 20% below the toxicity thresholds for all endpoints, if the incidence of toxicity was > 50% above the toxicity threshold for the most sensitive endpoint, and the overall correct classification rate was ≥ 80 for the most sensitive endpoint.

Probable effect concentration – Concentration of a chemical in sediment above which adverse biological effects are likely to occur.

Protozoa – Single-celled eukaryotes (organisms whose cells have nuclei) that commonly show characteristics usually associated with animals, most notably mobility and heterotrophy.

Receptor – A plant or animal that may be exposed to a stressor.

Reference envelope - A statistical representation of data from reference locations that is used to evaluate data for test sites.

Reference sample – A comparatively uncontaminated sample used for comparison to samples from contaminated sites in environmental monitoring studies. It can be from the least impacted (or unimpacted) area of the site or from a nearby site that is ecologically similar, but not affected by the contaminants at the site under investigation (often incorrectly referred to as a control).

Reliability – A measure of accuracy of a toxicity threshold in terms of correctly classifying a sediment sample as toxic or not toxic, based on the data that were used to derive the toxicity threshold. A threshold was considered reliable if < 20% incidence of toxicity was observed below the toxicity threshold, > 50% incidence of toxicity was observed above the toxicity threshold, and the overall correct classification rate was $\geq 80\%$.

Remedial action objectives – Objectives intended to describe the narrative intent of any remedial actions that are undertaken to mitigate risks to the ecological receptors that are exposed to contaminants of concern.

Remediation goal – Concentration limits for chemical in environmental media that are anticipated to protect human health or the environment.

Riparian – Pertaining to the banks of a natural water course.

Risk – The probability or likelihood an adverse effect will occur.

Risk assessor – The person who analyzes information from a cleanup/Superfund site to determine if there is the possibility of harm to the local ecosystem.

Risk characterization – An element of conventional risk assessment procedure. A systematic, scientific assessment of potential adverse health effects resulting from exposure to hazardous agents or situations which uses information from the site characterization.

Risk management – Actions, including monitoring, designed to prevent or mitigate risks to human health or the environment caused by contamination at a site.

Sediment – Particulate material that usually lies below the ponds, lakes, stream, and rivers.

Sediment-associated contaminants – Contaminants that are present in sediments, including whole sediments or pore water.

Sediment chemistry data – Information on the concentrations of chemical substances in whole sediments or pore water.

Sediment-dwelling organisms – The organisms that live in, on, or near bottom sediments, including both epibenthic and infaunal species.

Sediment quality guidelines – Chemical benchmark that is intended to define the concentration of sediment-associated contaminants that is associated with a high or a low probability of observing harmful biological effects or unacceptable levels of bioaccumulation, depending on its purpose and narrative intent.

Simultaneously extracted metals – Divalent metals - commonly cadmium, copper, lead, mercury, nickel, and zinc - that form less soluble sulfides than does iron or manganese and are solubilized during the acidification step (0.5M HCl for 1 hour) used in the determination of acid volatile sulfides in sediments.

Threshold effect concentration – Concentration of a chemical in sediment below which adverse biological effects are unlikely to occur.

T_{10} – Low risk threshold associated with a 10% reduction in a measured endpoint.

T_{20} – High risk threshold associated with a 20% reduction in a measured endpoint.

Threshold effect concentration – Concentration of a chemical in sediment below which adverse biological effects are unlikely to occur.

Toxic – Capable of causing injury or death. In this study, the toxicity of sediment samples was evaluated using a reference envelope approach.

Toxicity threshold – Chemical benchmark for water or sediment quality which define the concentration of chemicals of potential concern that are associated with high or low probabilities of observing harmful biological effects, depending on the narrative intent; or, a chemical benchmark that is intended to define the concentration of a substance in the tissues of fish or invertebrates that will protect wildlife against effects that are associated with dietary exposure to hazardous substances.

Trophic level – The position that an organism occupies in a food chain, food web, or food pyramid, as pertaining to nutrition.

Trustee – Any Federal natural resources management agency designated in the National Contingency Plan and any State agency designated by the Governor of each State, pursuant to Section 107(f)(2)(B) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), that may prosecute claims for damages under Section 107(f) or 111(b) of CERCLA; or an Indiana tribe, that may commence an action under Section 126(d) of CERCLA.

Type I Error – Incorrectly classifying a not toxic sample as toxic. Also referred to as a false positive.

Type II Error – Incorrectly classifying a toxic sample as not toxic. Also referred to as a false negative.

Whole sediment – Sediment and associated pore water.

Executive Summary

ES1.0 Introduction

The Tri-State Mining District (TSMD) is a historical lead and zinc mining area that includes portions of Kansas, Missouri, and Oklahoma. The TSMD was one of the world's foremost lead and zinc mining areas, yielding about 460 million tons of ore between 1885 and 1970 (Black and Veatch Special Projects Corp. 2006). The lead and zinc deposits within the TSMD, an area of about 500 square miles, were associated with the geologic region known as the Ozark Plateau. The ore deposits were typically accessed using underground mining methods, with recovered ore typically crushed on site and concentrated using gravity separation and/or floatation. These two ore-concentration processes resulted in the production of sand- and gravel-sized particles called chat (i.e., coarse tailings) and sand- and silt-sized particles called tailings. Further smelting and refining of these ore concentrates was conducted at various locations within the study area or elsewhere. Historical mining activities in the TSMD have resulted in contamination of surface water, groundwater, sediments, and/or floodplain soils in the Neosho River and Spring River basins by lead, zinc, and other heavy metals.

In response to public concerns regarding the potential for adverse effects on human health and ecological receptors associated with exposure to site-related chemicals of interest (COIs), USEPA and its partners have conducted numerous investigations within the study area to provide the data and information needed to evaluate the nature and extent of contamination in the study area, to assess risks to human health associated with exposure to contaminants, and to evaluate risks to ecological receptors utilizing habitats within the TSMD. This document describes the results of two ecological risk assessments (ERAs) that were conducted to determine if exposure to contaminants in aquatic habitats within the TSMD posed potential risks to ecological receptors, including:

- A screening-level ERA (SLERA) to evaluate potential risks to aquatic organisms utilizing aquatic habitats in the study area; and,
- A detailed ERA (DERA) to assess risks to benthic invertebrates utilizing habitats within the study area.

Together, these two ERAs are referred to as the Advanced SLERA for the TSMD. The Advanced SLERA is not intended to obviate the need for baseline ERAs (BERAs) of the TSMD, but rather to provide risk managers with additional information for identifying in-stream sources of contaminants, evaluating candidate source control measures, and assessing other risk management options in the near term. In addition, the information contained in this document is intended to assist the Natural Resources Trustees in the development of restoration goals for aquatic habitats in the TSMD.

It is important to note that the SLERA and DERA were conducted in general accordance with USEPA (1997a) guidance. Accordingly, the results of these ERAs can be integrated into

ongoing remedial investigations (RIs; e.g., those underway in Cherokee, Jasper, and/or Newton counties) and/or RIs that may be conducted in the future (e.g., OU-5 of the Tar Creek Site).

ES1.1 Study Objectives

The goal of this study was to assess the risks to ecological receptors exposed to environmental media in aquatic habitats within the TSMD. The primary objectives of this study were to:

- Evaluate the potential risks posed to ecological receptors exposed to abiotic media within aquatic habitats in the TSMD (i.e., conduct a SLERA for aquatic habitats);
- Evaluate risks to benthic invertebrates utilizing aquatic habitats in the TSMD (i.e., conduct a DERA for benthic invertebrates);
- Provide the information needed by risk managers to determine the need for additional source control measures and to establish candidate clean-up goals for the site; and,
- Provide the information needed by the Natural Resources Trustees to identify restoration goals for the site.

ES1.2 Study Approach

A step-wise approach was used to evaluate risks to ecological receptors utilizing aquatic habitats within the TSMD. More specifically, the study approach involved the following steps:

- Compiling information that describes current conditions within the watershed (i.e., data collected between 2002 and 2009; which is considered to represent current conditions);
- Conducting a screening-level problem formulation and ecological effects evaluation;
- Completing a screening-level exposure estimate and risk calculation;
- Developing a detailed problem formulation to support evaluation of risks to the benthic invertebrate community;
- Establishing assessment and measurement endpoints for evaluating risks to the benthic invertebrate community and refining the preliminary analysis plan to direct the risk assessment;
- Evaluating risks to benthic invertebrates using multiple lines-of-evidence; and,

- Formulating preliminary remedial action objectives to guide risk management activities.

These steps are in general accordance with the ERA framework and the eight-step process for conducting an ERA described in *Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessment* (USEPA 1997a). Detailed descriptions of the procedures used in the SLERA are described in Chapters 3 and 4 of this document. Chapters 5, 6, and 7 describe the general approach and detailed procedures that were used in the DERA to evaluate the nature, severity, and areal extent of risks to benthic invertebrates utilizing habitats in the study area. The results of the DERA are presented in Chapter 8, while uncertainties associated with the assessment are discussed in Chapter 9. Preliminary remedial action objectives for the TSMD are presented in Chapter 10. This data compilation and analysis may also be useful to the Natural Resources Trustees as they conduct natural resource damage assessments and evaluate restoration goals.

ES1.3 Screening-Level Ecological Risk Assessment

A SLERA was conducted to determine if exposure to contaminants in abiotic media poses potential risks to ecological receptors utilizing aquatic habitats in the TSMD. Screening-level problem formulation involved describing the environmental setting, identifying suspected contaminants, evaluating contaminant transport and fate, assessing ecotoxicology, identifying potential receptors and potentially-complete exposure pathways, and establishing assessment and measurement endpoints. Evaluation of the available information indicated that metals (e.g., cadmium, lead, and zinc) were the principal COIs in the study area and that several other substances could be identified as additional COIs [i.e., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides, and various semi-volatile organic compounds (SVOCs)]. The potentially-complete exposure pathways included direct exposure to surface water, sediment, and pore water. As the organisms that utilize aquatic habitats were identified as the receptors potentially at risk, the assessment endpoint that was evaluated in the SLERA included:

- Survival, growth, and reproduction of ecological receptors associated with exposure to contaminants in surface water, sediment, and/or pore water.

Toxicity screening values (TSVs) were identified for each of the three abiotic media types, as part of the screening level ecological effects evaluation. More specifically, ambient water quality criteria (i.e., criteria continuous concentrations; USEPA 1999; 2006a) or functionally-equivalent values (e.g., water quality guidelines; CCME 2002) were selected for evaluating surface-water and pore-water chemistry data. Consensus-based threshold effect concentrations (MacDonald *et al.* 2000a) or sediment quality benchmarks with similar narrative intent (MacDonald *et al.* 2008) were selected to evaluate sediment chemistry data. In all cases, the TSVs that were selected were intended to provide conservative estimates of no observed adverse effect levels (NOAELs) for the COIs.

To support this evaluation, data and information from multiple sources were acquired, reviewed, and evaluated. The data that met the evaluation criteria were compiled in a project database in MS Access format. Following translation into database format, the data were verified using a combination of electronic and manual procedures. Subsequently, the database was audited to identify potential outliers (which were further checked to determine if the data were correct), assure data completeness, examine qualifier codes, and verify sample identification numbers. The audited watershed database was considered a reliable tool for evaluating risks to ecological receptors in the study area.

Potential exposure of ecological receptors to site-related contaminants was evaluated using data on the concentrations of suspected contaminants in three abiotic media, including surface water, sediment, and pore water. The surface-water chemistry data (n = up to 694, depending on the analyte) provided broad spatial coverage of the study area and were considered to be sufficient to support the SLERA. Similarly, the available sediment-chemistry data (n = up to 1156, depending on the analyte) were considered to provide an adequate basis for assessing the potential risk to ecological receptors. While the data set for pore-water chemistry was limited (n = up to 70, depending on the analyte), the spatial coverage was considered to be sufficient to support a screening-level assessment. For all media types, the exposure point concentration (EPC) was estimated using the highest concentration of each substance measured in the study area (i.e., maximum values; USEPA 1997).

The screening-level risk calculations involved determination of hazard quotients (HQs; where $HQ = EPC \div TSV$) for each contaminant in each environmental medium. An HQ of < 1.0 was considered to indicate that exposure to the measured concentrations of the contaminant or contaminant mixture [e.g., sum equilibrium partitioning-based sediment benchmarks-toxic units (\sum ESB-TUs); sum simultaneously extracted metals minus acid volatile sulfides (\sum SEM-AVS); USEPA 2003a; 2005] would not pose potential risks to ecological receptors. The results of this evaluation showed that the levels of one or more substances in surface water, sediment, and pore water exceeded the selected TSVs. Therefore, the available information indicated that there was a potential for adverse effects on ecological receptors (via all three of these exposure routes) and that a more thorough assessment was needed to evaluate risks to ecological receptors in the TSMD. The substances that were identified as chemicals of potential concern (COPCs) for further evaluation included metals, PAHs, PCBs, organochlorine pesticides, various SVOCs, and nutrients (i.e., ammonia, chlorine; Table ES-1).

ES1.4 Detailed Ecological Risk Assessment for the Benthic Invertebrate Community

The results of the SLERA indicated that the concentrations of contaminants in surface water, sediment, and/or pore water posed potential risks to ecological receptors utilizing aquatic habitats in the TSMD. For this reason, a DERA was undertaken to further evaluate risks to ecological receptors associated with exposure to site-related COPCs in the TSMD. The

results of conceptual site modeling indicated that a variety of ecological receptor groups could be adversely affected by exposure to COPCs in aquatic and riparian habitats within the study area, including microbiota, aquatic and terrestrial plants, aquatic and terrestrial invertebrates, fish, amphibians, reptiles, aquatic-dependent birds, and aquatic-dependent mammals. While risks to all of these receptor groups may ultimately need to be evaluated [and, in some cases, were evaluated previously; See Dames and Moore (1993) and Black and Veatch Special Projects Corp. (1998) for additional information], this DERA was focused on evaluating contemporary risks (i.e., 2002 to 2009) to the benthic invertebrate community posed by exposure to COPCs in surface water, sediment, and pore water within the TSMD.

Information on six lines-of-evidence was used to determine if the survival, growth, or reproduction of benthic invertebrates (i.e., the assessment endpoint) have been adversely affected or are likely to have been adversely affected by exposure to contaminated surface water or sediments in the TSMD relative to reference conditions. The six lines-of-evidence that were considered in the assessment included:

- Surface-water chemistry;
- Sediment chemistry;
- Sediment toxicity;
- Pore-water chemistry;
- Invertebrate-tissue chemistry; and,
- Freshwater mussel species richness.

The measurement endpoints in this assessment included: the concentrations of COPCs in surface water; the concentrations of COPCs in sediment; the concentrations of COPCs in pore water; the survival and biomass of amphipods, *Hyalella azteca*, in 28-d sediment toxicity tests; the survival and biomass of midges, *Chironomus dilutus*, in 10-d sediment toxicity tests; the survival and biomass of freshwater mussels, *Lampsilis siliquoidea*, in 28-d sediment toxicity tests; the concentrations of COPCs in invertebrate tissues, and species richness of freshwater mussels.

Sediment-chemistry data were available for 1162 samples collected within the TSMD. By comparison, surface-water chemistry (n = 537), pore-water chemistry (n = 96), sediment toxicity (n = 76), invertebrate-tissue chemistry (n = 239), mussel taxa richness (n = 16) data were somewhat less robust. Accordingly, sediment chemistry was used as a primary line-of-evidence for evaluating risks to the benthic community. For this line of evidence, risks to benthic invertebrates were evaluated using site-specific toxicity thresholds (SSTTs) derived using matching sediment chemistry and sediment toxicity data from the study area. These SSTTs were demonstrated to provide a reliable basis for classifying sediment samples from the study area as toxic and not toxic.

The results of this assessment indicated that exposure to COPCs in sediment from the TSMD posed low risks to benthic invertebrate communities at 51% of the locations (596 of 1162) that were sampled within the study area (Figure ES-1; Table ES-2). By comparison, the

concentrations of cadmium, lead, and/or zinc in surficial sediments were sufficient to pose moderate risks to benthic invertebrates at about 9% (110 of 1162) of the sampling stations within the TSMD. High risks to the benthic invertebrate community were indicated for 39% (456 of 1162) of the locations sampled (Table ES-2). Of the 23 areas of interest (AoIs) that were evaluated, the locations with the highest proportions of sediment samples with COPC concentrations sufficient to pose high risks to the benthic invertebrate community were [note: sediment samples with sum probable effects concentration quotients for cadmium, lead, zinc ($\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$) of > 10.04 were classified as posing high risks to benthic invertebrates]:

- Short Creek AoI (100%; 44 of 44 samples);
- Middle Tar Creek AoI (100%; 52 of 52 samples);
- Lytle Creek AoI (95%; 39 of 41 samples);
- Empire Lake AoI (93%; 38 of 41 samples);
- Spring Brook AoI (93%; 14 of 15 samples);
- Elm Creek AoI (85%; 22 of 26 samples);
- Turkey Creek AoI (83; 40 of 48 samples);
- Lower Tar Creek AoI (81%; 88 of 108 samples);
- Beaver Creek AoI (51%; 33 of 65 samples);
- Shoal Creek AoI (49%; 55 of 112 samples);
- Lower Spring River AoI (48%; 32 of 66 samples);
- Willow Creek AoI (47%; 14 of 30 samples);
- Center Creek AoI (46%; 37 of 81 samples);
- Middle Spring River AoI (23%; 27 of 115 samples); and
- Upper Tar Creek AoI (21%; 8 of 39 samples).

Risks to the benthic invertebrate community were classified as moderate in the Cow Creek AoI [predicted incidence of toxicity (PIoT) of 15%; $n = 34$], Brush Creek AoI (PIoT of 14%; $n = 14$), and Lost Creek AoI PIoT of 12%; $n = 33$). The remaining AoIs (i.e., Upper Spring River, North Fork Spring River, Shawnee Creek, Warren Branch, and Neosho River) were all classified as posing low risks to benthic invertebrates, based on the measured concentrations of cadmium, lead, and zinc in surficial sediment samples (i.e., $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$; Table ES-2). Risks to the benthic invertebrate community were considered to be low for all of the reference sediment samples (Table ES-2). It is important to note that sediment hot spots may exist within AoIs that are considered to pose low risks to benthic invertebrates based on the frequency of exceedance of the selected toxicity thresholds.

Evaluation of the other five lines-of-evidence also indicated that risks to benthic invertebrates are elevated at numerous locations within the study area. More specifically, the available data confirmed that exposure to divalent metals in surface water posed moderate or high risks to benthic invertebrates in 17 of the 23 AoIs examined (Table ES-3; Figure ES-2). Similarly, examination of the available pore-water chemistry data indicated that exposure to a primary

risk driver (zinc) posed moderate or high risks in 12 of the 23 AoIs (Table ES-4; Figure ES-3). Furthermore, the incidence of toxicity to amphipods, midges, or mussels in laboratory toxicity tests (endpoints: survival or biomass) exceeded 50% in 8 of the 23 AoIs within the study area (Table ES-5; Figures ES-4 to ES-7). By comparison, invertebrate-tissue samples in 9 of the 16 AoIs had concentrations of metals sufficient to pose moderate or high risks to benthic invertebrates (Table ES-6; Figure ES-8). Finally, Angelo *et al.* (2007) reported that streams draining heavily mined areas exhibited depauperate (or fully extirpated) native mussel assemblages and correspondingly elevated concentrations of cadmium, lead, and zinc in water, sediment, and bivalve tissue. Collectively, these five additional lines-of-evidence confirmed that exposure to metal-contaminated surface water, sediment, and pore water posed elevated risks to benthic invertebrates throughout a large portion of the TSMD (Table ES-7).

The results of the biological investigations conducted during site investigations indicated that surface-water ($\sum TU_{\text{DIVALENT METALS}}$), sediment (i.e., $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$), pore-water (i.e., PW-TU_{Zn}), or invertebrate-tissue ($\sum \text{Metals-TUs}$) chemistry data provided reliable bases for classifying risks to benthic invertebrates in the TSMD (MacDonald *et al.* 2009; Tables ES-8 to ES-11). More specifically, these results showed that the magnitude of effects tended to increase with increasing risk to the benthic invertebrate community. For example, the survival of amphipods was lower for the locations that were designated as posing moderate and high risks than was the case for the locations that were classified as posing low risk to benthic invertebrates or those that were designated as reference sediment samples (Table ES-9). Likewise, the survival and biomass of midges and freshwater mussels tended to be lowest in the samples that were classified as posing high risks to the benthic invertebrate community (Table ES-9). Importantly, species richness of freshwater mussels was lowest in the locations that had the highest concentrations of metals in sediments (as measured by mean $\text{PEC-Q}_{\text{Cd,Pb,Zn}}$; Table ES-9). Together, these results implied that the survival and biomass of benthic invertebrates have been impaired in response to exposure to contaminated sediments in the TSMD. As the reproduction of benthic invertebrates is highly correlated with growth or biomass, it is likely that benthic invertebrate reproduction has also been adversely affected in the study area. These results also indicated that the low risk thresholds utilized in the DERA would provide a relevant basis for establishing restoration goals for the TSMD.

The results of this assessment indicated that a number of substances are causing or substantially contributing to adverse effects on the benthic invertebrate community in the TSMD (i.e., relative to reference conditions). More specifically, cadmium, lead, and zinc were identified as the primary contaminants of concern (COCs) in the study area. Several other metals may also be contributing to adverse effects on benthic invertebrates, including chromium, copper, mercury, and nickel. In certain locations (e.g., Turkey Creek), it is possible that PAHs may be contributing to sediment toxicity and other adverse effects on the benthic invertebrate community.

ES1.5 Conclusions

In general accordance with USEPA (1997a) guidance, two ERAs of the TSMD were conducted following an eight-step process (See Appendix 1 for more information). These ERAs consisted of a SLERA for aquatic habitats and a DERA for the benthic invertebrate community. The results of the SLERA indicated that the presence of contaminants in surface water, sediment, and/or pore water posed potential risks to ecological receptors. Accordingly, risks to the benthic invertebrate community were further evaluated in the DERA. The results of the detailed assessment indicated that exposure to metals in sediment posed moderate or high risks to benthic invertebrates at about 78% of the locations that have been sampled in the study area (Table ES-2). The available surface-water chemistry, pore-water chemistry, sediment toxicity, invertebrate-tissue chemistry and freshwater mussel species richness data confirm that elevated risks to benthic invertebrates occurred in many AoIs within the TSMD (Tables ES-7, ES-11). Cadmium, lead, and zinc were identified as the primary COCs in the TSMD, with chromium, copper, mercury, nickel, and/or silver likely contributing to adverse effects on benthic invertebrates. The information provided by the SLERA, DERA, and companion documents (i.e., Ingersoll *et al.* 2008; MacDonald *et al.* 2009) is intended to support decisions regarding the need for remedial actions, including source control and other early action, within the Spring River and Neosho River watersheds. This data compilation and analysis may also be useful to the Natural Resources Trustees as they conduct natural resource damage assessments and evaluate restoration goals.

Table ES-1. Refined list of chemicals of potential concern in surface water, pore water, sediment, and biological tissues for evaluation in the detailed ecological risk assessment of the Tri-State Mining District.

Chemical of Potential Concern/Mixture	Surface Water¹	Sediment¹	Pore Water¹	Tissue²
<i>Metals</i>				
Aluminum, total	Y	Y	U	N
Arsenic, total	N	Y	N	Y
Barium, total	N	Y	N	N
Cadmium, total	Y	Y	U	Y
Chromium, total	N	Y	U	N
Cobalt, total	N	N	U	N
Copper, total	Y	Y	U	Y
Iron, total	Y	Y	U	N
Lead, total	Y	Y	U	Y
Mercury, total	N	Y	U	Y
Molybdenum, total	N	U	U	N
Nickel, total	Y	Y	N	N
Selenium, total	N	N	U	Y
Silver, total	N	N	U	N
Zinc, total	Y	Y	U	Y
Aluminum, dissolved	N	N	N	N
Cadmium, dissolved	Y	N	Y	N
Chromium, dissolved	N	N	N	N
Cobalt, dissolved	N	N	Y	N
Copper, dissolved	N	N	N	N
Iron, dissolved	Y	N	N	N
Lead, dissolved	N	N	Y	N
Molybdenum, dissolved	N	N	N	N
Mercury, dissolved	U	N	U	N
Nickel, dissolved	Y	N	N	N
Selenium, dissolved	N	N	N	N
Silver, dissolved	N	N	N	N
Zinc, dissolved	Y	N	Y	N
<i>Polycyclic Aromatic Hydrocarbons (PAHs)</i>				
2-Methylnaphthalene	N	N	N	N
Acenaphthene	N	N	N	N
Acenaphthylene	N	N	N	Y
Anthracene	N	Y	N	Y
Benz(<i>a</i>)anthracene	N	Y	N	Y
Benzo(<i>a</i>)pyrene	N	Y	N	Y
Benzo(<i>b</i>)fluoranthene	N	N	N	Y
Benzo(<i>g,h,i</i>)perylene	N	Y	N	Y
Benzo(<i>k</i>)fluoranthene	N	Y	N	Y

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Chemical of Potential Concern/Mixture	Surface Water¹	Sediment¹	Pore Water¹	Tissue²
<i>PAHs (cont.)</i>				
Biphenyl	N	N	N	N
Carbazole	N	N	N	N
Chrysene	N	Y	N	Y
Dibenz(<i>a,h</i>)anthracene	N	Y	N	Y
Dibenzofuran	N	N	N	N
Fluoranthene	N	Y	N	Y
Fluorene	N	N	N	Y
Indeno(1,2,3- <i>c,d</i>)pyrene	N	Y	N	Y
Naphthalene	N	N	N	N
Phenanthrene	N	Y	N	Y
Pyrene	N	Y	N	Y
Total high molecular weight PAHs	N	Y	N	Y
Total low molecular weight PAHs	N	Y	N	Y
Total PAHs	N	Y	N	Y
<i>Polychlorinated Biphenyls (PCBs)</i>				
Aroclor 1016	N	N	N	Y
Aroclor 1221	N	N	N	Y
Aroclor 1232	N	N	N	Y
Aroclor 1242	N	N	N	Y
Aroclor 1248	N	N	N	Y
Aroclor 1254	N	N	N	Y
Aroclor 1260	N	N	N	Y
Aroclor 1262	N	N	N	Y
Aroclor 1268	N	N	N	Y
PCBs, total	N	N	N	Y
<i>Organochlorine Pesticides</i>				
Aldrin	N	N	N	Y
Chlordane, cis-	N	N	N	Y
Chlordane, trans-	N	N	N	Y
Dieldrin	N	N	N	Y
Endosulfan sulfate	N	N	N	Y
Endosulfan-alpha	N	N	N	Y
Endosulfan-beta	N	N	N	Y
Endrin	N	N	N	Y
Endrin aldehyde	N	N	N	Y
Endrin ketone	N	N	N	Y
Heptachlor	N	N	N	Y
Heptachlor epoxide	N	N	N	Y

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Chemical of Potential Concern/Mixture	Surface Water¹	Sediment¹	Pore Water¹	Tissue²
<i>Organochlorine Pesticides (cont.)</i>				
Hexachlorobenzene	N	N	N	Y
Hexachlorocyclohexane-alpha	N	N	N	Y
Hexachlorocyclohexane-beta	N	N	N	Y
Hexachlorocyclohexane-delta	N	N	N	Y
Hexachlorocyclohexane-gamma	N	N	N	Y
Hexachlorocyclopentadiene	N	N	N	Y
Isophorone	N	N	N	Y
Methoxychlor	N	N	N	Y
<i>p,p'</i> -DDD	N	N	N	Y
<i>p,p'</i> -DDE	N	N	N	Y
<i>p,p'</i> -DDT	N	N	N	Y
Toxaphene	N	N	N	Y
<i>Semi-Volatile Compounds</i>				
1,2,4-Trichlorobenzene	N	N	N	Y
1,2-Dichlorobenzene	N	N	N	Y
1,3-Dichlorobenzene	N	N	N	Y
1,4-Dichlorobenzene	N	N	N	Y
2,4,5-Trichlorophenol	N	N	N	Y
2,4,6-Trichlorophenol	N	N	N	Y
2,4-Dichlorophenol	N	N	N	Y
2,4-Dimethylphenol	N	N	N	Y
2,4-Dinitrophenol	N	N	N	Y
2,4-Dinitrotoluene	N	N	N	Y
2,6-Dinitrotoluene	N	N	N	Y
2-Chloronaphthalene	N	N	N	Y
2-Chlorophenol	N	N	N	Y
2-Methylphenol	N	N	N	Y
2-Nitroaniline	N	N	N	Y
2-Nitrophenol	N	N	N	Y
3&/or4 Methylphenol	N	N	N	Y
3,3'-Dichlorobenzidine	N	N	N	Y
3-Nitroaniline	N	N	N	Y
4-Bromophenyl phenyl ether	N	N	N	Y
4-Chloro-3-methylphenol	N	N	N	N
4-Chloroaniline	N	N	N	N
4-Chlorophenyl phenyl ether	N	N	N	Y
4-Nitroaniline	N	N	N	N
4-Nitrophenol	N	N	N	N
Acetophenone	N	N	N	N
Atrazine	N	N	N	N

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Chemical of Potential Concern/Mixture	Surface Water¹	Sediment¹	Pore Water¹	Tissue²
<i>Semi-Volatile Compounds (cont.)</i>				
Benzaldehyde	N	N	N	N
Benzoic acid	N	N	N	N
Benzyl alcohol	N	N	N	N
bis(2-chloroethoxy)methane	N	N	N	N
bis(2-chloroethyl)ether	N	N	N	N
bis(2-chloroisopropyl) ether	N	N	N	N
bis(2-ethylhexyl) phthalate	N	N	N	Y
Butylbenzyl phthalate	N	Y	N	Y
Caprolactam	N	N	N	N
Diethyl phthalate	N	N	N	Y
Dimethyl phthalate	N	N	N	N
Di- <i>n</i> -butyl phthalate	N	N	N	Y
Dinitro- <i>o</i> -cresol	N	N	N	N
Di- <i>n</i> -octyl phthalate	N	N	N	Y
Hexachlorobutadiene	N	N	N	Y
Hexachloroethane	N	N	N	Y
<i>n</i> -nitrosodi- <i>n</i> -propylamine	N	N	N	N
<i>n</i> -nitrosodiphenylamine	N	N	N	N
Nitrobenzene	N	N	N	Y
Pentachlorophenol	N	N	N	Y
Phenol	N	N	N	N
<i>Nutrients/Inorganics/Conventionals</i>				
Ammonia	Y	N	N	N
Chlorine, dissolved	U	N	N	N
Nitrate, dissolved, NO3-N	N	N	N	N
Nitrate, total, NO3-N	N	N	N	N

TSMD = Tri-State Mining District; COPC = chemical of potential concern; Y = yes; N = no; U = uncertain.
 HQ = hazard quotient; TSV = toxicity screening value; COC = contaminant of concern.

¹ A COPC was retained as a preliminary COC if the HQ was >1.0 and if the 95th percentile concentration for the TSMD exceeded the 95th percentile concentration for reference samples by a factor of two or more for a given COPC. COPCs were also retained as uncertain COCs if no TSV or no data were available.

² All bioaccumulative COPCs were retained because no basis for COPC refinement was available (ie., it was not possible to make comparisons to levels in tissues from reference areas).

Table ES-2. Frequency of exceedance of the site-specific toxicity thresholds for sediment that were developed for the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Samples Predicted to be Toxic (%) ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
Upper/Middle Spring River Sub-basin							
Upper Spring River AoI	18	1.07	1 (6%)	17	1	0	Low
North Fork Spring River AoI	27	0.54	0 (0%)	27	0	0	Low
Middle Spring River AoI	115	2.29	27 (23%)	88	15	12	High
Cow Creek AoI	34	1.87	5 (15%)	29	2	3	Moderate
Center Creek AoI	81	5.39	37 (46%)	44	7	30	High
Turkey Creek AoI	48	18.1	40 (83%)	8	5	35	High
Shawnee Creek AoI	27	1.37	2 (7%)	25	2	0	Low
Short Creek AoI	44	74.2	44 (100%)	0	2	42	High
<i>Sub-basin Subtotal</i>	<i>394</i>	<i>4.30</i>	<i>156 (40%)</i>	<i>238</i>	<i>34</i>	<i>122</i>	<i>High</i>
Lower Spring River Sub-basin							
Empire Lake AoI	41	20.90	38 (93%)	3	2	36	High
Lower Spring River AoI	66	5.04	32 (48%)	34	20	12	High
Shoal Creek AoI	112	5.56	55 (49%)	57	24	31	High
Brush Creek AoI	14	1.47	2 (14%)	12	1	1	Moderate
Willow Creek AoI	30	6.79	14 (47%)	16	8	6	High
Spring Brook AoI	15	27.31	14 (93%)	1	0	14	High
Beaver Creek AoI	65	7.51	33 (51%)	32	7	26	High
Warren Branch AoI	9	1.23	0 (0%)	9	0	0	Low
Lost Creek AoI	33	1.49	4 (12%)	29	1	3	Moderate
<i>Sub-basin Subtotal</i>	<i>385</i>	<i>5.87</i>	<i>192 (50%)</i>	<i>193</i>	<i>63</i>	<i>129</i>	<i>High</i>
Neosho River Sub-basin							
Neosho River AoI	117	1.26	9 (8%)	108	5	4	Low
Upper Tar Creek AoI	39	3.12	8 (21%)	31	0	8	High
Middle Tar Creek AoI	52	79.9	52 (100%)	0	1	51	High
Lytle Creek AoI	41	62.5	39 (95%)	2	2	37	High
Lower Tar Creek AoI	108	13.6	88 (81%)	20	3	85	High
Elm Creek AoI	26	34.1	22 (85%)	4	2	20	High
<i>Sub-basin Subtotal</i>	<i>383</i>	<i>8.41</i>	<i>218 (57%)</i>	<i>165</i>	<i>13</i>	<i>205</i>	<i>High</i>

Table ES-2. Frequency of exceedance of the site-specific toxicity thresholds for sediment that were developed for the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Samples Predicted to be Toxic (%) ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
<i>Study Area as a Whole</i>	<i>1162</i>	<i>6.09</i>	<i>566 (49%)</i>	<i>596</i>	<i>110</i>	<i>456</i>	<i>High</i>
Reference Sediment Samples	10	0.46	0 (0%)	10	0	0	Low

Σ PEC-Q = sum probable effect concentration quotient; Cd = cadmium; Pb = lead; Zn = zinc; d = day; n = sample size; AoI = area of interest; SSTT = site-specific toxicity thresholds.

¹ Sediment samples were predicted to be toxic to benthic invertebrates if the SSTT was exceeded: i.e., if Σ PEC-Q_{Cd,Pb,Zn} \geq 6.47.

² Risk classification: Low if Σ PEC-Q_{Cd,Pb,Zn} < 6.47; Moderate if Σ PEC-Q_{Cd,Pb,Zn} = 6.47 to 10.04; and High if Σ PEC-Q_{Cd,Pb,Zn} > 10.04.

³ Based on frequency of exceedance of the SSTT of 6.47: Low if <10%; Moderate if 10 to 20%; and High if >20% (i.e. based on 20% increase in frequency of toxicity compared to that for reference sediment samples).

Table ES-3. Frequency of exceedance of site-specific toxicity thresholds for divalent metals in surface water (i.e., Σ SW-TUs_{DIVALENT METALS}) in the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ SW-TUs _{DIVALENT METALS}	Number of Samples Predicted to be Toxic ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
Upper/Middle Spring River Sub-basin							
Upper Spring River AoI	5	0.408	0 (0%)	5	0	0	Low
North Fork Spring River AoI	8	0.556	0 (0%)	8	0	0	Low
Middle Spring River AoI	20	0.857	9 (45%)	11	4	5	High
Cow Creek AoI	5	0.919	1 (20%)	4	0	1	Moderate
Center Creek AoI	36	1.02	14 (39%)	22	0	14	High
Turkey Creek AoI	19	1.51	16 (84%)	3	3	13	High
Shawnee Creek AoI	7	0.635	2 (29%)	5	1	1	High
Short Creek AoI	6	50.6	6 (100%)	0	0	6	High
<i>Sub-basin Subtotal</i>	<i>106</i>	<i>1.16</i>	<i>48 (45%)</i>	<i>58</i>	<i>8</i>	<i>40</i>	<i>High</i>
Lower Spring River Sub-basin							
Empire Lake AoI	2	0.954	1 (50%)	1	1	0	High
Lower Spring River AoI	32	0.543	3 (9%)	29	3	0	Low
Shoal Creek AoI	50	0.623	8 (16%)	42	3	5	Moderate
Brush Creek AoI	1	NC	1 (100%)	0	1	0	High
Willow Creek AoI	5	3.74	5 (100%)	0	1	4	High
Spring Brook AoI	3	31.6	3 (100%)	0	0	3	High
Beaver Creek AoI	87	0.998	39 (45%)	48	10	29	High
Warren Branch AoI	5	0.500	0 (0%)	5	0	0	Low
Lost Creek AoI	23	0.617	1 (4%)	22	0	1	Low
<i>Sub-basin Subtotal</i>	<i>208</i>	<i>0.820</i>	<i>61 (29%)</i>	<i>147</i>	<i>19</i>	<i>42</i>	<i>High</i>
Neosho River Sub-basin							
Neosho River AoI	37	0.433	3 (8%)	34	2	1	Low
Upper Tar Creek AoI	3	6.19	3 (100%)	0	1	2	High
Middle Tar Creek AoI	53	5.97	44 (83%)	9	2	42	High
Lytle Creek AoI	4	16.7	4 (100%)	0	0	4	High
Lower Tar Creek AoI	121	3.66	101 (83%)	20	2	99	High
Elm Creek AoI	5	8.38	4 (80%)	1	0	4	High
<i>Sub-basin Subtotal</i>	<i>223</i>	<i>3.04</i>	<i>159 (71%)</i>	<i>64</i>	<i>7</i>	<i>152</i>	<i>High</i>

Table ES-3. Frequency of exceedance of site-specific toxicity thresholds for divalent metals in surface water (i.e., Σ SW-TUs_{DIVALENT METALS}) in the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ SW-TUs _{DIVALENT METALS}	Number of Samples Predicted to be Toxic ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
<i>Study Area as a Whole</i>	537	1.52	268 (50%)	269	34	234	High
Reference Surface Water Samples	18	0.54	1 (6%)	17	0	1	Low

Σ SW-TUs = sum of surface water toxic units; Divalent metals = dissolved copper, dissolved cadmium, dissolved lead, dissolved nickel, dissolved silver, dissolved zinc;

SSTT = site-specific toxicity threshold; AoI = area of interest; n = sample size; ND = no data; NC = not calculated.

¹ Surface water samples were predicted to be toxic to benthic invertebrates if the SSTT was exceeded: i.e., Σ SW-TUs_{DIVALENT METALS} \geq 1.03.

² Risk classification: Low if Σ SW-TUs < 1.03; Moderate if Σ SW-TUs = 1.03 to 1.41; and High if Σ SW-TUs > 1.41.

³ Based on frequency of exceedance of the SSTT of 1.03: Low if <10%; Moderate if 10 to 20%; and High if >20% (i.e. based on 20% increase in frequency of exceedance compared to that for surface water samples from the selected reference area).

Table ES-4. Frequency of exceedance of the site-specific toxicity thresholds for pore water that were developed for the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of PW-TU _{Zn}	Number of Samples Predicted to be Toxic ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
Upper/Middle Spring River Sub-basin							
Upper Spring River AoI	5	0.010	0 (0%)	5	0	0	Low
North Fork Spring River AoI	7	0.017	1 (14%)	6	1	0	Moderate
Middle Spring River AoI	6	0.066	1 (17%)	5	0	1	Moderate
Cow Creek AoI	5	0.198	1 (20%)	4	0	1	Moderate
Center Creek AoI	13	0.469	8 (62%)	5	1	7	High
Turkey Creek AoI	12	0.560	6 (50%)	6	1	5	High
Shawnee Creek AoI	2	0.007	0 (0%)	2	0	0	Low
Short Creek AoI	3	9.59	3 (100%)	0	0	3	High
<i>Sub-basin Subtotal</i>	<i>53</i>	<i>0.163</i>	<i>20 (38%)</i>	<i>33</i>	<i>3</i>	<i>17</i>	<i>High</i>
Lower Spring River Sub-basin							
Empire Lake AoI	1	NC	0 (0%)	1	0	0	Low
Lower Spring River AoI	4	0.160	1 (25%)	3	0	1	High
Shoal Creek AoI	11	0.114	1 (9%)	10	0	1	Low
Brush Creek AoI	ND	ND	ND	ND	ND	ND	ND
Willow Creek AoI	2	0.051	0 (0%)	2	0	0	Low
Spring Brook AoI	ND	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	1	NC	1 (100%)	0	0	1	High
Warren Branch AoI	ND	ND	ND	ND	ND	ND	ND
Lost Creek AoI	4	0.021	0 (0%)	4	0	0	Low
<i>Sub-basin Subtotal</i>	<i>23</i>	<i>0.0859</i>	<i>3 (13%)</i>	<i>20</i>	<i>0</i>	<i>3</i>	<i>Moderate</i>
Neosho River Sub-basin							
Neosho River AoI	6	0.026	0 (0%)	6	0	0	Low
Upper Tar Creek AoI	3	0.028	0 (0%)	3	0	0	Low
Middle Tar Creek AoI	2	0.904	1 (50%)	1	0	1	High
Lytle Creek AoI	2	0.634	1 (50%)	1	0	1	High
Lower Tar Creek AoI	5	0.816	3 (60%)	2	1	2	High
Elm Creek AoI	2	0.553	1 (50%)	1	0	1	High
<i>Sub-basin Subtotal</i>	<i>20</i>	<i>0.166</i>	<i>6 (30%)</i>	<i>14</i>	<i>1</i>	<i>5</i>	<i>High</i>

Table ES-4. Frequency of exceedance of the site-specific toxicity thresholds for pore water that were developed for the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of PW-TU _{Zn}	Number of Samples Predicted to be Toxic ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
<i>Study Area as a Whole</i>	<i>96</i>	<i>0.141</i>	<i>29 (30%)</i>	<i>67</i>	<i>4</i>	<i>25</i>	<i>High</i>
Reference Sediment Samples	8	0.006	0 (0%)	8	0	0	Low

PW-TU = pore-water toxic units; Zn = zinc; n = sample size; SSTT = site-specific toxicity threshold; ND = no data; NC = not calculated.

AoI = area of interest

¹ Pore-water samples were predicted to be toxic to benthic invertebrates if the SSTT was exceeded: i.e., PW-TU_{Zn} ≥ 0.581.

² Risk classification: Low if PW-TU_{Zn} < 0.581; Moderate if PW-TU_{Zn} = 0.581 to 0.867; and High if PW-TU_{Zn} > 0.867.

Table ES-5. Incidence-of-toxicity to amphipods, midges, and mussels exposed to sediment samples from the Tri-State Mining District.

Area of Interest (AoI)	Incidence of Toxicity (IOT) to Benthic Invertebrates							
	Amphipod (<i>H. azteca</i>) ¹		Midge (<i>C. dilutus</i>) ¹		Mussel (<i>L. siliquoidea</i>) ¹		Overall Toxicity for Amphipod, Midge, or Mussel ²	
	IOT	Number Toxic	IOT	Number Toxic	IOT	Number Toxic	IOT	Number Toxic
Upper/Middle Spring River Sub-basin								
Upper Spring River AoI	0%	0 of 5	40%	2 of 5	0%	0 of 3	40%	2 of 5
North Fork Spring River AoI	0%	0 of 5	0%	0 of 5	0%	0 of 2	0%	0 of 5
Middle Spring River AoI	0%	0 of 7	33%	1 of 3	33%	2 of 6	43%	3 of 7
Cow Creek AoI	0%	0 of 2	100%	2 of 2	0%	0 of 1	100%	2 of 2
Center Creek AoI	36%	4 of 11	44%	4 of 9	40%	4 of 10	64%	7 of 9
Turkey Creek AoI	60%	6 of 10	80%	8 of 10	57%	4 of 7	90%	9 of 10
Shawnee Creek AoI	0%	0 of 2	0%	0 of 2	0%	0 of 2	0%	0 of 2
Short Creek AoI	100%	3 of 3	100%	3 of 3	100%	2 of 2	100%	3 of 3
<i>Sub-basin Subtotal</i>	<i>29%</i>	<i>13 of 45</i>	<i>51%</i>	<i>20 of 39</i>	<i>36%</i>	<i>12 of 33</i>	<i>58%</i>	<i>26 of 45</i>
Lower Spring River Sub-basin								
Empire Lake AoI	0%	0 of 1	0%	0 of 1	ND	ND	0%	0 of 1
Lower Spring River AoI	0%	0 of 2	50%	1 of 2	ND	ND	50%	1 of 2
Shoal Creek AoI	0%	0 of 7	29%	2 of 7	0%	0 of 2	29%	2 of 7
Brush Creek AoI	ND	ND	ND	ND	ND	ND	ND	ND
Willow Creek AoI	0%	0 of 2	50%	1 of 2	0%	0 of 2	50%	1 of 2
Spring Brook AoI	ND	ND	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	100%	1 of 1	100%	1 of 1	100%	1 of 1	100%	1 of 1
Warren Branch AoI	ND	ND	ND	ND	ND	ND	ND	ND
Lost Creek AoI	0%	0 of 3	33%	1 of 3	0%	0 of 2	33%	1 of 3
<i>Sub-basin Subtotal</i>	<i>6%</i>	<i>1 of 16</i>	<i>38%</i>	<i>6 of 16</i>	<i>14%</i>	<i>1 of 7</i>	<i>38%</i>	<i>6 of 16</i>
Neosho River Sub-basin								
Neosho River AoI	25%	1 of 4	25%	1 of 4	0%	0 of 3	25%	1 of 4
Upper Tar Creek AoI	0%	0 of 2	50%	1 of 2	50%	1 of 2	50%	1 of 2
Middle Tar Creek AoI	100%	2 of 2	100%	2 of 2	ND	ND	100%	2 of 2
Lytle Creek AoI	50%	1 of 2	50%	1 of 2	0%	0 of 1	50%	1 of 2

Table ES-5. Incidence-of-toxicity to amphipods, midges, and mussels exposed to sediment samples from the Tri-State Mining District.

Area of Interest (AoI)	Incidence of Toxicity (IOT) to Benthic Invertebrates						Overall Toxicity for Amphipod, Midge, or Mussel ²	
	Amphipod (<i>H. azteca</i>) ¹		Midge (<i>C. dilutus</i>) ¹		Mussel (<i>L. siliquoidea</i>) ¹		IOT	Number Toxic
	IOT	Number Toxic	IOT	Number Toxic	IOT	Number Toxic		
Neosho River Sub-basin (cont.)								
Lower Tar Creek AoI	75%	3 of 4	75%	3 of 4	100%	2 of 2	100%	4 of 4
Elm Creek AoI	100%	1 of 1	100%	1 of 1	ND	ND	100%	1 of 1
<i>Sub-basin Subtotal</i>	<i>53%</i>	<i>8 of 15</i>	<i>60%</i>	<i>9 of 15</i>	<i>38%</i>	<i>3 of 8</i>	<i>67%</i>	<i>10 of 15</i>
Study Area as a Whole	29%	22 of 76	50%	35 of 70	33%	16 of 48	55%	42 of 76
Reference Sediment Samples	0%	0 of 10	0%	0 of 8	0%	0 of 5	0%	0 of 10

ND = no data; AoI = area of interest; IOT = incidence of toxicity.

¹ Sediment samples were designated as toxic if the sample was designated as toxic based on the survival or biomass endpoints.

Table ES-6. Frequency of exceedance of selected toxicity thresholds for evaluating invertebrate-tissue chemistry data from the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of ΣMetal-TUs ¹	Number of Samples with ΣMetal-TUs ≥ 6.01 ¹	Number of Samples Predicted to be Toxic ²	Number of Samples/Risk Category ³			Risk to Benthic Community ⁴
					Low	Moderate	High	
Upper/Middle Spring River Sub-basin								
Upper Spring River AoI	13	1.80	0	0 (0%)	13	0	0	Low
North Fork Spring River AoI	16	1.95	0	0 (0%)	16	0	0	Low
Middle Spring River AoI	130	4.34	38	38 (29%)	92	7	31	High
Cow Creek AoI	21	2.49	0	0 (0%)	21	0	0	Low
Center Creek AoI	7	3.49	1	1 (14%)	6	0	1	Moderate
Turkey Creek AoI	6	7.46	5	5 (83%)	1	1	4	High
Shawnee Creek AoI	1	NC	0	0 (0%)	1	0	0	Low
Short Creek AoI	1	NC	1	1 (100%)	0	0	1	High
<i>Sub-basin Subtotal</i>	<i>195</i>	<i>3.67</i>	<i>45</i>	<i>45 (23%)</i>	<i>150</i>	<i>8</i>	<i>37</i>	<i>High</i>
Lower Spring River Sub-basin								
Lower Spring River AoI	11	3.06	1	1 (9%)	10	0	1	Low
Shoal Creek AoI	26	3.96	6	6 (23%)	20	4	2	High
Willow Creek AoI	1	NC	0	0 (0%)	1	0	0	Low
Beaver Creek AoI	1	NC	1	1 (100%)	0	0	1	High
Lost Creek AoI	1	NC	0	0 (0%)	1	0	0	Low
<i>Sub-basin Subtotal</i>	<i>40</i>	<i>3.26</i>	<i>8</i>	<i>8 (20%)</i>	<i>32</i>	<i>4</i>	<i>4</i>	<i>High</i>
Neosho River Sub-basin								
Middle Tar Creek AoI	1	NC	1	1 (100%)	0	0	1	High
Lytle Creek AoI	1	NC	1	1 (100%)	0	0	1	High
Lower Tar Creek AoI	2	13.1	2	2 (100%)	0	0	2	High
<i>Sub-basin Subtotal</i>	<i>4</i>	<i>20.9</i>	<i>4</i>	<i>4 (100%)</i>	<i>0</i>	<i>0</i>	<i>4</i>	<i>High</i>
Study Area as a Whole	239	3.81	57	57 (24%)	182	12	45	High

Table ES-6. Frequency of exceedance of selected toxicity thresholds for evaluating invertebrate-tissue chemistry data from the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ Metal-TUs ¹	Number of Samples with Σ Metal-TUs \geq 6.01 ¹	Number of Samples Predicted to be Toxic ²	Number of Samples/Risk Category ³			Risk to Benthic Community ⁴
					Low	Moderate	High	
Reference Sediment Samples	2	2.85	0	0 (0%)	2	0	0	Low

Σ Metal-TUs = sum of metal toxic units; Cd = cadmium; Cu = copper; Hg = Mercury; Pb = lead; Zn = zinc; n = sample size; NC = not calculated; TT = toxicity threshold.

¹ Σ Metal-TUs calculated by summing the hazard quotients for Cd, Cu, Pb, Hg, and Zn.

² Tissue samples were designated as having metal concentrations sufficient to adversely affect benthic invertebrates if the selected TT was exceeded: i.e., Σ Metal-TUs \geq 6.01.

³ Risk classification: Low if Σ Metal-TUs <6.01; Moderate if Σ Metal-TUs = 6.01 to 7.45; and High if Σ Metal-TUs >7.45.

⁴ Based on predicted frequency of toxicity: Low if <10%; Moderate if 10 to 20%; and High if >20%.

Table ES-7. Evaluation of risks to benthic invertebrates exposed to chemicals of potential concern in the Tri-State Mining District, based on multiple lines-of-evidence.

Area of Interest (AoI)	Chemistry								Sediment Toxicity					
	Sediment		Pore-Water		Invertebrate-Tissue		Surface Water		Amphipod		Mussel		Midge	
	n	Number Predicted Toxic	n	Number Predicted Toxic	n	Number Predicted Toxic	n	Number of Exceedences	n	Observed Toxicity	n	Observed Toxicity	n	Observed Toxicity
Upper/Middle Spring River Sub-basin														
Upper Spring River AoI	18	1 (6%)	5	0 (0%)	13	0 (0%)	5	0 (0%)	5	0%	3	0%	5	40%
North Fork Spring River AoI	27	0 (0%)	7	1 (14%)	16	0 (0%)	8	0 (0%)	5	0%	2	0%	5	0%
Middle Spring River AoI	115	27 (23%)	6	1 (17%)	130	38 (29%)	20	9 (45%)	7	0%	6	33%	3	33%
Cow Creek AoI	34	5 (15%)	5	1 (20%)	21	0 (0%)	5	1 (20%)	2	0%	1	0%	2	100%
Center Creek AoI	81	37 (46%)	13	8 (62%)	7	1 (14%)	36	14 (39%)	11	36%	10	40%	9	44%
Turkey Creek AoI	48	40 (83%)	12	6 (50%)	6	5 (83%)	19	16 (84%)	10	60%	7	57%	10	80%
Shawnee Creek AoI	27	2 (7%)	2	0 (0%)	1	0 (0%)	7	2 (29%)	2	0%	2	0%	2	0%
Short Creek AoI	44	44 (100%)	3	3 (100%)	1	1 (100%)	6	6 (100%)	3	100%	2	100%	3	100%
<i>Sub-basin Subtotal</i>	<i>394</i>	<i>156 (40%)</i>	<i>53</i>	<i>20 (38%)</i>	<i>195</i>	<i>45 (23%)</i>	<i>106</i>	<i>48 (45%)</i>	<i>45</i>	<i>29%</i>	<i>33</i>	<i>36%</i>	<i>39</i>	<i>51%</i>
Lower Spring River Sub-basin														
Empire Lake AoI	41	38 (93%)	1	0 (0%)	ND	ND	2	1 (50%)	1	0%	ND	ND	1	0%
Lower Spring River AoI	66	32 (48%)	4	1 (25%)	11	1 (9%)	32	3 (9%)	2	0%	ND	ND	2	50%
Shoal Creek AoI	112	55 (49%)	11	1 (9%)	26	6 (23%)	50	8 (16%)	7	0%	2	0%	7	29%
Brush Creek AoI	14	2 (14%)	ND	ND	ND	ND	1	1 (100%)	ND	ND	ND	ND	ND	ND
Willow Creek AoI	30	14 (47%)	2	0 (0%)	1	0 (0%)	5	5 (100%)	2	0%	2	0%	2	50%
Spring Brook AoI	15	14 (93%)	ND	ND	ND	ND	3	3 (100%)	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	65	33 (51%)	1	1 (100%)	1	1 (100%)	87	39 (45%)	1	100%	1	100%	1	100%
Warren Branch AoI	9	0 (0%)	ND	ND	ND	ND	5	0 (0%)	ND	ND	ND	ND	ND	ND
Lost Creek AoI	33	4 (12%)	4	0 (0%)	1	0 (0%)	23	1 (4%)	3	0%	2	0%	3	33%
<i>Sub-basin Subtotal</i>	<i>385</i>	<i>192 (50%)</i>	<i>23</i>	<i>3 (14%)</i>	<i>40</i>	<i>8 (20%)</i>	<i>208</i>	<i>61 (29%)</i>	<i>16</i>	<i>6%</i>	<i>7</i>	<i>14%</i>	<i>16</i>	<i>38%</i>
Neosho River Sub-basin														
Neosho River AoI	117	9 (8%)	6	0 (0%)	ND	ND	37	3 (8%)	4	25%	3	0%	4	25%
Upper Tar Creek AoI	39	8 (21%)	3	0 (0%)	ND	ND	3	3 (100%)	2	0%	2	50%	2	50%
Middle Tar Creek AoI	52	52 (100%)	2	1 (50%)	1	1 (100%)	53	44 (83%)	2	100%	ND	ND	2	100%
Lytle Creek AoI	41	39 (95%)	2	1 (50%)	1	1 (100%)	4	4 (100%)	2	50%	1	0%	2	50%

Table ES-7. Evaluation of risks to benthic invertebrates exposed to chemicals of potential concern in the Tri-State Mining District, based on multiple lines-of-evidence.

Area of Interest (AoI)	Chemistry								Sediment Toxicity					
	Sediment		Pore-Water		Invertebrate-Tissue		Surface Water		Amphipod		Mussel		Midge	
	n	Number Predicted Toxic	n	Number Predicted Toxic	n	Number Predicted Toxic	n	Number of Exceedences	n	Observed Toxicity	n	Observed Toxicity	n	Observed Toxicity
Neosho River Sub-basin (cont.)														
Lower Tar Creek AoI	108	88 (81%)	5	3 (60%)	2	2 (100%)	121	101 (83%)	4	75%	2	100%	4	75%
Elm Creek AoI	26	22 (85%)	2	1 (50%)	ND	ND	5	4 (80%)	1	100%	ND	ND	1	100%
<i>Sub-basin Subtotal</i>	<i>383</i>	<i>218 (57%)</i>	<i>20</i>	<i>6 (30%)</i>	<i>4</i>	<i>4 (100%)</i>	<i>223</i>	<i>159 (71%)</i>	<i>15</i>	<i>53%</i>	<i>8</i>	<i>38%</i>	<i>15</i>	<i>60%</i>
<i>Study Area as a Whole</i>	1162	566 (49%)	96	29 (31%)	239	57 (24%)	537	268 (50%)	76	29%	48	33%	70	50%
Reference Sediment Samples	10	0 (0%)	8	0 (0%)	2	0 (0%)	18	1 (6%)	10	0%	5	0%	8	0%

Table ES-8. Survival, weight, and biomass of amphipods (*H. azteca*), midges (*C. dilutus*), and mussels (*L. siliquoidea*) exposed to surface-water samples from the Tri-State Mining District that were classified into reference, low risk, moderate risk, and high risk categories using the selected surface-water toxicity thresholds of 1.03 and 1.41 for $\Sigma\text{TU}_{\text{Divalent Metals}}$ (control-adjusted results are reported for each endpoint).

Toxicity Test Organism	Test Duration	Endpoint Measured	Control-Adjusted Survival, Weight, or Biomass			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
<i>H. azteca</i>	28-d	Survival	98.8% ± 6.3% (8)	98.6% ± 10.% (49)	93.1% ± 13.7% (6)	25.1% ± 34.6% (15)
		Weight	115.% ± 49.6% (8)	93.9% ± 28.9% (49)	99.1% ± 16.8% (6)	82.1% ± 72.% (15)
		Biomass	115.9% ± 54.5% (8)	93.8% ± 33.1% (49)	92.4% ± 13.1% (6)	27.7% ± 40.5% (15)
<i>C. dilutus</i>	10-d	Survival	99.2% ± 3.9% (3)	98.8% ± 4.2% (30)	94.9% ± 3.6% (4)	71.7% ± 30.8% (8)
		Weight	79.9% ± 20.4% (3)	88.6% ± 16.2% (30)	95.3% ± 4.9% (4)	64.3% ± 24.7% (8)
		Biomass	79.1% ± 19.8% (3)	87.3% ± 16.% (30)	90.1% ± 2.6% (4)	50.6% ± 30.5% (8)
<i>L. siliquoidea</i>	28-d	Survival	104.7% ± 7.4% (8)	101.4% ± 9.7% (49)	97.7% ± 4.7% (6)	84.2% ± 11.9% (15)
		Weight	99.5% ± 18.% (8)	81.9% ± 25.6% (49)	86.9% ± 13.9% (6)	64.1% ± 29.2% (15)
		Biomass	105.7% ± 21.8% (8)	83.3% ± 25.4% (49)	83.3% ± 12.3% (6)	54.3% ± 25.3% (15)

d = day; n = sample size; divalent metals include Cadmium (Cd), Copper (Cu), Lead (Pb), Nickel (Ni), Silver (As), and Zinc (Zn); TSV = toxicity screening value (see Table 3).

$$^1 \Sigma\text{TU}_{\text{Divalent Metals}} < 1.03, \text{ where } \Sigma\text{TU}_{\text{Divalent Metals}} = \frac{[\text{Cd}]}{\text{TSV}_{\text{Cd}}} + \frac{[\text{Cu}]}{\text{TSV}_{\text{Cu}}} + \frac{[\text{Pb}]}{\text{TSV}_{\text{Pb}}} + \frac{[\text{Ni}]}{\text{TSV}_{\text{Ni}}} + \frac{[\text{As}]}{\text{TSV}_{\text{As}}} + \frac{[\text{Zn}]}{\text{TSV}_{\text{Ni}}}$$

$$^2 \Sigma\text{TU}_{\text{Divalent Metals}} = 1.03 \text{ to } 1.41.$$

$$^3 \Sigma\text{TU}_{\text{Divalent Metals}} > 1.41.$$

Note: TSVs for divalent metals were calculated by assuming a water hardness of 100 mg/L.

Table ES-9. Survival, weight, and biomass of amphipods (*H. azteca*), midges (*C. dilutus*), and mussels (*L. siliquoidea*) exposed to sediment samples from the Tri-State Mining District that were classified into reference, low risk, moderate risk, and high risk categories using the selected sediment toxicity thresholds of 6.47 and 10.04 for Σ PEC-Q_{Cd,Pb,Zn} (control-adjusted results are repeated for each endpoint).

Toxicity Test Organism	Test Duration	Endpoint Measured	Control-Adjusted Survival, Weight, or Biomass			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
<i>H. azteca</i>	28-d	Survival	98.5% ± 5.6% (10)	100.5% ± 5.6% (46)	92.2% ± 13.4% (6)	49.1% ± 42.8% (24)
		Weight	112.8% ± 45.% (10)	97.6% ± 31.4% (46)	94.6% ± 20.0% (6)	86.6% ± 58.3% (24)
		Biomass	112.9% ± 49.3% (10)	99.0% ± 33.7% (46)	87.4% ± 22.0% (6)	49.1% ± 45.7% (24)
<i>C. dilutus</i>	10-d	Survival	104.7% ± 7.4% (8)	100.3% ± 10.2% (41)	104.6% ± 8.3% (6)	90.4% ± 13.0% (23)
		Weight	99.5% ± 18.% (8)	85.2% ± 25.4% (41)	64.1% ± 26.8% (6)	70.4% ± 25.5% (23)
		Biomass	105.7% ± 21.8% (8)	85.9% ± 26.0% (41)	65.6% ± 19.8% (6)	64.5% ± 25.2% (23)
<i>L. siliquoidea</i>	28-d	Survival	100.7% ± 3.9% (5)	97.8% ± 9.4% (28)	98.1% ± 4.4% (4)	83.9% ± 24.7% (16)
		Weight	82.6% ± 18.6% (5)	94.1% ± 21.8% (28)	93.0% ± 13.2% (4)	76.7% ± 23.6% (16)
		Biomass	83.4% ± 20.5% (5)	91.2% ± 19.1% (28)	91.5% ± 14.3% (4)	68.1% ± 29.1% (16)
			Average Number of Taxa ⁴			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
Mussels	NA	Number of Live Mussel Taxa	ND (0)	8.17 ± 6.12 (12)	3.75 ± 4.35 (4)	ND (0)
	NA	Number of Live Mussel Taxa Classified as Threatened, Endangered, or of Special Concern	ND (0)	3.25 ± 3.52 (12)	0.25 ± 0.5 (4)	ND (0)
	NA	Total Number of Mussel Taxa	ND (0)	11.3 ± 7.94 (12)	5.75 ± 6.13 (4)	ND (0)

Σ PEC-Q_{Cd,Pb,Zn} = sum probable effect concentration quotient for cadmium, lead, and zinc; d = day; n = sample size; ND = no data or limited data.

¹ Σ PEC-Q_{Cd,Pb,Zn} < 6.47

² Σ PEC-Q_{Cd,Pb,Zn} = 6.47 to 10.04

³ Σ PEC-Q_{Cd,Pb,Zn} > 10.04

⁴ Includes data for sampling sites that had matching mussel taxa abundance and sediment chemistry data only.

Table ES-10. Survival, weight, and biomass of amphipods (*H. azteca*), midges (*C. dilutus*), and mussels (*L. siliquoidea*) exposed to pore-water samples from the Tri-State Mining District that were classified into reference, low risk, moderate risk, and high risk categories using the selected pore-water toxicity thresholds of 0.581 and 0.867 for PW-TU_{Zn} (control-adjusted results are repeated for each endpoint).

Toxicity Test Organism	Test Duration	Endpoint Measured	Control-Adjusted Survival, Weight, or Biomass			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
<i>H. azteca</i>	28-d	Survival	98.8% ± 6.3% (8)	98.8% ± 9.7% (52)	80.6% ± 15.8% (2)	29.4% ± 37.8% (16)
		Weight	115.% ± 49.6% (8)	93.8% ± 28.1% (52)	131.7% ± 33.1% (2)	80.4% ± 67.8% (16)
		Biomass	115.9% ± 54.5% (8)	93.8% ± 32.2% (52)	110.8% ± 48.3% (2)	29.1% ± 35.7% (16)
<i>C. dilutus</i>	10-d	Survival	104.7% ± 7.4% (8)	101.2% ± 9.5% (52)	93.4% ± 13.% (2)	85.6% ± 12.1% (16)
		Weight	99.5% ± 18.% (8)	81.8% ± 24.9% (52)	111.7% ± 28.% (2)	63.7% ± 25.4% (16)
		Biomass	105.7% ± 21.8% (8)	83.% ± 24.8% (52)	97.5% ± 5.3% (2)	55.4% ± 24.6% (16)
<i>L. siliquoidea</i>	28-d	Survival	99.2% ± 3.9% (3)	98.8% ± 4.1% (31)	94.9% (1)	75.9% ± 28.5% (10)
		Weight	79.9% ± 20.4% (3)	88.6% ± 15.9% (31)	98.9% (1)	70.8% ± 25.8% (10)
		Biomass	79.1% ± 19.8% (3)	87.4% ± 15.7% (31)	93.9% (1)	58.4% ± 31.5% (10)

PW-TU_{Zn} = pore-water toxic unit for zinc; d = day; n = sample size.

¹ PW-TU_{Zn} < 0.581

² PW-TU_{Zn} = 0.581 to 0.867

³ PW-TU_{Zn} > 0.867

Table ES-11. Survival, weight, and biomass of amphipods (*H. azteca*), midges (*C. dilutus*), and mussels (*L. siliquoidea*) exposed to sediment samples from the Tri-State Mining District that were classified into reference, low risk, moderate risk, and high risk categories using the selected toxicity thresholds for invertebrate tissues (i.e., Σ Metals-TU of 6.01 and 7.45; i.e., using oligochaete tissue residue data from the 28-d bioaccumulation tests).

Toxicity Test Organism	Test Duration	Endpoint Measured	Control-Adjusted Survival, Weight, or Biomass			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
<i>H. azteca</i>	28-d	Survival	107% ± 5.9% (2)	101.4% ± 7.2% (9)	89.7% (1)	55.8% ± 42.4% (11)
		Weight	170% ± 47.6% (2)	98.2% ± 46.4% (9)	66.1% (1)	79.2% ± 42.1% (11)
		Biomass	182% ± 39.7% (2)	101.7% ± 51.3% (9)	59.9% (1)	52.5% ± 40.4% (11)
<i>C. dilutus</i>	10-d	Survival	101% ± 1.8% (2)	102.4% ± 6.5% (9)	117% (1)	95.0% ± 8.8% (11)
		Weight	112% ± 1.1% (2)	85.1% ± 25.1% (9)	39.8% (1)	68.1% ± 26.1% (11)
		Biomass	112% ± 5.5% (2)	86.9% ± 22.7% (9)	49.2% (1)	65.0% ± 26.1% (11)
<i>L. siliquoidea</i>	28-d	Survival	101% ± 1.8% (2)	99.7% ± 2.5% (8)	97.5% (1)	86.2% ± 20.7% (8)
		Weight	81.4% ± 27.2% (2)	85.2% ± 13.6% (8)	90.0% (1)	74.3% ± 22.1% (8)
		Biomass	81.9% ± 27.2% (2)	84.5% ± 12.1% (8)	87.9% (1)	67.5% ± 28.2% (8)
			Average Number of Taxa ⁴			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
Mussels	NA	Number of Live Mussel Taxa	ND (0)	7.64 ± 6.31 (11)	6.0 (1)	10.5 ± 4.95 (2)
	NA	Number of Live Mussel Taxa	ND (0)	7.64 ± 6.31 (11)	6.0 (1)	10.5 ± 4.95 (2)
	NA	Classified as Threatened, Endangered, or of Special Concern	ND (0)	2.64 ± 3.59 (11)	3.0 (1)	3.5 ± 4.95 (2)
	NA	Number of Total Mussel Taxa	ND (0)	11.18 ± 8.33 (11)	7.0 (1)	13.0 ± 4.24 (2)

Σ Metal-TUs = sum of metal toxic units for cadmium, copper, mercury, lead, and zinc; d = day; n = sample size; ND = no data; HQ = hazard quotient; NA = not applicable.

Σ Metal-TUs calculated by summing the HQs for Cd, Cu, Pb, Hg, and Zn.

Σ Metal-TUs based on concentrations of metals in tissues were calculated on a wet weight basis. Concentrations of metals in tissues that were reported in dry weight were converted to a wet weight equivalent for the Σ Metal-TUs calculation by multiplying the dry weight concentration by 5.

¹ Σ Metal-TUs < 6.01

² Σ Metal-TUs = 6.01 to 7.45

³ Σ Metal-TUs > 7.45

⁴ Includes data for sampling sites that had matching mussel taxa abundance and tissue chemistry data only

Figure ES-1. Map of Study Area, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

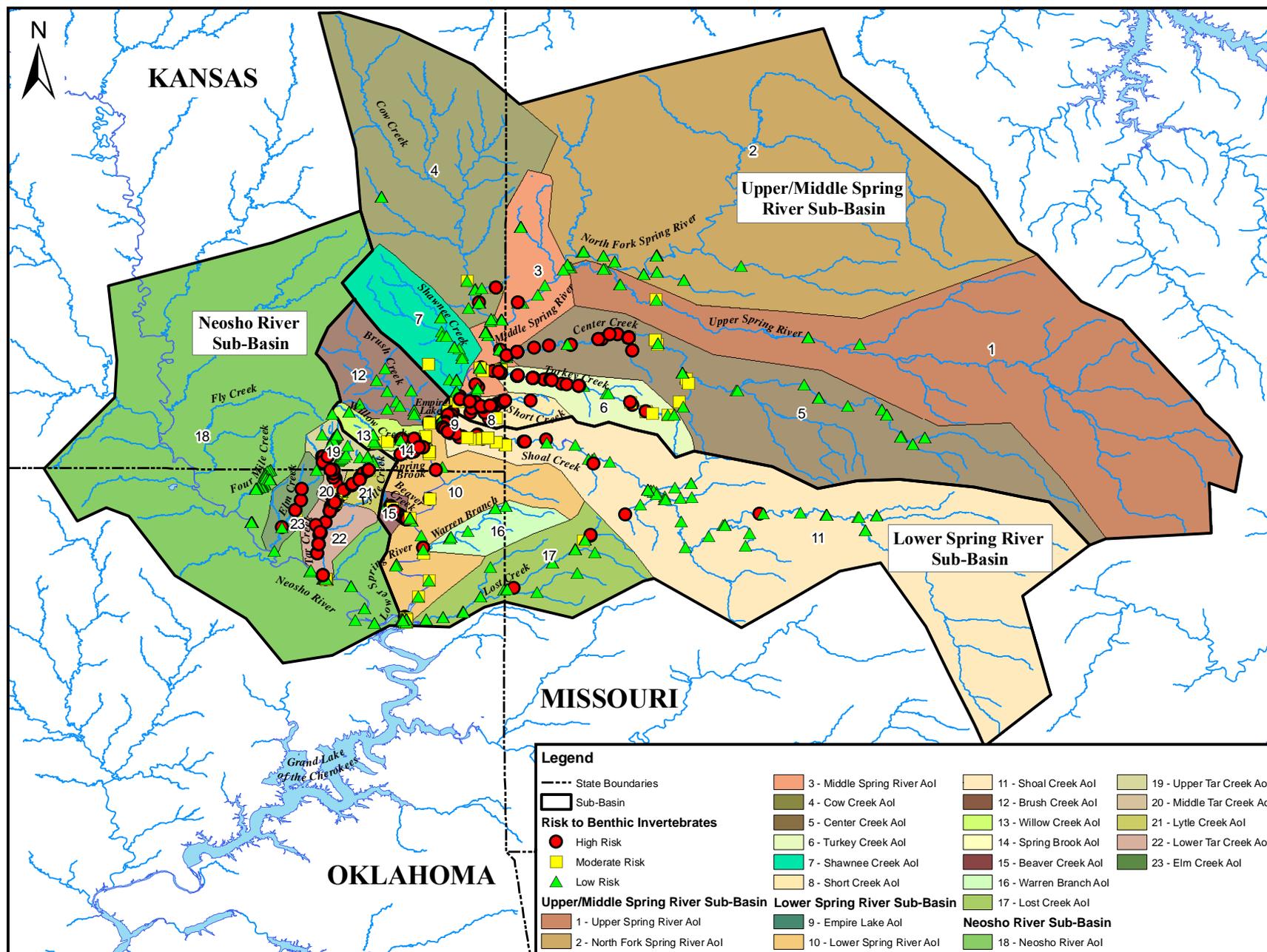


Figure ES-2. Map of Study Area, showing locations where exposure to surface water poses low ($\sum SW - TU_{\text{DIVALENT METALS}} < 1.03$), moderate ($\sum SW - TU_{\text{DIVALENT METALS}} 1.03 - 1.41$), or high ($\sum SW - TU_{\text{DIVALENT METALS}} > 1.41$) risks to the benthic community in the Tri-State Mining District.

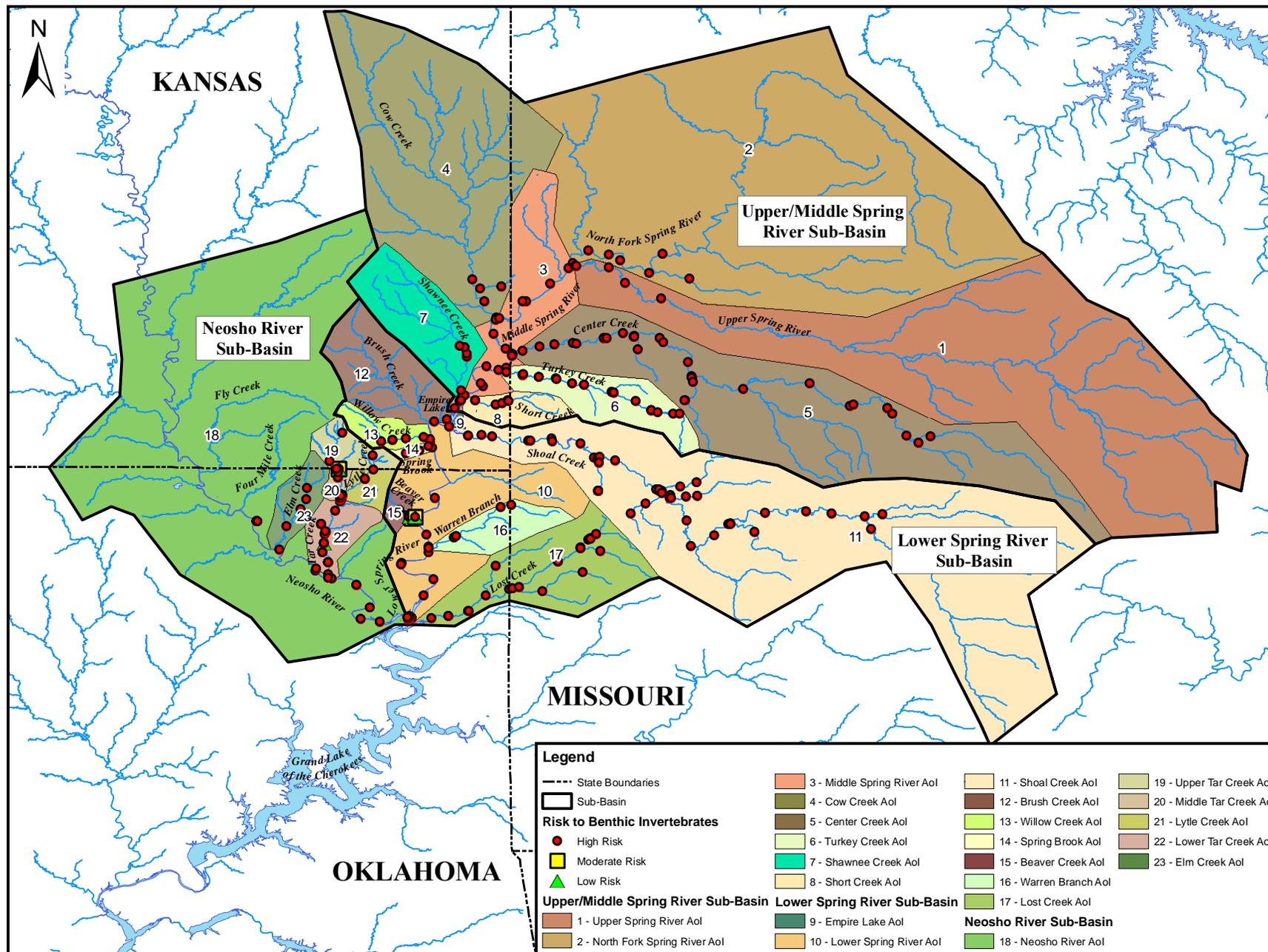


Figure ES-3. Map of Study Area, showing locations where exposure to pore water poses low ($\sum PW-TU_{Zn} < 0.581$), moderate ($\sum PW-TU_{Zn} 0.581 - 0.867$), or high ($\sum PW-TU_{Zn} > 0.867$) risks to the benthic community in the Tri-State Mining District.

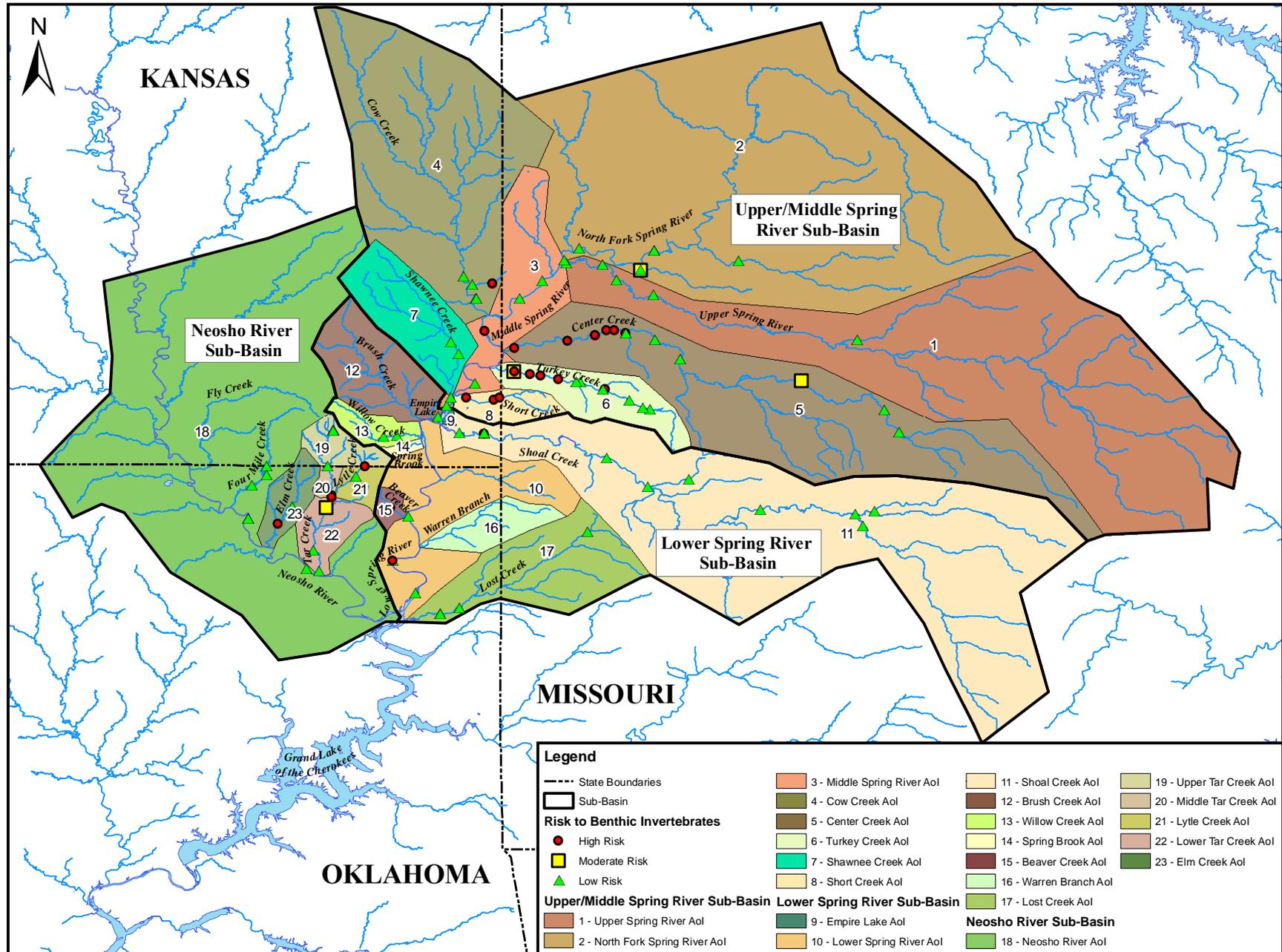


Figure ES-4. Map of Study Area, showing locations with sediments that are toxic or not toxic to the amphipod, *Hyaella azteca* (Endpoints Measured: Survival or Biomass).

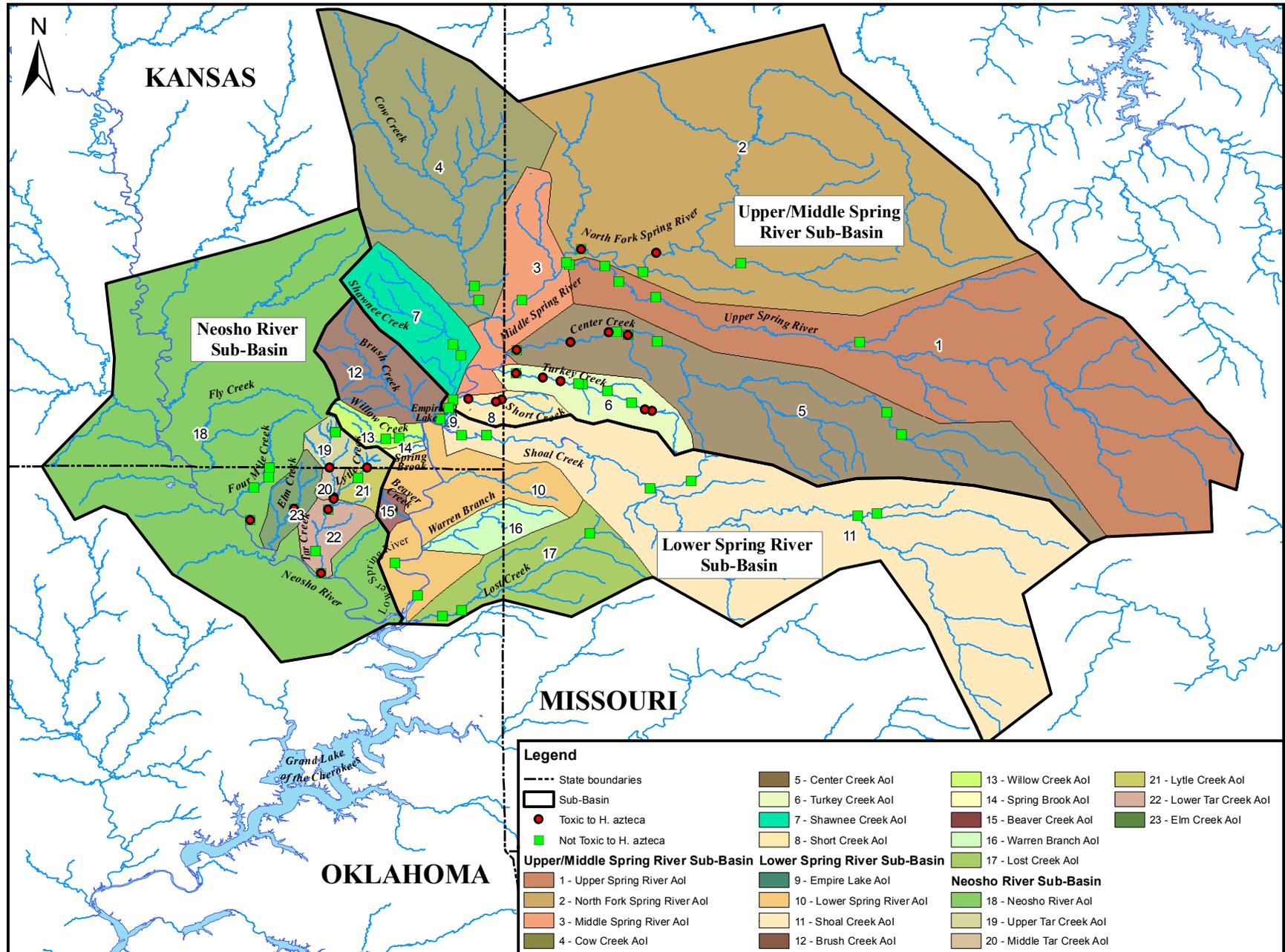


Figure ES-5. Map of Study Area, showing locations with sediments that are toxic or not toxic to the midge, *Chironomus dilutus* (Endpoints Measured: Survival or Biomass).

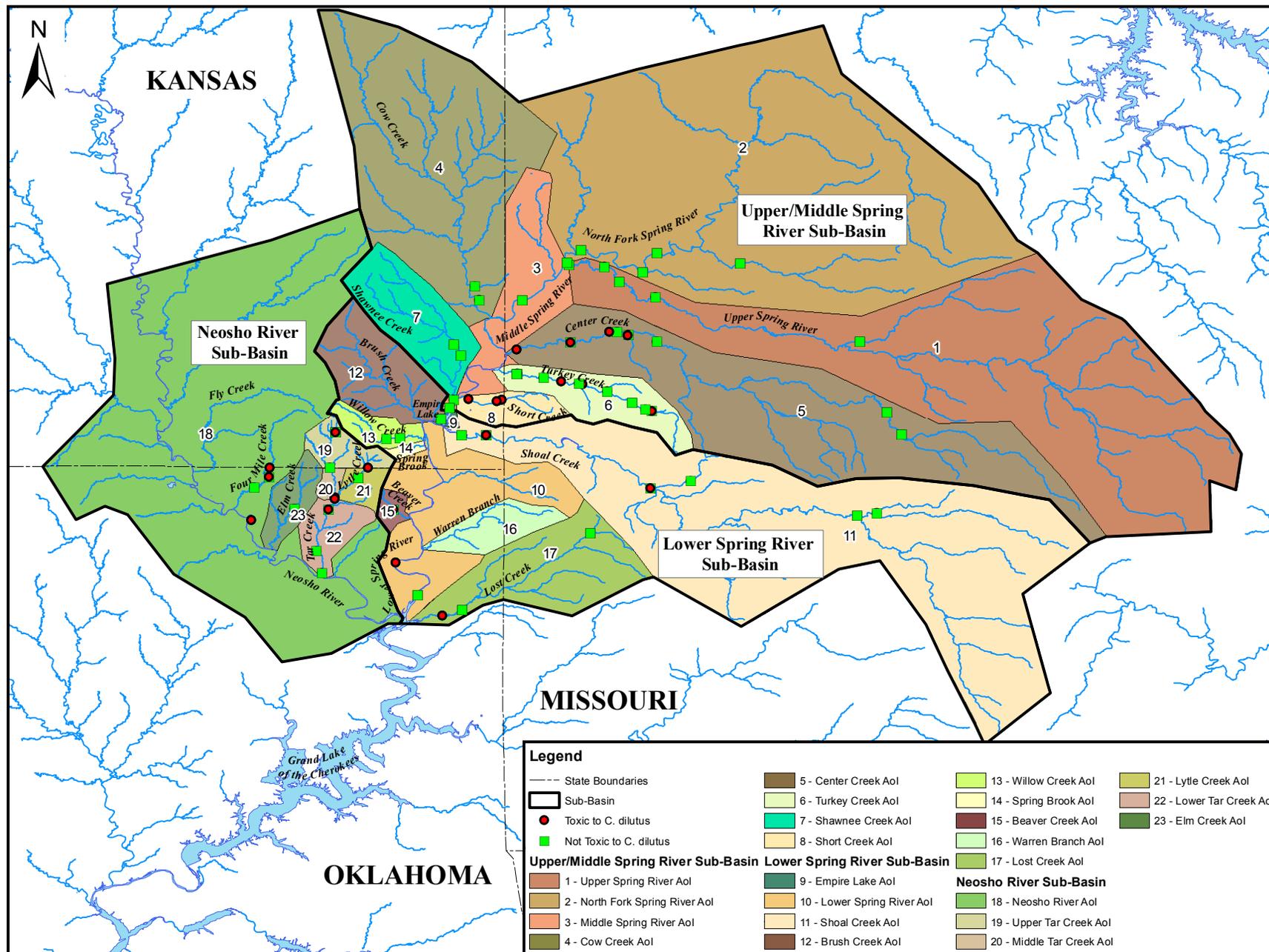


Figure ES-6. Map of Study Area, showing locations with sediments that are toxic or not toxic to the mussel, *Lampsilis siliquoidea* (Endpoints Measured: Survival or Biomass).

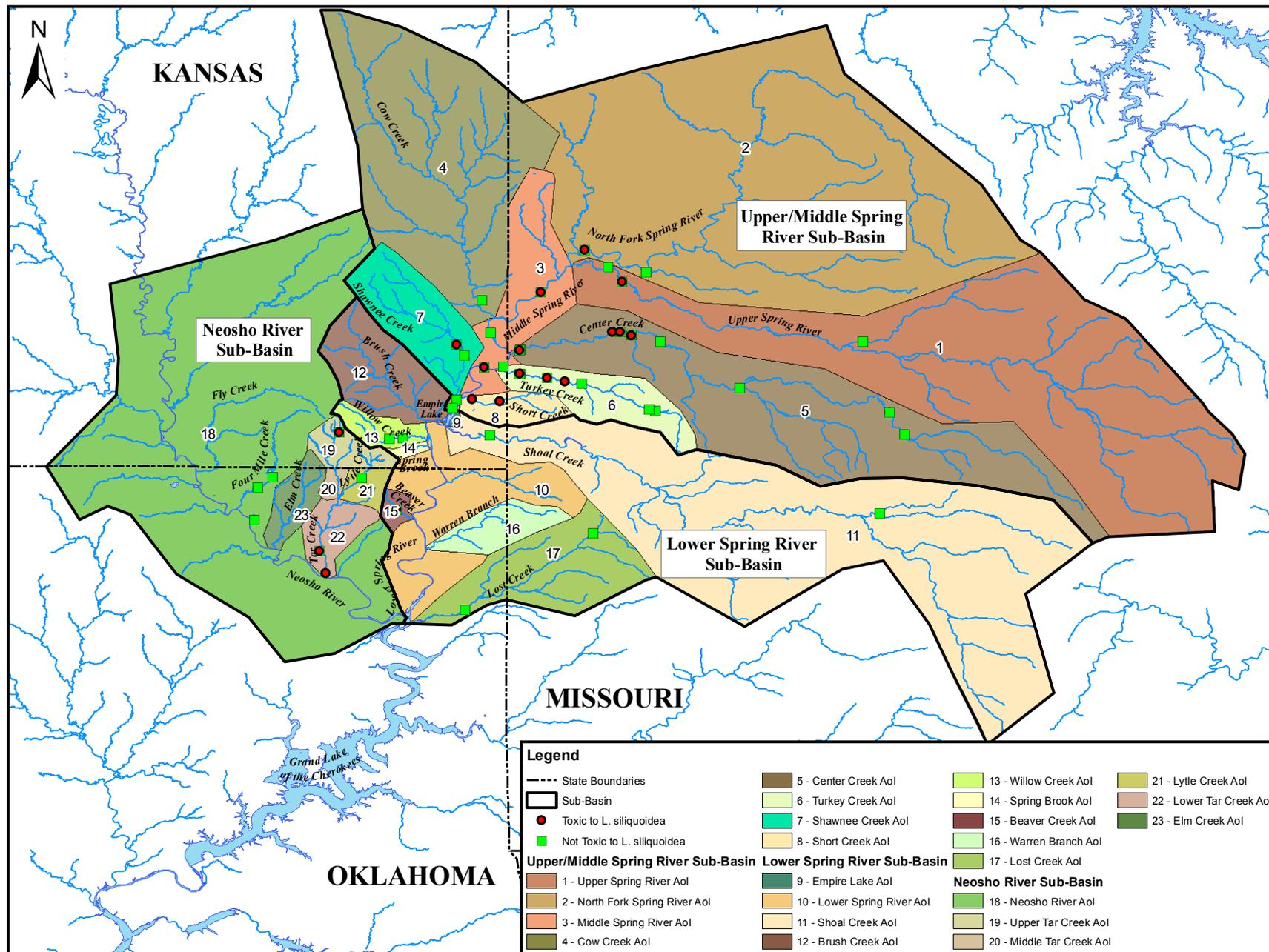


Figure ES-7. Map of Study Area, showing locations that are toxic or not toxic to amphipods (*Hyalella azteca*), midges (*Chironomus dilutus*), or mussels (*Lampsilis siliquoidea*). (Endpoints Measured: Survival or Biomass).

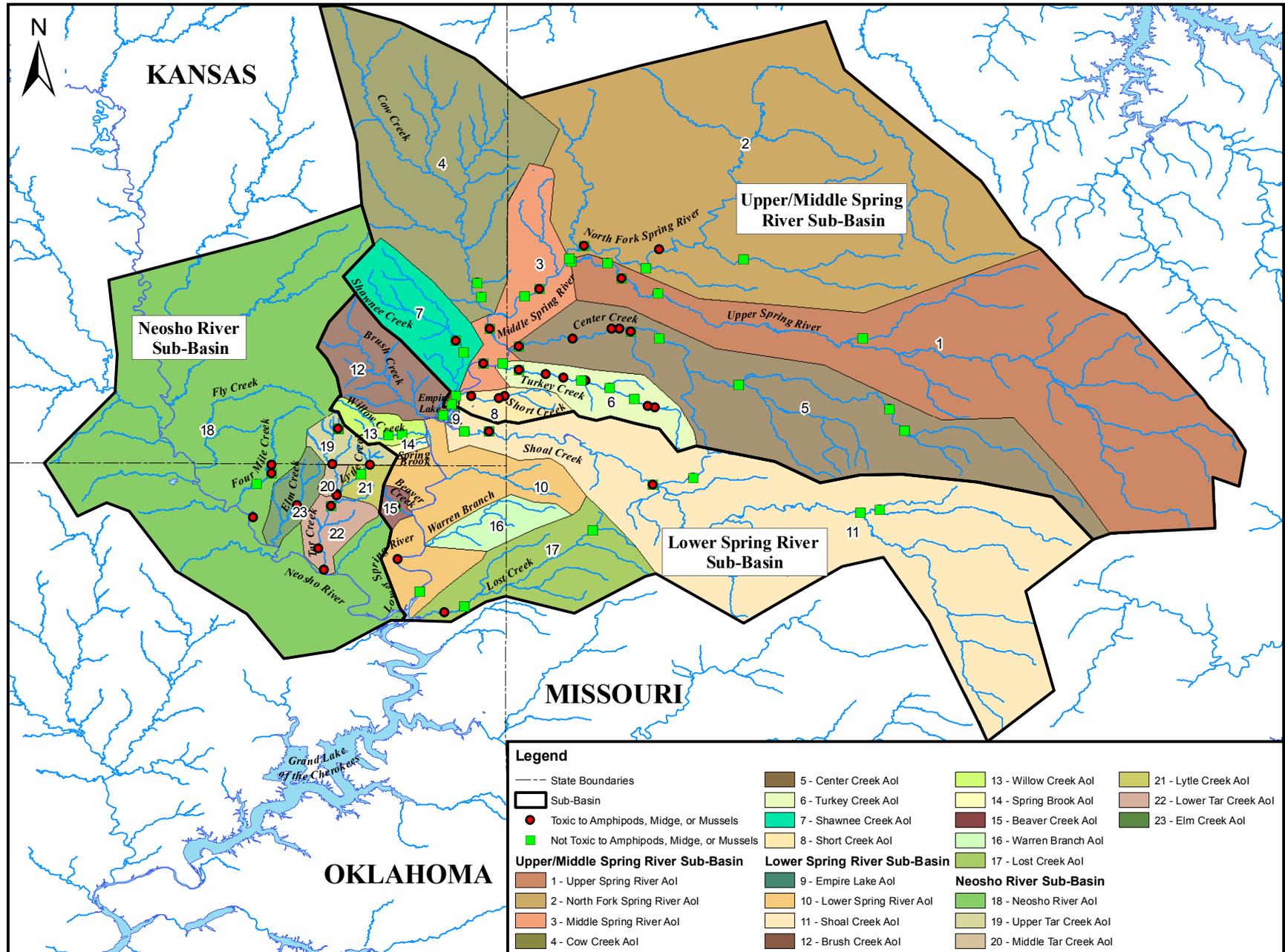
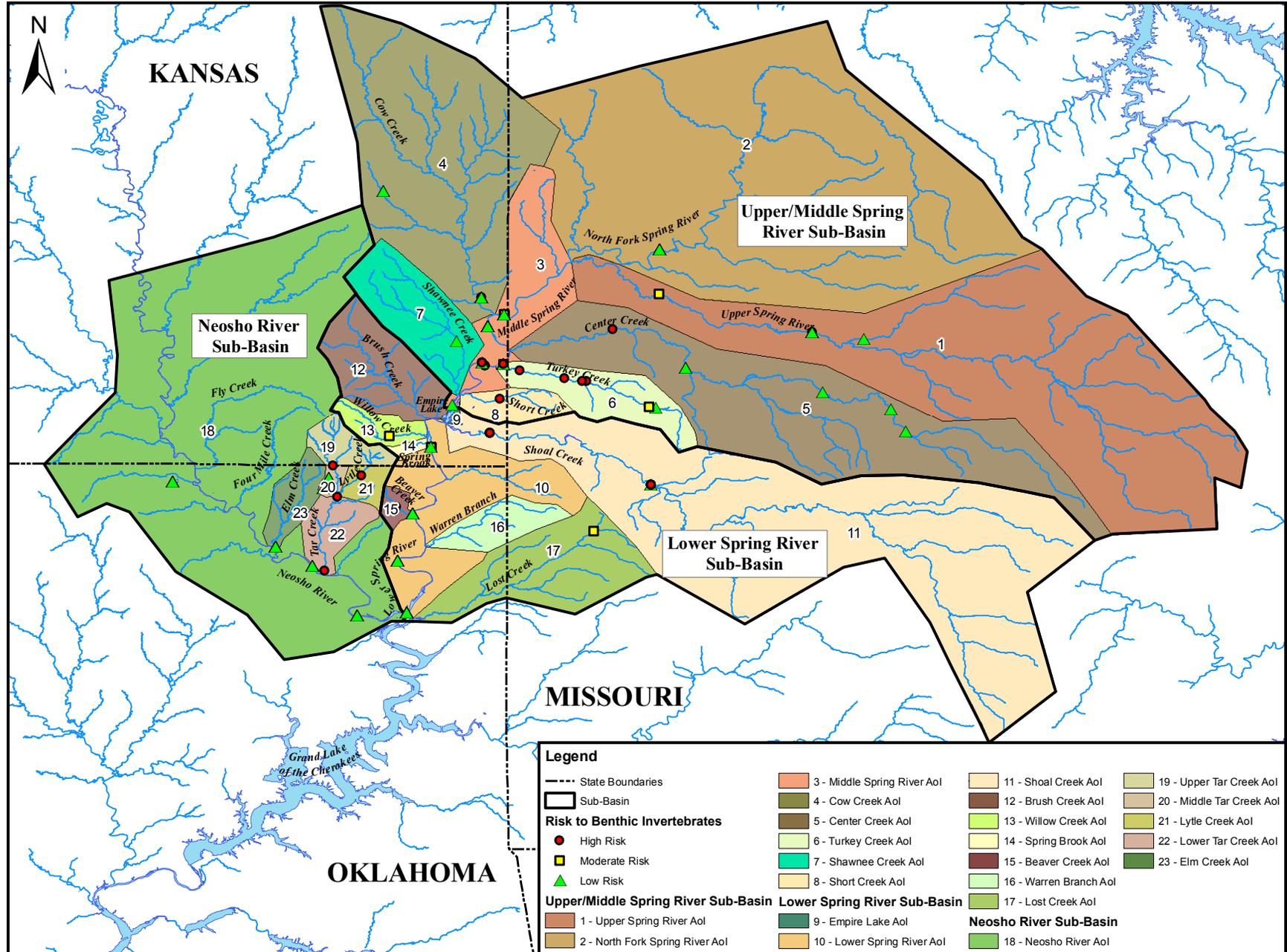


Figure ES-8. Map of Study Area, showing locations where accumulation of metals in invertebrate tissues poses low ($\sum \text{Metal} - \text{TU} < 6.01$), moderate ($\sum \text{Metal} - \text{TU} 6.01 - 7.45$), or high ($\sum \text{Metal} - \text{TU} > 7.45$) risks to the benthic community in the Tri-State Mining District.



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Disclaimer: The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Chapter 1 Background

1.0 Introduction

The Tri-State Mining District (TSMD) is a historical lead and zinc mining area that includes portions of Kansas, Missouri, and Oklahoma (Figure 1). The TSMD was one of the world's foremost lead and zinc mining areas, yielding about 460 million tons of crude ore between 1850 and 1970 (Black and Veatch Special Projects Corp. 2006). The lead and zinc deposits within the TSMD, an area of about 500 square miles, were associated with the geologic region known as the Ozark Plateau, which is characterized by the presence of Mississippian rocks. The ore deposits were typically accessed using underground mining methods, with recovered ore typically crushed on site and concentrated using gravity separation and/or floatation. These two ore-concentration processes resulted in the production of sand- and gravel-sized particles called chat (i.e., coarse tailings) and sand- and silt-sized particles called tailings. Further smelting and refining of these ore concentrates were conducted at various locations within the study area or elsewhere. Historical mining activities in the TSMD have resulted in contamination of surface water, groundwater, sediments, and/or floodplain soils in the Tar Creek, Neosho River, and Spring River basins by lead, zinc, and other heavy metals.

In response to public concern regarding the potential for adverse effects on human health and ecological receptors associated with exposure to site-related contaminants, a number of sites within the TSMD have been included on the National Priorities List (NPL). These include two sites within Missouri (Oronogo-Duenweg Mining Belt Site, Jasper County and the Newton County Mine Tailings Site), one site within Kansas (Cherokee County Site), and one site within Oklahoma (Tar Creek Site, Ottawa County). A systematic process (i.e., remedial investigation/feasibility study; RI/FS) is typically used to investigate and remediate sites on the NPL. The RI process is intended to provide the information needed to:

- Characterize site conditions;
- Determine the nature of the waste;
- Assess risks to human health and the environment; and,
- Conduct treatability testing to evaluate the potential performance and cost of the treatment technologies that are being considered.

The feasibility study is the mechanism for developing, screening, and evaluating the alternative remedial options that are proposed for the site. Together, the RI and FS are intended to provide the information needed to make informed decisions regarding the management of risks to human health and the environment at hazardous waste sites.

Unique issues and concerns have dictated different approaches and schedules for conducting investigations and evaluating remedial alternatives at each of the NPL sites in the TSMD. As a result, site investigations have generally proceeded independently for the sites located within Spring and Neosho river watersheds. In certain operable units (OUs) of these sites, RIs have already been completed (e.g., OU-2, OU-3, and OU-4 of the Oronogo-Duenweg Mining Belt Site). In other OUs, the RI process has not yet been initiated (e.g., OU-5 within the Tar Creek Site). This phasing of investigations has allowed risk managers to effectively address serious and imminent risks to human health and the environment through implementation of source control, time critical removal, and other actions in upland and riparian areas.

In recent years, the United States Environmental Protection Agency (USEPA) and its partners have recognized that effective assessment of risks to human health and ecological receptors associated with exposure to site-related contaminants in aquatic habitats cannot be effectively addressed without applying a watershed-based approach. This is particularly important in the Spring River and Tar Creek watersheds, where contaminated sediments and flood-plain soils not only pose potential risks to ecological receptors, but also represent source materials to downstream areas. As a result, risk management decisions in upstream areas will need to consider issues related to the stability of in-stream sediments and flood-plain soils and the potential for downstream transport of these materials.

In recognition of the need for more comprehensive information on sediment quality conditions within the Spring and Neosho river watersheds, USEPA (Region 6 and Region 7) and its partners conducted focused studies in 2006 and 2007. These studies were intended to provide further information for determining the nature and extent of sediment contamination, assessing the toxicity of contaminated sediments, and evaluating the bioavailability of sediment-associated contaminants in the TSMD. In 2006, 310 sediment samples were collected and submitted for chemical characterization to evaluate the nature and extent of contamination throughout the TSMD. In 2007, a further 70 sediment samples were collected and tested to evaluate sediment chemistry, sediment toxicity, and bioaccumulation. Collectively, the resultant data from these two recent studies and information from previous

studies provide a basis for better identifying in-stream source areas and for evaluating potential risks to aquatic receptors throughout these important watersheds.

This document describes the results of two ecological risk assessments (ERA) that were conducted to determine if exposure to site-related contaminants poses potential risks to ecological receptors utilizing aquatic habitats within the TSMD. First, a screening-level ERA (SLERA) was conducted using the surface-water chemistry, sediment chemistry, and pore-water chemistry data that have been generated for the TSMD since 2002 (i.e., to reflect contemporary conditions in the study area). While various types of ERAs have been conducted previously for Jasper County, MO (Black and Veatch Special Projects Corp. 1999), for Cherokee County, KS (Dames and Moore 1993), and for Ottawa County, OK (Schmitt *et al.* 2006), these studies do not reflect the results of recent investigations that provide broad spatial coverage of the study area. Accordingly, the SLERA is intended to provide a conservative, watershed-wide evaluation of the potential risks to ecological receptors posed by exposure to chemicals of potential concern (COPCs) associated with exposure to abiotic media in aquatic habitats within the TSMD.

Second, a detailed evaluation of risks to benthic invertebrates utilizing aquatic habitats within the TSMD was conducted. Benthic invertebrates were selected as a key ecological receptor group in the study area because they represent the essential elements of aquatic food webs and tend to be among the most sensitive organisms when exposed to sediment-associated contaminants. The detailed ERA (or DERA) utilized multiple lines-of-evidence to assess risks to benthic invertebrate communities associated with exposure to COPCs in surface water, sediment, and pore water. Importantly, the DERA relied on the site-specific toxicity thresholds (SSTTs) for sediments and pore water that were developed using matching toxicity and chemistry from the study area, as well as information on several additional lines-of-evidence (i.e., surface-water chemistry, invertebrate-tissue chemistry, and mussel distribution and abundance). As a result, uncertainty in the estimates of risks to benthic invertebrates is likely to be substantially reduced. Accordingly, the DERA provides risk managers with useful information for identifying source areas, evaluating candidate source control measures, and assessing various risk management options for these watersheds.

1.1 Approach to Ecological Risk Assessment

As indicated above, two ERAs were conducted to evaluate potential risks to aquatic organisms associated with exposure to contaminated environmental media located throughout the TSMD. These ERAs were conducted in general accordance with the *Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessment* (USEPA 1997) to ensure that the results can be integrated into ongoing RIs (e.g., Cherokee County, Jasper County, and Newton County) and/or future RIs for relevant subsites within the TSMD (e.g., Ottawa County). The USEPA guidance document describes an ERA framework (Figure 2) and an eight-step process for conducting an ERA (Figure 3), including:

- Step 1: Screening-Level Preliminary Problem Formulation and Ecological Effects Evaluation;
- Step 2: Screening-Level Preliminary Exposure Estimate and Risk Calculation [there is a Scientific Management Decision Point (SMDP) at the end of this step to determine if a full ERA is necessary];
- Step 3: Baseline Risk Assessment Problem Formulation (SMDP to establish agreement on CSM, assessment endpoints, exposure pathways, and risk questions);
- Step 4: Study Design and Data Quality Objectives (SMDP to establish agreement on measurement endpoints, study design, and analysis plan);
- Step 5: Field Verification of Sampling Design (SMDP to approve work plan and sampling and analysis plan for ERA);
- Step 6: Site Investigation and Analysis of Exposure and Effects (SMDP only if change in sampling and analysis plan is necessary);
- Step 7: Risk Characterization; and,
- Step 8: Risk Management (SMDP to sign Record of Decision).

In accordance with the USEPA guidance, the ERAs of the TSMD were conducted using this stepwise approach. The objectives of these ERAs were to:

- Evaluate the potential risks posed to ecological receptors exposed to abiotic media within aquatic and riparian habitats in the TSMD;
- Evaluate risks to benthic invertebrates utilizing aquatic habitats in the TSMD;

- Provide the information needed by risk managers to determine the need for additional source control measures and to establish clean-up goals for the site; and,
- Provide the information needed by Natural Resources Trustees to develop restoration goals for the TSMD.

1.2 Purpose of this Report

Ecological risk assessment is a process that evaluates the likelihood that adverse ecological effects are occurring or may occur as a result of exposure to one or more stressors (USEPA 1998). The process is used to systematically evaluate and organize data, information, assumptions, and uncertainties in order to help understand and predict the relationships between stressors and receptors (i.e., ecological effects) in a way that is useful for environmental decision-making (USEPA 1998). An assessment may involve one or more chemical, physical, or biological stressors.

The ERA process consists of three phases, problem formulation, analysis, and risk characterization (Figure 3). The first phase, problem formulation, is a systematic planning process that identifies the factors to be addressed in an ERA and consists of five major activities (USEPA 1997a). First, a preliminary list of COPCs at the site is established. Next, the potential ecological effects of the COPCs at the site are characterized. In addition, the available information on the transport and fate of the COPCs, on potential exposure pathways, and on the biota potentially at risk is reviewed and evaluated. Together, this information provides a basis for selecting the assessment and measurement endpoints that will be used in the risk assessment. Finally, a conceptual model, with testable hypotheses (or risk questions) that the site investigation will address, is developed in a manner that links the assessment and measurement endpoints. At the conclusion of the problem formulation, there is a scientific/management decision point, which consists of agreement on four items: the assessment endpoints; the exposure pathways; the risk questions; and, the conceptual model that integrates these components (Figure 3; USEPA 1997a).

The analysis phase of the ERA process, which is driven by the problem formulation, consists of two main elements, exposure characterization and effects characterization (Figure 2; USEPA 1998). Exposure is the contact or co-occurrence of a contaminant and a receptor (Suter *et al.* 2000). The exposure assessment is intended to provide an estimate of the magnitude of exposure to stressors, over time and space. In the analysis of effects, the nature of the effects that are associated with exposure to one or more stressors is evaluated, along with their magnitude as a function of exposure. Collectively, the information compiled during this phase of the process supports characterization of the nature of potential or actual exposure and of the ecological responses under the circumstances defined in the conceptual model (USEPA 1998). The two main products of the analysis phase, the exposure profile and the stressor-response profile, provide a basis for the third and final phase of the process, risk characterization (Figure 2). At the conclusion of the analysis phase, a SMDP is required if new information becomes available that necessitates alteration of measurement endpoints, testable hypotheses, and/or sampling design.

During the risk characterization, the exposure and stressor-response profiles are integrated through the risk estimation process (USEPA 1998). Risk characterization is undertaken to determine if significant effects are occurring or are likely to be occurring at the site under investigation. In addition, the nature, magnitude, and areal extent of effects on the selected assessment endpoints are determined. Finally, the stressors that are causing or substantially contributing to such effects are identified. Risk characterization includes a summary of assumptions, scientific uncertainties, and the strengths and weaknesses of the analyses (i.e., an uncertainty analysis).

This document was prepared to present the results of two watershed-wide ERAs for the TSMD. More specifically, this report was prepared to present the results of the SLERA that was conducted for the study area. In addition, the report is intended to present the detailed problem formulation, describe the conceptual model for the site, and identify the assessment and measurement endpoints that were selected for evaluating risks to the benthic invertebrate community. Detailed exposure profiles and stressor-response profiles are presented in the report. The nature, magnitude, and spatial extent of risks to benthic invertebrates are also described. Finally, the major areas of uncertainty in the assessment, along with the approaches that were used to address them, are identified and discussed in this report. Collectively, the SLERA and DERA are intended to provide contemporary information on

the risks posed to selected ecological receptors associated with exposure to site-related COPCs in the TSMD.

The approaches used to conduct the SLERA and DERA are generally consistent with the guidance that has been issued by USEPA (1997a; 1998). In addition, the methods used are consistent with the procedures described in the Guidance Manuals for Assessing Contaminated Sediments in Freshwater Ecosystems (MacDonald and Ingersoll 2002a; 2002b; Ingersoll and MacDonald 2002). The reader is directed to these documents for more information on the selected methods and the rationale for their application.

1.3 Organization of this Report

This report is organized into a number of sections to facilitate access to the information associated with the SLERA and the DERA of the TSMD, including:

- Background (Chapter 1);
- Geographic Scope of Study Area (Chapter 2);
- Screening-Level Problem Formulation and Ecological Effects Evaluation (Chapter 3);
- Screening-Level Exposure Estimate and Risk Calculation (Chapter 4);
- Development of Ecosystem Goals and Objectives for the Tri-State Mining District (Chapter 5);
- Overview of Problem Formulation for Detailed Assessment of Risks to the Benthic Invertebrate Community (Chapter 6);
- Approach to the Assessment of Risks to the Benthic Invertebrate Community (Chapter 7);
- Detailed Assessment of Risks to the Benthic Invertebrate Community (Chapter 8);
- Uncertainty Analysis (Chapter 9);

- Development of Preliminary Remedial Action Objectives for the Tri-State Mining District (Chapter 10);
- Summary and Conclusions (Chapter 11); and,
- References (Chapter 12).

Appendix 1 presents the preliminary problem formulation for the DERA of aquatic habitats in the TSMD. More detailed information on the environmental fate and effects of site-related COPCs is provided in Appendix 2. Relationships between the concentrations of metals in various particle size classes of sediment are presented in Appendix 3. Procedures for interpreting the results of sediment toxicity tests are described in Appendix 4. A description of the data sets that were compiled to support the SLERA and DERA is provided in Appendix 5. An overview of the quality of the data collected during the 2007 sediment sampling program of the TSMD is presented in Appendix 6. An overview of the approach that was used to compile, evaluate, and analyze the surface-water chemistry, sediment chemistry, pore-water chemistry, invertebrate tissue chemistry, sediment toxicity, and mussel taxa richness data that were used to support the advanced SLERA of the TSMD is presented in Appendix 7. Finally, a glossary of terms and a list of acronyms are provided (after the Table of Contents) to define the various scientific terms that are used throughout this document.

Chapter 2 Geographic Scope of Study Area

2.0 Introduction

The TSMD is comprised of a total of four NPL sites in Missouri (MO), Kansas (KS), and Oklahoma (OK), including: the Cherokee County site, Cherokee County, KS; the Orong-Duenweg Site, Jasper County, MO; the Newton County Mine Tailings Site, Newton County, MO; and, the Tar Creek Site, Ottawa County, OK (Figure 1). Although there are a variety of land use activities within the Spring River and Neosho River watersheds, environmental concerns in the area have focused primarily on releases of metals from historical mining activities. Ores bearing lead, zinc, and other base metals were mined, milled, and smelted in the TSMD between about 1850 and 1970. During this period, metals may have been released from a vast number of mining, milling, and smelting operations in the study area. The total mass of metals released to the environment from these operations is unknown, however.

In response to public concerns regarding the potential effects on human health and the environment associated with exposure to site-related COPCs, a SLERA and a DERA are being conducted to assess risks to ecological receptors utilizing aquatic habitats in the study area. Although the TSMD consists of four separate NPL sites, there are a number of similarities among the sites. Importantly, historical land use activities were similar for the four sites, with mining and smelting occurring throughout the TSMD. There are also numerous similarities in terms of the physical, chemical, and biological characteristics of the areas. For this reason, USEPA has decided to assess risks to selected ecological receptors over the entire TSMD. In this way, the results of the SLERA and DERA will provide a consistent basis for identifying priorities for further investigation within each of the individual NPL sites. This chapter describes the geographic scope of the study area.

2.1 Considerations for Determining the Geographic Scope of the Study Area

For the purposes of assessing risks to ecological receptors, it is necessary to define the geographic scope of the study area. According to Suter *et al.* (2000), the spatial extent of a site can be established based on one or more of the following criteria:

- The areas in which wastes have been deposited;
- The areas believed to be contaminated;
- The areas owned or controlled by the responsible party;
- The extent of transport processes; and,
- The buffer zones.

While a site-wide approach was adopted for the advanced SLERA, it was useful to identify a number of areas of interest (i.e., spatial units) within the study area (i.e., to provide an understanding of spatial patterns of potential risks to ecological receptors and to support risk management decisions at an appropriate spatial scale). The decision about how to divide the site into spatial units must be based on two considerations, the location of the contaminants and the dynamics of the site (i.e., both hydrological and biological; Suter *et al.* 2000). Therefore, detailed biological surveys and habitat evaluations are often conducted to facilitate the identification of ecologically-relevant areas of interest and reaches within each area of interest. Reference areas are also commonly identified to support evaluations of risks to ecological receptors.

2.2 Geographic Scope of the Study Area

The geographic scope of the TSMD is defined as the in-channel, riparian, and floodplain areas from the headwaters of the Spring River to Grand Lake for the Spring River watershed and from Oswego, KS to Grand Lake for the Neosho River watershed. However, that definition of the study area did not provide a basis for evaluating spatial patterns of contamination or

associated risks to aquatic receptors. For this reason, the study area was initially divided into eight areas of interest (AoIs) to facilitate the design of the 2007 Sediment Sampling Program. While these divisions were relevant and appropriate for designing the sampling program, it was decided that it would be beneficial to report the results of the DERA with greater spatial resolution. For this reason, the study area was re-divided into a total of 23 AoIs (Figure 4). The AoIs that are located within Missouri, Kansas, and Oklahoma are shown in Figures 5, 6, and 7, respectively. The AoIs were grouped into sub-basins including the Upper/Middle Spring River, Lower Spring River, and Neosho River sub-basins as follows:

Upper/Middle Spring River Sub-Basin

- Upper Spring River AoI (Spring River and associated tributaries located upstream of the confluence with the North Fork Spring River);
- North Fork Spring River AoI;
- Middle Spring River AoI (Spring River mainstem from the confluence with the North Fork Spring River to Empire Lake, including the tributaries that are not included in the other AoIs);
- Cow Creek AoI;
- Center Creek AoI;
- Turkey Creek AoI;
- Shawnee Creek AoI; and,
- Short Creek AoI.

Lower Spring River Sub-Basin

- Empire Lake AoI;
- Lower Spring River AoI (Spring River from Empire Lake to Grand Lake, including the tributaries that are not included in other AoIs);
- Shoal Creek AoI;
- Brush Creek AoI;
- Willow Creek AoI;
- Spring Brook AoI;

- Beaver Creek AoI;
- Warren Branch AoI; and,
- Lost Creek AoI.

Neosho River Sub-Basin

- Neosho River AoI (Neosho River from approximately Oswego to Grand Lake);
- Upper Tar Creek AoI (Tar Creek and associated tributaries from the headwaters to the Kansas-Oklahoma border);
- Middle Tar Creek AoI (Tar Creek and associated tributaries from the Kansas-Oklahoma border to the confluence with Lytle Creek);
- Lytle Creek AoI;
- Lower Tar Creek AoI (Tar Creek and associated tributaries from the confluence with Lytle Creek to the confluence with the Neosho River); and,
- Elm Creek and associated tributaries.

Because mining activities have been conducted throughout the study area (Figure 8), it was difficult to identify reference areas within the TSMD. However the results of investigations conducted recently by the Quapaw Tribe suggested that Four-Mile Creek and Upper Tar Creek may represent suitable reference areas for the TSMD (Kirshner 2008). In addition, investigations conducted by USEPA and its partners in 2006 and 2007 demonstrated that additional reference sites could be identified elsewhere within the TSMD. MacDonald *et al.* (2009) provided a listing of the locations that were selected for establishing reference conditions in the TSMD.

Chapter 3 Screening-Level Problem Formulation and Ecological Effects Evaluation

3.0 Introduction

In accordance with USEPA guidance, the problem formulation for a SLERA is intended to provide three main products, including: assessment endpoints; a conceptual model(s); and, a risk analysis plan (USEPA 1997a; 1998). The conceptual site model (CSM) represents a particularly important component of the problem formulation because it enhances the level of understanding regarding the relationships between human activities and ecological receptors at the site under consideration. Specifically, the conceptual model describes key relationships between stressors and assessment endpoints. In so doing, the CSM provides a framework for predicting effects on ecological receptors and a template for generating risk questions and testable hypotheses (USEPA 1997a; 1998). The CSM also provides a means of highlighting what is known and what is not known about a site. In this way, the conceptual model provides a basis for identifying data gaps and designing monitoring programs to acquire the information necessary to complete the assessment.

Conceptual site models consist of two main elements, including: 1) a set of hypotheses that describe predicted relationships between stressors, exposures, and assessment endpoint responses (along with a rationale for their selection); and, 2) diagrams that illustrate the relationships presented in the risk hypotheses. The following sections of this chapter summarize information on the sources and releases of COPCs, the transport and fate of these substances, the pathways by which ecological receptors are exposed to the COPCs, and the potential effects of these substances on the ecological receptors that occur in the TSMD. In turn, this information is used to develop a series of hypotheses that provide predictions about how ecological receptors will be exposed to and respond to the COPCs present in the study area.

3.1 Environmental Setting

The TSMD encompasses an area of about 1,188 square miles (3,118 km²) in southwestern Missouri, southeastern Kansas, and northeastern Oklahoma (Andrews *et al.* 2009). This area was one of the most productive lead and zinc mining areas in the United States, with more than 4,000 subsurface mines producing about 1.7 million tons of lead and 8.8 million tons of zinc over a period of roughly 120 years (Andrews *et al.* 2009; Angelo *et al.* 2007).

The Spring River and Neosho River represent the principal watercourses in the TSMD. The Spring River drains about 6,600 km² of land in Missouri, Kansas, and Oklahoma (Angelo *et al.* 2007). From its headwaters in the Ozark Highlands, the Spring River flows some 200 km to its confluence with the Neosho River, which together constitute the headwaters of Grand Lake O' the Cherokees (Grand Lake; Angelo *et al.* 2007). Over that distance, the Spring River is joined by a number of tributaries, including the North Fork of the Spring River, Center Creek, Turkey Creek, Cow Creek, Short Creek, Shoal Creek, Brush Creek, Willow Creek, Five-Mile Creek, Beaver Creek, Warren Branch, Lost Creek, and Shawnee Creek. Empire Lake represents the largest reservoir in the river basin.

The Neosho River drains an area of 33,225 km² of land, primarily in Kansas and Oklahoma. Its headwaters are located in Morris County, KS, near the town of Parkerville. From that location, the Neosho River flows some 736 km to its confluence with the Spring River. The Cottonwood River and Lightning Creek represent the largest tributaries to the Neosho River in Kansas. Fly Creek, Four-Mile Creek, Elm Creek, and Tar Creek are the principal tributaries that join the Neosho River in Oklahoma.

The Spring River and the tributaries in the eastern portion of the watershed originate in the Ozark Highlands. These watercourses flow through the Springfield Plain, which has low-moderate relief (< 46 meters) and is underlain by Mississippian cherty limestones. As expected in areas with Karst topography, there is substantial communication between surface water and groundwater resources. Numerous springs occur throughout the area. Pre-settlement vegetation was mostly prairie, with timber along stream courses. These streams are characterized by relatively stable flow patterns, gravelly substrate, and clear water.

The Neosho River, its tributaries, and the western tributaries to the Spring River flow through the Cherokee Plains. This portion of the study area has very low relief (usually < 25 meters) and is underlain by Pennsylvanian sandstones and shales. Thin-bedded limestones and coal are also present in this area. Wetlands are abundant throughout the wide, flat alluvial floodplains. Pre-settlement vegetation was both upland and wet prairie. Most of the land is currently in pasture and cropland, with local areas of extensive strip mines. Substantial prairie remnants are still apparent in certain locations. Streams flowing through this portion of the study area generally have less reliable flow patterns, fine-grained stream-bed substrates, and greater turbidity.

3.2 Sources and Releases of Contaminants

There are a number of natural and anthropogenic sources of toxic and bioaccumulative substances in the TSMD. Anthropogenic sources of environmental contaminants in the watershed are dominated by releases and discharges associated with historical mining, milling, and smelting operations. When mining ended in the mid-1970s, hundreds of millions of tons of coarse mine tailings (waste rock, locally known as chat) were distributed in piles and elsewhere throughout the TSMD (Figure 8). By 2000, about 75 million tons of chat remained in the study area. In addition, fine tailings (i.e., clay- and silt-sized particles) were also distributed in numerous tailings ponds located throughout the TSMD. Ongoing releases from these structures, as well as minewater discharges, represent continuing sources of contaminants to the Spring and Neosho river basins. In addition, municipal wastewater treatment plant discharges, stormwater discharges, surface-water recharge by contaminated groundwater, non-point source discharges, spills associated with production and transport activities, and deposition of substances that were originally released into the atmosphere represent potential sources of contaminants within the study area. Participants attending an ecological risk assessment workshop (convened on January 17 and 18, 2007) indicated that the potential sources of contaminants within the TSMD include (MESL and CH2M Hill 2007):

- NPDES permitted outfalls;
- Agricultural runoff;

- Urban stormwater runoff;
- Chat piles and chat bases;
- Mill ponds (including tailings ponds, slime ponds, and tailings impoundments);
- Chat washing facilities (which result in the production of fines, which may be routed to floatation ponds; in some cases, floatation ponds exist under chat piles and represent sources of contaminants during and following rain events);
- Relocation of chat for other uses (e.g., construction of roads, driveways, railroad beds, foundations for houses, and sewer lines);
- Groundwater discharges and seeps (including perched groundwater within chat piles, groundwater seeps, and groundwater upwelling into streambeds. The area has Karst-type geology east of the Spring River and Pennsylvania shale west of the Spring River);
- Minewater discharge (this type of source includes direct minewater discharges to Lytle Creek and discharges from boreholes);
- Historical smelting operations (resulting in aerial dispersion of metals and direct releases of slag into river systems; at Galena, Short Creek runs through a slag pile);
- Runoff from contaminated floodplain soils (this is particularly important in Center Creek, Turkey Creek, and in the vicinity of the smelters; this source is likely to be most active during periods of high precipitation and/or elevated streamflows);
- Dust deposition from chat piles (the Quapaw Tribe has conducted air monitoring upwind and downwind of chat sales operations and observed that the levels of lead never exceeded ambient air quality standards; levels of lead were highest closest to the source. USEPA models identified air as a potential source of metals to areas that have been cleaned-up previously, but concluded that air was not a significant source); and,
- Streambed sediments (sediments represent an important secondary source of COPCs to downstream areas, particularly during periods of elevated streamflow).

It was also noted that chat is currently being used in the production of asphalt, which represents an effective source control measure as encapsulation in asphalt is thought to render the metals largely unavailable.

3.3 Chemicals of Interest

Based on the information provided by participants at the January 17 and 18, 2007 Ecological Risk Assessment Workshop (MESL and CH2M Hill 2007), a wide variety of substances may have been released into aquatic ecosystems located within the TSMD. While cadmium, lead and zinc are known to occur at elevated levels in the TSMD, many other contaminants have also been identified as chemicals of interest (COIs). Using information on the environmental transport and fate of these substances, it is reasonable to suggest that the following substances represent the COIs in the TSMD:

- Metals (aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, mercury, molybdenum, nickel, selenium, silver, zinc);
- Polycyclic aromatic hydrocarbons (PAHs; 13 parent PAHs + alkylated PAHs);
- Polychlorinated biphenyls (PCBs);
- Organochlorine pesticides; and,
- Various semi-volatile organic compounds (SVOCs).

The substances that were identified as COIs for evaluation under the SLERA are identified in Tables 1 and 2.

3.4 Contaminant Transport and Fate

There are a number of processes that can transport COIs from their source to the exposure locations for ecological receptors. These processes differ depending on how the COIs are

released into the environment (i.e., depending on whether the COIs are released into air, water, or soils) and the form of the COI. Each of these processes are briefly described in this section of the problem formulation to support the identification of key routes of exposure to COIs at the TSMD Site.

For COIs that are released into air, aerial transport and subsequent deposition of airborne particulates represents the primary mechanism that results in contamination of environmental media. In general, larger diameter particulates are deposited in the immediate vicinity of the release point, resulting in contamination of riparian and upland soils and/or surface waters, depending on the locations of these physical features and prevailing wind directions and velocities. Certain substances can remain airborne for substantial periods of time and be transported over long distances (e.g., VOCs), while other COIs can be repeatedly cycled through the air due to serial volatilization and precipitation in response to prevailing climatic conditions (e.g., certain SVOCs, such as PCBs).

For COIs that are released into water, downstream transport can be influenced by a variety of factors. First, substances that are released in the aqueous phase or those that dissolve readily in water are typically transported downstream in the surface-water flow. Such substances are likely to be transported out of the study area if conditions favorable to remaining in the dissolved phase persist throughout the study area. However, many contaminants that are released in the aqueous phase form associations with colloidal or particulate matter (i.e., through such fate processes as precipitation and adsorption). These COIs can also remain in the flow for extended periods of time, but are likely to be deposited onto the streambed or lake bed when water velocities are reduced (i.e., in the slow-moving sections of the river or the reservoir).

For substances that partition into the surface microlayer, volatilization can result in losses to air and subsequent transport elsewhere in or outside the TSMD Site. Alternatively, downstream transport is likely to occur for the substances that have low volatility. For example, slag has reportedly been observed to float on the surface of the water in small mats and be transported considerable distances downstream. This material is likely to sink when the surface tension is broken, such as often occurs in the turbulent sections of the river.

Some COIs are released into water in the particulate phase (i.e., in association with fine particulate matter). For these substances, downstream transport is dependent on maintaining water velocities sufficient to keep the particulate matter in suspension. Accordingly, deposition on the streambed can occur very rapidly (i.e., for large, dense particles) or can occur in downstream areas that have lower water velocities. It is important to note that deposited materials can be transported further downstream through bed load transport or through resuspension when water velocities increase. Slumping and erosion of the banks can also result in the transport of COIs from the margins of the stream or reservoir to deeper water areas. During high and extreme flow events, suspended materials can be deposited in floodplain areas and become associated with floodplain soils.

For COIs that are released to upland or riparian soils (i.e., by direct placement of contaminated material, deposition of suspended sediment, or deposition of airborne material), wind and water erosion represent the principal transport processes that result in translocation of COIs. While water erosion typically results in down gradient movement to COIs (i.e., to lower elevation soils and/or to surface water), wind erosion can result in relocation of COIs in virtually any direction. Volatilization of COIs from upland or riparian soils can result in the further transport of soil-associated COIs to other areas, with the distance that the COIs are being transported dependent on the physical-chemical characteristics of the substance and the local climatic conditions. For substances that dissolve readily in water, movement through soils and into groundwater represents a potential transport process. Such COIs can remain in groundwater for extended periods of time or can recontaminate surface water through groundwater recharge.

For many of the COIs that are released into the environment, uptake by biological organisms represents an important fate process. Such biological uptake can result in the removal of COIs from surface water, sediment, or soil, with plants and invertebrates being the most important ecosystem components that facilitate bioaccumulation. Because such plants and invertebrates are eaten by higher order consumers, these bioaccumulative COIs can be transferred and, potentially biomagnified, through aquatic, aquatic-dependent, and/or terrestrial food webs. Hence, bioaccumulation represents another important process through which water-borne, sediment-associated, and/or soil-associated COIs can be transported within and outside the TSMD Site. Bioavailability is a key factor that needs to be considered during evaluations of the bioaccumulation of COIs at the site. In addition, biotransformation

can result in the formation of substances different from the parent COIs, frequently with different physical-chemical properties.

While the preceding discussion was focused on describing COI transport processes in the study area, there are a number of fate processes that can reduce the concentrations of COIs in environmental media and/or result in the transformation of COIs. For example, chemical-oxidation, photo-oxidation, or hydrolysis can transform COIs to other, frequently less toxic, substances. Similarly, biodegradation can result in losses and/or transformations of organic substances. In addition, chemically- or biologically-mediated reduction reactions can alter the form of a chemical in the environment and, in the case of metals, render them less available to biological organisms (e.g., through the formation of metal sulfides). Furthermore, decrepitation (i.e., physical breakdown) can result in the breaking-up of particulate matter, such as chat, into smaller size fractions, potentially altering its fate in the environment.

Collectively, environmental transport and fate processes result in partitioning of COIs into environmental media (i.e., water, sediment, soil, and/or biota) in accordance with their physical and chemical properties and the characteristics of the receiving water body. As a result of such partitioning, elevated levels of COIs can occur in surface water (including the surface microlayer), bottom sediments, and/or the tissues of aquatic organisms. Accordingly, information on the environmental fate can be used to classify the COIs into three groups, including:

- Bioaccumulative substances (i.e., substances that accumulate in the tissues of aquatic organisms);
- Toxic substances that partition into sediment and/or soil; and,
- Toxic substances that partition into surface water (including pore water and the surface microlayer).

3.5 Potentially Complete Exposure Pathways

Once released to the environment, there are three pathways through which ecological receptors can be exposed to COIs. These routes of exposure include direct contact with

contaminated environmental media, ingestion of contaminated environmental media, and inhalation of contaminated air. For bioaccumulative substances, the ingestion of contaminated prey species represents the most important route of exposure for the majority of aquatic organisms and aquatic-dependent wildlife species. Direct contact with contaminated water and/or contaminated sediment and ingestion of contaminated sediment also represent an important route of exposure to bioaccumulative COIs for many aquatic organisms.

For toxic substances that partition into sediments and soil, direct contact with contaminated sediment (and pore water) and soil represents the most important route of exposure for exposure for most aquatic and terrestrial organisms. However, ingestion of contaminated sediment and/or soil can also represent an important exposure pathway for certain organisms (e.g., oligochaetes that process sediment or soil to obtain food).

For toxic substances that partition into surface water, direct contact with contaminated water represents the most important route of exposure for aquatic organisms (i.e., uptake through the gills and/or through the skin). For wildlife species, ingestion of contaminated water represents the principal route of exposure to toxic substances that partition into surface water.

For toxic substances that partition into the surface microlayer, direct contact with the contaminated surface microlayer represents the most important route of exposure for aquatic organisms (i.e., uptake through the gills and/or through the skin). However, aquatic-dependent wildlife species can be exposed to substances that volatilize from the surface microlayer through inhalation. This route of exposure could become important during and following accidental spills of VOCs, when such substances are present as slicks on the water surface. Such spills of VOCs are not expected to occur in the study area and, hence, VOCs have not been identified as COIs in the study area. A more detailed description of the pathways through which ecological receptors can be exposed to environmental contaminants is presented in Chapter 6.

3.6 Ecological Receptors Potentially at Risk

There are a wide variety of ecological receptors that could be exposed to contaminated environmental media in the TSMD. The receptor groups for which potentially complete exposure pathways exist within the TSMD can be classified into ten main receptor groups, including:

- Microbiota (e.g., bacteria, fungi and protozoa);
- Aquatic plants (including phytoplankton, periphyton, and aquatic macrophytes);
- Aquatic invertebrates (including zooplankton and benthic invertebrates);
- Fish (including benthic and pelagic fish);
- Amphibians;
- Terrestrial plants (including riparian plants and other terrestrial plants that inhabit floodplain areas);
- Terrestrial invertebrates;
- Reptiles (e.g., turtles, snakes);
- Birds (including a number of feeding guilds); and,
- Mammals (including a number of feeding guilds).

The COIs in the TSMD were classified into three categories based on their predicted environmental fate (MESL *et al.* 2007). By considering this information, in conjunction with the exposure pathways that apply to these groups of COIs, it is possible to identify the receptors that are potentially at risk due to exposure to contaminated environmental media. For bioaccumulative substances, the groups of aquatic organisms that are most likely to be exposed to tissue-associated contaminants include benthic invertebrates, fish, amphibians, reptiles, birds, and mammals.

Toxic substances that partition into sediments and floodplain soils pose a potential risk to a variety of aquatic organisms and aquatic-dependent wildlife species. The groups of aquatic organisms that are most likely to be exposed to sediment-associated contaminants include decomposers (i.e., microbiota), aquatic plants (i.e., rooted aquatic macrophytes), benthic

invertebrates, benthic fish, and amphibians. Although reptiles can come in contact with contaminated sediments, it is unlikely that significant dermal uptake would occur. Terrestrial plants, terrestrial invertebrates, amphibians, reptiles, birds, and mammals represent the receptor groups most likely to be exposed to COIs in floodplain soils.

For toxic substances that partition into surface water, aquatic plants, aquatic invertebrates, fish, and amphibians represent the principal groups of exposed aquatic organisms. By comparison, aquatic invertebrates and pelagic fish, are likely to have the highest potential for exposure to toxic substances that partition into the surface microlayer.

3.7 Conceptual Site Model

Exposure to environmental contaminants has the potential to adversely affect aquatic and terrestrial organisms utilizing habitats within the study area. The nature and severity of such effects are dependent on the substance under consideration, its bioavailability, the characteristics of the exposure medium, the duration of exposure, the species and life stage of the exposed biota, and several other factors. Evaluation of the environmental fate of COIs and identification of the types of effects that could occur in the various groups of organisms found in the TSMD provides a basis for developing fate and effects hypotheses (i.e., using the information presented in Appendix 2). In turn, these hypotheses provide a basis for evaluating the logical consequences of exposing ecological receptors to environmental contaminants (i.e., predicting the responses of assessment endpoints when exposed to chemical stressors; USEPA 1998).

Certain metals, high molecular weight-PAHs [HMW-PAHs; e.g., benzo(a)pyrene], PCBs, organochlorine pesticides, and various SVOCs are the bioaccumulative substances of potential concern at the TSMD. Short- and long-term exposure to these substances have been demonstrated to adversely affect the survival, growth, and/or reproduction of aquatic invertebrates, fish, amphibians, birds, and mammals. Extended exposure to some of these substances can also result in tumor induction and/or immune system suppression (see Chapter 4 of Appendix 1 and Appendix 2 for more information). The following fate and effects

hypothesis was developed to identify the key stressor-effect relationships that need to be evaluated during the analysis phase of the assessment:

- Based on the physical-chemical properties [e.g., octanol water partition coefficient (K_{ow})] of the bioaccumulative substances of concern, the nature of the food web in the TSMD Site, and the effects that have been documented in field and laboratory studies, metals, HMW-PAHs, PCBs, organochlorine pesticides, and certain SVOCs that are released into surface waters will accumulate in the tissues of aquatic organisms to levels that will adversely affect the survival, growth, and/or reproduction of benthic invertebrates, fish, and/or amphibians. The survival, growth, and/or reproduction of reptiles, birds, and mammals feeding on aquatic and/or terrestrial prey organisms will also be adversely affected by food-web transfer of bioaccumulative substances.

Many of the COIs in the TSMD Site were classified as toxic substances that partition into soil and/or sediments, including metals, PAHs (parent and alkylated), PCBs, organochlorine pesticides, and SVOCs. Adverse effects on the survival, growth, and/or reproduction have been observed in aquatic plants, aquatic invertebrates, fish, and amphibians exposed to one or more of these substances in sediments (see Chapter 4 of Appendix 1 and Appendix 2 for more information). Exposure to sediment-associated contaminants also has the potential to adversely affect the microbial community (i.e., decomposers). Similarly, one or more of these substances has been documented to adversely affect the survival, growth, and/or reproduction of terrestrial plants, terrestrial invertebrates, birds, and mammals exposed to contaminated soil. The following fate and effect hypothesis was developed to identify the key stressor-effect relationships that need to be evaluated during the analysis phase of the assessment:

- Based on the environmental fate of the toxic substances that partition into sediments and the effects that have been documented in laboratory studies, metals, PAHs (parent and alkylated), PCBs, organochlorine pesticides, and SVOCs will accumulate in sediments and/or pore water to levels that will adversely affect the activity of the microbial community (e.g., reduce the rate of carbon processing by decomposers), the survival and/or growth of aquatic plants, and/or the survival, growth, and/or reproduction of benthic invertebrates, fish, and/or amphibians.

The survival, growth, and/or reproduction of terrestrial plants, terrestrial invertebrates, reptiles, birds, and/or mammals will also be adversely affected by exposure to toxic substances that partition into floodplain and/or upland soils. However, the soil pathway was not evaluated in this SLERA.

The toxic COIs that partition into water in the TSMD include metals. Adverse effects on survival, growth, and/or reproduction have been observed in aquatic plants, aquatic invertebrates, and fish exposed to one or more of these substances in water (see Chapter 4 of Appendix 1 and Appendix 2). The following fate and effect hypothesis was developed to identify the key stressor-effect relationships that need to be evaluated during the analysis phase of the assessment:

- Based on the environmental fate of the toxic substances that partition into water (including pore water and the surface microlayer) and the effects that have been documented in laboratory studies, metals will occur in surface water at levels that will adversely affect the survival, growth, and/or reproduction of aquatic plants, aquatic invertebrates, fish, and/or amphibians.

A general CSM diagram was developed to show the principal routes of exposure to contaminated water, sediment, soil, air, and biota (Figure 9).

3.8 Assessment and Measurement Endpoints

In the environment, a variety of plant and animal species can be exposed to COIs (these species are referred to as receptors potentially at risk). Each of these receptors can be exposed to COIs through different exposure routes and have the potential to exhibit different types and severities of effects. While information on the effects of each COI on each component of the ecosystem would provide comprehensive information for evaluating ecological risks, it is neither practical nor feasible to directly evaluate risks to all of the individual components of the ecosystem that could be adversely affected by environmental contamination at a site (USEPA 1997a). For this reason, risk assessment activities should be

focused on the receptors that represent valued ecosystem components (e.g., fish species) and on the receptors that support valued ecosystem functions (e.g., carbon processing by the microbial community, which is needed to support healthy fish populations). Of particular interest are those receptors that are most likely to be adversely affected by the presence of COIs at the site (USEPA 1998).

As part of the preliminary problem formulation (MacDonald *et al.* 2007), a number of candidate assessment endpoints were considered for potential use in the SLERA of the TSMD Site. Importantly, the SLERA is primarily focused on aquatic receptors, including microbiota, aquatic plants, aquatic invertebrates (i.e., benthic invertebrates and zooplankton), fish, and amphibians. Terrestrial plants, terrestrial invertebrates, reptiles, birds, and mammals were excluded from the assessment, as risks to these receptor groups have, at least in part, been evaluated previously (Dames and Moore 1993; Black and Veatch Special Projects Corp. 1998; Schmitt *et al.* 2006) and may be further evaluated in the future. Accordingly, the assessment endpoint for the SLERA is:

- Survival, growth, and reproduction of ecological receptors associated with exposure to COIs in surface water, sediment, or pore water.

While such an assessment endpoint is essential for defining the environmental values that need to be protected at the TSMD Site, it is not possible to measure the effects on all of the members of the various aquatic receptor groups that are associated with exposure to COIs in surface water, sediment, or pore water at the site. For this reason, it is necessary to articulate specific risk questions (i.e., testable hypotheses) that can be answered through the collection and evaluation of focused data and information at the site. For a SLERA, such data typically include the concentrations of suspected contaminants in abiotic media (e.g., surface water, sediment). The risk questions that were considered in the SLERA for the TSMD include:

- Are the concentrations of COIs in surface water from the TSMD greater than conservative benchmarks for the protection of aquatic organisms (i.e., benchmarks that are equivalent to no observed effect levels; NOELs)?

- Are the concentrations of COIs in sediment samples from the TSMD greater than conservative benchmarks for the protection of aquatic organisms (i.e., benchmarks that are equivalent to NOELs)?
- Are the concentrations of COIs in pore-water samples from the TSMD greater than conservative benchmarks for the protection of aquatic organisms (i.e., benchmarks that are equivalent to NOELs)?

A measurement endpoint is defined as ‘a measurable ecological characteristic that is related to the valued characteristic that is selected as the assessment endpoint’ and it is a measure of biological effects (e.g., mortality, reproduction, growth; USEPA 1997a). Measurement endpoints are frequently numerical expressions of observations (e.g., toxicity test results, community diversity measures) that can be compared to similar observations for a control material and/or for reference sites. Such comparisons provide a basis for evaluating the effects that are associated with exposure to a COI or group of COIs at the site under consideration. Measurement endpoints can include measures of exposure (e.g., COI concentrations in water or sediments) or measures of effects (e.g., survival or biomass of amphipods in 10-d toxicity tests). At the SLERA stage of the ERA process, the measured or estimated concentrations of COIs in environmental media are selected measurement endpoints. Accordingly, the risk questions (RQs) and the highest priority measurement endpoints (MEs) for evaluating the status of the candidate assessment endpoint (AE) include:

AE: Survival, growth, and reproduction of ecological receptors associated with exposure to COIs in surface water, sediment, or pore water.

RQ-1: Are the concentrations of COIs in surface-water from the TSMD greater than conservative benchmarks for the protection of aquatic organisms (i.e., benchmarks that are equivalent to no observed adverse effect levels; NOAELs)?

ME-1: The concentrations of COIs in surface-water samples collected from the TSMD.

RQ-2: Are the concentrations of COIs in sediment samples from the TSMD greater than conservative benchmarks for the protection of aquatic organisms (i.e., benchmarks that are equivalent to NOAELs)?

ME-2: The concentrations of COIs in sediment samples collected from the TSMD.

RQ-3: Are the concentrations of COIs in pore-water samples from the TSMD greater than conservative benchmarks for the protection of aquatic organisms (i.e., benchmarks that are equivalent to NOAELs)?

ME-3: The concentrations of COIs in pore-water samples collected from the TSMD.

3.9 Screening-Level Ecological Effects Evaluation

The screening-level ecological effects evaluation involved identification and compilation of toxicity screening values (TSVs; which are also referred to as screening ecotoxicity values; SEVs) for water and sediment. The TSVs used in the SLERA are intended to provide conservative numerical estimates of the concentrations of COIs in abiotic environmental media below which there will be no or negligible adverse effects on the ecological receptor groups of concern. Accordingly, the selected TSVs are considered to be sufficiently conservative to support identification of the COIs that are not considered to pose potential risks to ecological receptors (i.e., when none of the samples have concentrations in excess of the TSV). Such COIs can be eliminated from further consideration if the existing data provide adequate spatial coverage of the study area. It is also important to note that such TSVs do not account for the potential for unacceptable levels of bioaccumulation or biomagnification in food webs.

Because the TSVs generally represent NOAELs for long-term (chronic) exposures to a COI, exceedance of a TSV does not necessarily indicate that unacceptable risks to ecological receptors exist at the site. Rather, exceedance of a TSV indicates that a COI warrants further assessment to determine if exposure is sufficient to pose unacceptable risks to one or more ecological receptor groups (i.e., in a detailed or baseline ERA; such COIs are referred to as COPCs). The TSVs selected for use in the SLERA were adopted from publically-available literature sources and are described below.

3.9.1 Toxicity Screening Values for Water

The chronic ambient water quality criteria (WQC) derived by USEPA [1999; 2006a; i.e., criteria continuous concentrations (CCCs)] were selected, as available, as the primary TSVs for surface water and pore water. For those COIs for which CCCs were not available, TSVs for freshwater that were available from various sources throughout North America (i.e., as identified by risk assessors at USEPA headquarters and each of the 10 USEPA regions) were compiled (REAC 2004). Then, the geometric mean of the candidate benchmarks was calculated for each COI and selected as the TSV for that substance (MacDonald *et al.* 2008). For substances for which the benchmark was originally expressed on a hardness-dependent basis (i.e., cadmium and nickel), a hardness of 100 mg/L was assumed for all exposure point concentrations (i.e., the maximum concentration of each COI; exposure point concentration). The selected TSVs for surface water and pore water are presented in Table 3. Evaluation of the available water chemistry data consisted of comparing the exposure point concentration of each COI in surface water or pore water to the selected TSV for that COI.

3.9.2 Toxicity Screening Values for Sediment

The consensus-based threshold effects concentrations (TECs) derived by MacDonald *et al.* (2000a) were selected as the primary TSVs for sediment. For those COIs for which TECs were not available, TSVs for freshwater sediments that were available from various sources throughout North America (i.e., as identified by risk assessors at USEPA headquarters and each of the 10 USEPA regions) were compiled (REAC 2004). Then, the geometric mean of the candidate benchmarks was calculated for each COI and selected as the TSV for that substance. For substances for which the benchmark was originally expressed on an organic carbon-normalized basis, these values were converted to a dry weight-concentration at 1% organic carbon (MacDonald *et al.* 2008). In some cases, TSVs from other sources were identified and selected if TSVs were not available from the two primary sources. The selected TSVs for sediment are presented in Table 4. Evaluation of the available sediment chemistry data consisted of comparing the maximum concentration of each COI in sediment to the selected TSV for that COI.

3.9.3 Toxicity Screening Values for Bioaccumulative Substances

The selected TSVs surface water, pore water, and sediment did not account for bioaccumulation of COIs in the tissues of aquatic organisms nor the potential for adverse effects on higher trophic-level consumers of aquatic organisms. For this reason, bioaccumulative COIs were carried forward to the DERA for site-specific evaluation of risks to ecological receptors. For screening purposes, any organic chemical with a $\log K_{ow} \geq 4.0$ was considered to be a bioaccumulative COI and would be further evaluated in the DERA (i.e., identified as a bioaccumulative COPC). Chemicals with $\log K_{ow}$ s of < 4.0 have fugacities < 1.0 and occur virtually entirely in the dissolved phase (Clark *et al.* 1995). Therefore, organic chemicals with low K_{ow} s (i.e., < 4.0) were not evaluated in the DERA unless they screened in based on comparison to the TSVs for water, sediment, and/or soil. Certain metals are also known to bioaccumulate in the tissues of aquatic organisms (e.g., cadmium, chromium, copper, lead, mercury, nickel, selenium, and zinc; Lemly 2002; Paquin *et al.* 2003; Suter *et al.* 2007). These metals required further evaluation in the DERA.

Chapter 4 Screening-Level Exposure Estimate and Risk Calculation

4.0 Introduction

Step 2 in the ecological risk assessment process (Figure 3) involves development of screening-level exposure estimates and calculation of potential risks to ecological receptors associated with exposure to abiotic media (i.e., water, sediment, and soil). The results of this evaluation provide a basis for determining if:

- Risks to ecological receptors are negligible;
- The ecological risk assessment should continue to determine whether risks exist; or,
- There is potential for adverse ecological effects and a more detailed ecological risk assessment, incorporating more site-specific information, is needed.

This chapter describes the data that were used to evaluate potential risks to ecological receptors utilizing aquatic and floodplain habitats within the TSMD, presents the screening-level exposure estimates that were generated using the existing data, and describes the results of the screening-level risk calculation. In addition, uncertainties associated with the evaluation of potential risks to ecological receptors associated with exposure to abiotic media in the TSMD are discussed.

4.1 Data Compilation and Evaluation

Development of a project database represents an essential element of the SLERA process. As the project database is likely to represent a useful tool for all of the partners in the RI/FS process and for the Natural Resources Trustees, USEPA Region VI agreed to play a lead role in the development of a database for the TSMD watershed. All of the members of the TSMD

Watershed Partnership were invited to identify candidate data sets that should be considered for inclusion in the database. As a result, a substantial list of candidate data sets was developed.

To ensure that the most relevant data sets were compiled into the project database, selection criteria were formulated to guide the database development process. The data set selection criteria included:

- Include data generated between 2002 and 2009 to provide a basis for evaluating current conditions in the TSMD;
- Preferentially include data sets for the Ottawa County and Newton County portions of the TSMD (i.e., because BERAs had been completed previously for the Jasper County and Cherokee County portions of the site; Dames and Moore 1993; Black and Veatch Special Projects Corp. 1998). Compile data from elsewhere in the watershed when provided in electronic format; and,
- Primarily focus on compilation of surface-water chemistry, sediment chemistry (for surficial sediment samples; i.e., the top 15 cm of sediment), sediment toxicity, and benthic invertebrate community data (i.e., to support assessment of risks to benthic invertebrates). Compile other data types (soil chemistry data, invertebrate-tissue chemistry data, or fish-tissue chemistry data) when provided in electronic format. Only the data on the concentrations of suspected contaminants in abiotic media (surface water, sediment, and pore water) were used to assess potential risks to aquatic receptors in the SLERA.

To support the compilation and subsequent analysis of the information on environmental quality conditions, a geographic information system (GIS)-compatible, relational project database was developed in MS Access format. All of the data compiled in the database were georeferenced to facilitate mapping and spatial analysis using GIS-based applications [i.e., Environmental Systems Research Institute (ESRI's) ArcMap and Spatial Analyst programs]. The database structure made it possible to retrieve data in several ways, including by data type (i.e., chemistry vs. toxicity), by sediment horizon (i.e., surficial vs. sub-surface sediments), by AoI (i.e., Center Creek vs. Tar Creek), and by date. As such, the database facilitated a variety of data analyses to support the SLERA (and DERA).

4.2 Data Treatment

A substantial quantity of data and information has been generated on the condition of aquatic habitats within the TSMD. To support the current assessment, the available data on surface-water quality, sediment quality, and pore-water quality conditions in the study area were assembled in the project database. A description of each of the studies that were used in this evaluation of sediment quality conditions is provided in Appendix 5.

All of the data sets that were retrieved during the course of the study were critically reviewed to determine their applicability to the assessment of environmental quality conditions in the study area. The selection criteria that were used to evaluate each of the candidate data sets are listed in Section 4.1 of this report. The data sets that contained information on the study area and met the selection criteria were incorporated into a relational database in MS Access format. Following translation into database format, the data were verified to assure the quality of the data used in the risk assessment. This auditing process involved analyses of outliers (i.e., to identify inconsistencies with units) and completeness (i.e., to identify missing samples or missing data), examination of data qualifier fields (i.e., to assure internal consistency in the project database), and, checking of sample identification numbers (i.e., to ensure that data were not duplicated or missing). Finally, the data were verified against the original data source. Appendix 7 provides further details on the data treatment and evaluation methods employed to ensure quality data were used in the analyses. The results of the data evaluation and data auditing indicated that the compiled information represents a reliable basis for conducting a SLERA.

In a number of studies, additional samples were collected and/or analyzed as part of the quality assurance program. Appendix 6 provides a detailed description of the data quality assurance methods used in MacDonald *et al.* (2009). In this report, field replicate samples were treated as unique samples in the data analyses (i.e., by providing information on the small scale spatial variability in sediment quality conditions). By comparison, laboratory split samples were treated as duplicates and averaged to support subsequent data analysis.

To support subsequent interpretation of the sediment chemistry data, the total concentrations of several chemical classes were determined for each sediment sample. Specifically, the concentrations of total PAHs were calculated by summing the concentrations of up to 13

individual PAHs, including acenaphthene, acenaphthylene, anthracene, fluorene, 2-methylnaphthalene, naphthalene, phenanthrene, benz(a)anthracene, dibenz(a,h)anthracene, benzo(a)pyrene, chrysene, fluoranthene, and pyrene. For PCBs, the concentrations of total PCBs were determined using various procedures, depending on how the data were reported in the original study. If only the concentrations of total PCBs was reported in the study, then those values were used directly. If the concentrations of various Aroclors (e.g., Aroclor 1242, Aroclor 1248) were reported, then the concentrations of the various Aroclors were summed to determine the concentration of total PCBs. In some cases, the concentrations of total PCBs may have been estimated by summing the concentrations of measured congeners and multiplying by 2.01 (Lauenstein and Cantillo 1993). This procedure has been shown to provide a reliable basis for estimating the sum of 209 PCB congeners when only a limited number of congeners was measured. For DDTs, the concentrations of p,p'-DDD and o,p'-DDD, p,p'-DDE and o,p'-DDE, and p,p'-DDT and o,p'-DDT were summed to calculate the concentrations of sum DDD, sum DDE, and, sum DDT, respectively. Total DDTs was calculated by summing the concentrations of sum DDD, sum DDE, and, sum DDT. Finally, the concentrations of total chlordane were determined by summing the concentrations of alpha- and gamma-chlordane isomers. If only the concentrations of total chlordane was reported in the study, then those values were used directly.

In calculating the total concentrations of the various chemical classes, less than detection limit values were assigned a value of one-half of the detection, except when the detection limit was greater than the selected TSV. In this latter case, the less than detection limit result was not used in the calculation of the total concentration of the substance. In addition, all of the data for individual COPCs with concentrations less than the reported detection was excluded from the analysis if the detection limit was greater than the TSV.

A variety of procedures have been used to collect, and prepare for chemical analysis, the sediment samples represented in the project database. In some cases, sediment samples were collected and submitted for chemical analysis. In other cases, the sediment samples were sieved to < 2.00 mm and/or < 250 µm to support the generation of matching sediment toxicity and sediment chemistry data. In addition, certain investigators sieved sediment samples to < 63 µm to support chemical analysis of the fine fraction. For the purposes of the SLERA, chemical analyses on all particle size fractions were treated as equivalent and included in the data set used to evaluate potential risks to ecological receptors (which may result in

overestimation of risks to aquatic receptors). In contrast, risks to benthic invertebrates were evaluated in the DERA by estimating the concentrations of COPCs in the < 2.00 mm fraction when data were available on chemical concentrations in other size fractions (i.e., using the procedures described in Appendix 3).

4.3 Screening-Level Exposure Estimates

Screening-level exposure estimation is intended to identify the probable maximum environmental concentrations of COIs to which ecological receptors may be exposed within the TSMD. Accordingly, the highest measured or estimated on-site concentrations were used to estimate exposures for each environmental medium (USEPA 1997a). The abiotic media that were considered in this evaluation included surface water, sediment, and pore water.

4.3.1 Estimation of Exposure to Surface Water

Table 5 presents the distributions of the chemistry data for all of the COIs that were measured in surface-water samples collected within the TSMD (Figure 10). For all COIs, the maximum concentration measured within the study area was selected as the exposure point concentration (EPC) for surface water (which provides the most conservative estimate of EPCs). The corresponding distributions of surface-water chemistry data for samples from the selected reference area are presented in Table 6 (Figure 11).

4.3.2 Estimation of Exposure to Sediment

Table 7 presents the distributions of the chemistry data for all of the COIs that were measured in sediment samples collected within the TSMD (Figure 12). For all COIs, the maximum concentration measured within the study area was selected as the EPC for sediment. The corresponding distributions of sediment chemistry data for reference sediment samples are presented in Table 8 (Figure 13).

4.3.3 Estimation of Exposure to Pore Water

Table 9 presents the distributions of the chemistry data for all of the COIs that were measured in pore-water samples collected within the TSMD (Figure 14). For all COIs, the maximum concentration measured within the study area was selected as the EPC for pore water. The corresponding distributions of pore-water chemistry data for reference pore-water samples are presented in Table 10 (Figure 13).

4.4 Screening-Level Risk Calculation

In this evaluation, potential risks to ecological receptors were estimated using a hazard quotient (HQ) approach. More specifically, the exposure estimates generated in Section 4.3 were used in conjunction with the TSVs to estimate potential risks to ecological receptors associated with exposure to surface water, sediment, or pore water, within the TSMD, using the following equation:

$$HQ = EPC / TSV$$

Where: HQ = Hazard Quotient;
EPC = Exposure Point Concentration; and,
TSV = Toxicity Screening Value (no observed adverse effect levels were selected preferentially; units must match units for EPC).

An HQ of less than unity (i.e., 1.0) was considered to indicate that exposure to the measured concentrations of the COI would not pose potential risks to ecological receptors. These results were used to eliminate negligible-risk combinations of COIs and exposure pathways from further consideration. The COIs with HQs > 1.0 were considered to pose potential risks to ecological receptors and were retained as COPCs, while COIs with insufficient data to support calculation of an EPC were retained as uncertain COPCs and carried forward to the DERA.

4.4.1 Estimation of Risks Posed by Exposure to Surface Water

The results of the screening evaluation of COIs in surface water are presented in Table 11. These results show that several metals occur in surface water from the TSMD at concentrations sufficient to pose potential risks to ecological receptors, including aluminum, cadmium, chromium, cobalt, copper, iron, lead, mercury, nickel, selenium, silver, and zinc. Insufficient data were available to determine if certain other COIs in surface water pose potential risks to aquatic organisms, including ammonia and chlorine (Table 11). In addition, no data were located on the levels of PAHs, PCBs, organochlorine pesticides, SVOCs or VOCs in surface water within the study area. These substances were identified as uncertain COPCs and were brought forward into the DERA.

4.4.2 Estimation of Risks Posed by Exposure to Sediment

The results of the screening evaluation of COIs in sediment are presented in Table 12. Examination of the underlying sediment chemistry data shows that a robust data set is available for evaluating the potential risks to aquatic organisms posed by exposure to sediment-associated metals in the TSMD. Fewer data are available for PAHs, PCBs, organochlorine pesticides, and SVOCs.

Comparison of measured concentrations of COIs in sediment to the corresponding TSVs indicate that a number of substances pose potential risks to sediment-dwelling organisms, including:

- Metals (aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, mercury, nickel, selenium, silver and zinc);
- PAHs [acenaphthene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, phenanthrene, pyrene, total high molecular weight PAHs, total low molecular weight PAHs, and total PAHs];
- Organochlorine pesticides (hexachlorocyclopentadiene); and,

- SVOCs [atrazine, 3,3'dichlorobenzidine, bis(2ethylhexyl) phthalate, butylbenzyl phthalate, di-n-butyl phthalate, dinitro-o-cresol, hexachlorobutadiene, hexachloroethane, 2,4,5-trichlorophenol and 2,4,6 trichlorophenol]

Insufficient data were available to evaluate the potential risks to aquatic organisms associated with exposure to molybdenum and certain PCB formulations (Aroclor 1016, Aroclor 1248, and Aroclor 1260), organochlorine pesticides (e.g., aldrin, dieldrin, endrin), and SVOCs (e.g., phthalates, chlorophenols). Therefore, these substances were identified as uncertain COPCs were brought forward into the DERA (Table 12).

4.4.3 Estimation of Risks Posed by Exposure to Pore Water

The results of the screening evaluation of COIs in pore water are presented in Table 13. These results show that a number of metals pose potential risks to aquatic organisms that are exposed to pore water in the TSMD, including aluminum, cadmium, chromium, cobalt, copper, iron, lead, and zinc. Insufficient data were available to assess the potential risk to aquatic organisms posed by exposure to mercury, molybdenum, selenium, or silver. Therefore, these substances were identified as uncertain COPCs and were carried forward into the DERA.

4.5 Uncertainty Analysis and Data Gaps

The existing surface-water chemistry, sediment chemistry, and pore-water chemistry data were compiled, evaluated, and used to determine if exposure to COIs posed potential risks to ecological receptors utilizing aquatic habitats in the TSMD. The approach that was used to evaluate potential risks to ecological receptors was consistent with USEPA (1997a; 1998) guidance and involved comparison of EPCs to TSVs for each media type. This approach employs conservative assumptions about exposure of ecological receptors to COIs and about the toxic effects of site-related COIs. The following describes the primary uncertainties associated with the SLERA.

4.5.1 Uncertainties Associated with the Screening-Level Exposure Estimates

There are a number of uncertainties associated with the screening-level exposure estimates. First, the available surface-water chemistry data collected between 2002 and 2009 are somewhat limited. More specifically, the analytes measured in surface-water samples were limited to metals, nutrients, and major ions. In addition, the temporal and spatial variability in surface-water quality conditions (i.e., contaminant concentrations) has not been adequately characterized for the entire study area. This represents an important data gap. The results of this assessment suggest that metals represent key COIs in surface water and require further evaluation in the DERA.

The existing data provide a robust basis for estimating exposure of ecological receptors to sediment-associated COIs throughout the TSMD, particularly for the principal COIs in the study area (i.e., metals). While the available sediment chemistry data are limited for certain classes of contaminants (e.g., PAHs, PCBs, organochlorine pesticides, and SVOCs) sufficient information is available to conclude that most of these substances are likely to pose minimal risks to ecological receptors throughout much of the study area. Site-specific investigations in the vicinity of known sources of these contaminants (e.g., RCRA-related investigations or facility-specific investigations conducted under CERCLA) are likely to provide a basis for filling any data gaps that currently exist and for addressing concerns related to these substances. Nevertheless, several PAHs were carried forward into the DERA as COIs, while many other substances were identified as uncertain COIs (due to elevated detection limits).

Limited data are available to evaluate potential risks to ecological receptors posed by exposure to COIs in pore water. This limitation is mitigated to a large extent by the availability of a substantial sediment chemistry data set and the application of conservative assumptions regarding the toxicity of sediment-associated contaminants. As pore-water metal concentrations represented the best predictors of toxicity to benthic invertebrates (i.e., amphipods, midges, or mussels) exposed to sediment samples from the TSMD (MacDonald *et al.* 2009), collection of data on the concentrations of other COIs (e.g., organics) in pore water should be considered to be a low priority.

Exposure of higher trophic-level ecological receptors to bioaccumulative substances was not evaluated in the SLERA of aquatic habitats. This represents a major uncertainty of the SLERA and results in considering all of the bioaccumulative COPCs (i.e., HMW-PAHs, PCBs, phthalates, chlorophenols, and organochlorine pesticides) in any BERA that is conducted subsequently. However, the results of the 28-d laboratory bioaccumulation tests with oligochaetes (*Lumbriculus variegatus*) and the existing fish-tissue chemistry data will provide useful information to support refinement of the list of bioaccumulative COPCs. The laboratory bioaccumulation data have the potential to over-estimate the concentrations of COPCs in invertebrate tissues because incomplete depuration of gut contents occurred within the depuration period. The results of a screening-level assessment conducted in northeastern Oklahoma confirmed that lead, cadmium, and zinc have accumulated in the tissues of fish and crayfish to levels that pose potential risks to fish and wildlife (Schmitt *et al.* 2006).

4.5.2 Uncertainties Associated with the Screening-Level Ecological Effects Evaluation

There are several uncertainties associated with the screening-level ecological effects evaluation that was conducted to support the SLERA. For surface water and pore water, the chronic WQC (i.e., CCCs) that have been developed by USEPA (2006a) or functionally-equivalent values were selected as the TSVs. These values have been subject to rigorous peer-review and are generally assumed by the scientific community to provide an adequate level of protection for fish and other aquatic organisms. However, they do not represent NOAELs because effects on some proportion of the aquatic community may occur below these values. This increases uncertainty in the results of the SLERA. These WQC can account for some of the factors that affect bioavailability and/or toxicity (e.g., hardness-dependent WQC for certain metals, pH- and temperature-dependent WQC for ammonia); however, the selected TSVs generally do not account for bioavailability or speciation of contaminants. As the results of various studies show that the presence of dissolved organic carbon (DOC) and other factors can reduce the bioavailability of metals (DiToro *et al.* 1991; 2001; 2005; USEPA 2003b), the selected TSVs for certain substances may represent over-estimates of NOAELs. Therefore, selection of TSVs for surface water and pore water that do not fully account for the factors that influence contaminant bioavailability increases uncertainty in the results of the SLERA. Because TSVs were unavailable for a number of

substances in surface water and pore water, the potential risks posed by those COIs is unknown. This represents an important data gap.

In general, the selected TSVs for sediment do not account for the factors that could influence the bioavailability of COIs. Accordingly, such TSVs could over-estimate the bioavailability of sediment-associated COIs. While selection of conservative TSVs assures that aquatic organisms will be adequately protected, their application could result in over-estimates of the potential risks that contaminated sediments pose to benthic invertebrates and other aquatic organisms. Uncertainty in the results of the SLERA is, thereby, increased. Because TSVs were unavailable for a number of COIs in sediment, the potential risks posed by those substances is unknown. This represents an important data gap.

4.6 Scientific Management Decision Point Evaluation

At the end of the second step in the eight-step ecological risk assessment process for Superfund, risk assessors communicate the results of the SLERA to the risk managers (Gary Baumgarten for Ottawa County, Dave Drake for Cherokee County, and Mark Doolan for Jasper County and Newton County). Then, the risk managers need to evaluate the results of the SLERA and make one of the following three decisions for each COI in each environmental medium:

- There is adequate information to conclude that ecological risks are negligible and, therefore, there is no need for remediation on the basis of the risk assessment;
- The available information is not adequate to make a decision at this point in the process and the ecological risk assessment will proceed to Step 3 (problem formulation for a BERA); or,
- The information indicates a potential for adverse ecological effects and a more thorough assessment (i.e., a BERA) is warranted.

In addition, the results of the SLERA should be used to identify the COIs and exposure pathways that can be eliminated from further assessment because they are unlikely to pose

potential risks to ecological receptors (USEPA 1997a). Such decisions must be adequately documented and technically defensible. The following recommendations are offered to the risk managers of these sites.

4.6.1 Surface Water

The existing data on the concentrations of contaminants in surface water provide broad spatial coverage of the TSMD. The EPCs derived using these data were compared to conservative TSVs to determine if exposure to contaminants in surface water posed potential risks to ecological receptors. The results of the SLERA demonstrated that one or more COIs or COI mixtures occurred in surface water at concentrations that posed potential risks to aquatic organisms (Table 11), including:

- Aluminum;
- Ammonia;
- Cadmium;
- Chromium;
- Cobalt;
- Copper;
- Iron;
- Lead;
- Mercury;
- Nickel;
- Selenium;
- Silver; and,
- Zinc.

Therefore, a more thorough assessment of the surface-water exposure pathways is warranted. Insufficient data were available on the concentrations of any COIs except metals to determine if they posed potential risks to aquatic organisms. While organic chemicals are not expected to represent contaminants in the TSMD (i.e., due to the absence of known sources), ammonia, nitrite, and chlorine could be present at elevated levels in those receiving water

bodies that receive municipal waste water treatment plant discharges. Therefore, metals, ammonia, nitrite, and chlorine are the contaminants that should be considered COPCs in the DERA of the aquatic habitats in the TSMD.

4.6.2 Sediment

A great deal of information is available on the concentrations of COIs in sediment samples obtained from the TSMD. These data provide broad spatial and temporal coverage of aquatic habitats within the TSMD. The EPCs derived using these data were compared to conservative TSVs to determine if exposure to COIs in sediment posed potential risks to ecological receptors in the study area. The results of the SLERA demonstrated that one or more substances occurred in sediment at concentrations that posed potential risks to aquatic organisms (Table 12), including:

- Metals (aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, mercury, molybdenum, nickel, selenium, silver, and zinc);
- PAHs (13 individual PAHs);
- Organochlorine pesticides (hexachlorocyclopentadiene); and,
- SVOCs [atrazine, 3,3'dichlorobenzidine, bis(2ethylhexyl) phthalate, butylbenzyl phthalate, di-n-butyl phthalate, dinitro-o-cresol, hexachlorobutadiene, hexachloroethane, 2,4,5-trichlorophenol, and 2,4,6 trichlorophenol].

None of the PCBs, organochlorine pesticides, or SVOCs occurred at concentrations sufficient to pose potential risks to ecological receptors. However, detection limits were too high, in many cases, to conduct the screen. Therefore, many of these substances remain uncertain COPCs. Information on pore-water chemistry provides a basis for confirming the COPCs that were identified using sediment chemistry data. These results showed that aluminum, cadmium, chromium, cobalt, copper, iron, lead, mercury, molybdenum and zinc should be considered in the DERA for benthic invertebrates (Table 13). Hence, metals, PAHs, organochlorine pesticides, and SVOCs should be considered to be COPCs that are addressed in the DERA of the aquatic habitats in the TSMD.

4.6.3 Pore Water

Data on the concentrations of metals in pore water are available for up to 70 samples from the TSMD (depending on the analyte under consideration). The EPCs derived from these data were compared to conservative TSVs to determine if exposure to COIs in pore water posed potential risks to ecological receptors in the study area. The results of the SLERA demonstrated that one or more COIs occurred in pore water at concentrations sufficient to pose potential risks to aquatic organisms (Table 13), including:

- Aluminum;
- Cadmium;
- Chromium;
- Cobalt;
- Copper;
- Iron;
- Lead;
- Selenium
- Silver; and,
- Zinc.

Therefore, a more thorough assessment of the pore-water exposure pathway is warranted. As sources of organic contaminants were not identified in the study area, the DERA of the TSMD should focus on selected metals, ammonia, and nitrite as COPCs.

4.6.4 Bioaccumulative Chemicals of Potential Concern

The potential effects of bioaccumulative substances on higher-trophic level ecological receptors were not evaluated in the SLERA. Therefore, bioaccumulative substances will need to be identified and addressed in future assessments of risks to ecological receptors. Accordingly, all of organic contaminants with $\log K_{ow}$ values > 4.0 should be carried forward into the future assessments of risks to ecological receptors. In addition, several metals with the potential to accumulate in the tissues of aquatic organisms should be carried forward. The bioaccumulative COPCs in the TSMD should include:

- Metals (arsenic, cadmium, copper, lead, mercury, selenium, and zinc);
- PAHs [acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, phenanthrene, pyrene];
- PCBs (Aroclor 1016, Aroclor 1221, Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254, Aroclor 1260, Aroclor 1262, Aroclor 1268; and/or PCB congeners);
- Organochlorine pesticides [aldrin, chlordane, cis-, chlordane, trans-, dieldrin, endosulfan sulfate, endosulfan-alpha, endosulfan-beta, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, hexachlorobenzene, hexachlorocyclohexane (HCH)-alpha, HCH-beta, HCH-delta, HCH-gamma, hexachlorocyclopentadiene, isophorone, methoxychlor, p,p'-DDD, p,p'-DDE, p,p'-DDT, toxaphene]; and,
- SVOCs [1,2,4-trichlorobenzene, 4-bromophenyl phenyl ether, 4-chlorophenyl phenyl ether, bis(2-ethylhexyl) phthalate, butylbenzyl phthalate, diethyl phthalate, di-n-butylphthalate, di-n-octyl phthalate, hexachlorobutadiene, hexachloroethane, nitrobenzene, pentachlorophenol].

4.7 Summary Results of the Screening Level Ecological Risk Assessment

The results of the SLERA showed that exposure to surface water, sediment, and pore water posed potential risks to ecological receptors utilizing aquatic habitats within the TSMD. Therefore, all of these exposure media require further evaluation in the study area. The substances that were carried forward into the DERA were identified using the following criteria:

- Substances for which the maximum concentration exceeded the TSVs were identified as COPCs and were carried forward to the DERA;

- Substances without a TSV were identified as uncertain COPCs and were carried forward into the DERA; and,
- Substances with the potential to bioaccumulate in the tissues of aquatic organisms were identified as COPCs and were carried forward into the DERA.

Using these criteria, metals, PAHs, PCBs, organochlorine pesticides, various SVOCs, ammonia and chlorine were identified as the substances that need to be further evaluated to assess the risks that they potentially pose to ecological receptors in the TSMD.

Chapter 5 Development of Ecosystem Goals and Objectives for the Tri-State Mining District

5.0 Introduction

Jurisdictions throughout North America are transitioning toward the implementation of comprehensive ecosystem-based approaches to address concerns related to environmental quality conditions (Allen *et al.* 1991; Environment Canada 1996; IJC 1997; Crane *et al.* 2000). The ecosystem approach is particularly relevant for addressing concerns relative to environmental contamination in the vicinity of hazardous waste sites because it helps to focus risk assessment and risk management activities on the issues of greatest importance to stakeholders and the public. This chapter defines the ecosystem approach and presents ecosystem goals and objectives for the study area that are consistent with the interests and needs that have been articulated at several ERA workshops that have been convened on the TSMD (MESL and CH2M Hill 2007; MESL *et al.* 2007). This information is intended to provide context for the selection of assessment endpoints during the problem formulation process (Chapter 6 and Appendix 1).

5.1 Defining the Ecosystem Approach

The ecosystem approach to planning, research and management is the most recent phase in an historical succession of approaches to environmental management. Previously, humans were considered to be separate from the environment in which they lived. This *anthropocentric approach* viewed the external environment only in terms of human uses. However, overwhelming evidence from many sources indicates that human activities can have significant and far-reaching impacts on the environment and on the humans who reside in these systems. Therefore, there is a need for a more holistic approach to environmental management, in which humans are considered as integral components of the ecosystem. The ecosystem approach provides this progressive perspective by integrating the *anthropocentric*

view that characterized earlier management approaches, with an *ecocentric view* that considers the broader implications of human activities.

The primary distinction between the environmental and ecosystem approaches is whether the system under consideration is external to (in the environmental approach) or contains (in the ecosystem approach) the human population in the study area (Vallentyne and Beeton 1988). The conventional concept of the environment is like that of a *house* - external and detached; in contrast, ecosystem implies *home* - something that we feel part of and see ourselves in, even when we are not there (Christie *et al.* 1986). The change from the environmental approach to the ecosystem approach necessitates a change in the view of the environment from a political or people-oriented context to an ecosystem-oriented context (Vallentyne and Beeton 1988). The essence of the ecosystem approach is that humans are considered to be integral components of the ecosystem rather than being viewed as separate from their environment (Christie *et al.* 1986).

The ecosystem approach is not a new concept and it does not hinge on any one program, definition, or course of action. It is a way of thinking and a way of doing things (RCFTW 1992). Adopting an ecosystem approach means viewing the basic components of an ecosystem (i.e., air, water, land, and biota) and its functions in a broad context, which effectively integrates environmental, social, and economic interests into a decision-making framework that embraces the concept of sustainability (Figure 1; CCME 1996). Importantly, the ecosystem approach recognizes human activities, rather than natural resources, need to be managed if we are to achieve our long-term goal of sustainability. The identifying characteristics of the ecosystem approach include (Vallentyne and Hamilton 1987):

- A synthesis of integrated knowledge on the ecosystem;
- A holistic perspective of interrelating systems at different levels of integration;
and,
- Actions that are ecological, anticipatory, and ethical.

This expanded view then shapes the planning, research, and management decisions pertaining to the ecosystem.

5.2 A Framework for Implementing Ecosystem-Based Management

Implementation of the ecosystem approach requires a framework in which to develop and implement environmental assessment and management initiatives. This framework consists of five main steps, including (Environment Canada 1996; CCME 1996):

- Collate the existing ecosystem knowledge base and identify and assess the issues;
- Develop and articulate ecosystem health goals and objectives;
- Select ecosystem health indicators;
- Conduct directed research and monitoring; and,
- Make informed decisions on the assessment, conservation, protection, and restoration of natural resources.

The first step in the framework is intended to provide all participants in the process with a common understanding of the key issues and the existing knowledge base for the ecosystem under investigation. While various types of information are collected, reviewed, evaluated, and collated at this stage of the process, emphasis is placed on assembling the available information on historical land and resource use patterns, on the structure, function, and status of the ecosystem, and on the socioeconomic factors that can influence environmental management decisions. Both contemporary scientific data and traditional knowledge are sought to provide as complete an understanding as possible on the ecosystem. The information assembled at this stage of the process should be readily accessible to all participants in the process (i.e., by completing and distributing a state of the knowledge report, preparing and making available a detailed technical report, and disseminating the underlying data).

In the second step of the process, participants cooperatively develop a series of broad ecosystem goals and more specific ecosystem health objectives to articulate the long-term vision for the ecosystem. The *ecosystem goals* are based on the participants' common understanding of the ecosystem knowledge base and reflect the importance of the ecosystem to the community and to other stakeholder groups. A set of *ecosystem health objectives* are

also formulated at this stage of the process to clarify the scope and intent of the ecosystem goals. Societal values are reflected in the goals and objectives by ensuring that competing resource users are involved in their development. It is important that each of the ecosystem health objectives includes a target schedule for being achieved to help participants prioritize their programs and activities. Importantly, the designated uses of the aquatic ecosystem that require protection and/or restoration emerge directly from the goals and objectives that are established by stakeholders.

The third step of the ecosystem management framework involves the selection of a suite of ecosystem health indicators, which provide a basis for measuring the level of attainment of the goals and objectives. Initially, a broad suite of candidate indicators of ecosystem health are identified and evaluated to determine their applicability. Typically, selection criteria are established and applied on *a priori* bases to provide a consistent means of identifying the indicators that are most relevant to the assessment and/or management initiative. Each of the selected ecosystem health indicators must be supported by specific metrics and targets, which identify the acceptable range for each of the variables that will be measured in the monitoring program. If all of the measured attributes or metrics fall within acceptable ranges for all of the indicators, then the ecosystem as a whole is considered to be healthy and vital.

In the fourth step of the process, environmental monitoring and directed research are undertaken to evaluate the status of the ecosystem and to fill any data gaps that have been identified. In this application, the term monitoring is used to describe a wide range of activities that are focused on assessing the health of the ecosystem under consideration. Such monitoring could be implemented under a broad array of environmental assessment programs or conducted to address site-specific concerns regarding environmental quality conditions. Directed research activities may be needed to address priority data gaps for the ecosystem under consideration. Evaluation of the adequacy of the knowledge base provides a basis for identifying data gaps, including those associated with the application of the ecosystem health indicators chosen (i.e., to establish baseline conditions) or with the existing knowledge base. The results of monitoring activities (i.e., to assess the status of each indicator) provide the information needed to determine if the ecosystem goals and objectives are being met, to revise the metrics and targets, and to refine the monitoring program design.

Overall, the framework for implementing ecosystem-based management is intended to support informed decision-making. That is, the ecosystem goals and ecosystem health objectives establish the priorities that need to be reflected in decisions regarding the conservation of natural resources, protection of the environment, and socioeconomic development. As a final step in the process, the information on the status of the ecosystem health indicators is used by decision-makers to evaluate the efficacy of their management activities and to refine their approaches, if necessary (i.e., within an adaptive management context; by systematically evaluating the efficacy of management decisions and using that information to refine management strategies in the future). Successful adoption of this framework requires a strong commitment from all stakeholders and a willingness to explore new decision-making processes (Environment Canada 1996).

5.3 Establishment of Ecosystem Goals and Objectives

Ecosystem goals are broad narrative statements that define the management goals that have been established for a specific ecosystem. Definition of management goals for the aquatic ecosystem is a fundamental step towards the development of defensible management plans for the system. Definition of these ecosystem goals requires input from a number of sources to ensure that societal values are adequately represented. Open consultation with the public should be considered a primary source of information for defining these goals. Government agencies, non-government agencies, and other stakeholders may also be consulted during this phase of the process. Specifically, information on the existing and potential uses of the aquatic resources within the basin should be solicited. Participants at the TSMD ERA workshops identified the following as an important long-term management goal:

***Protection and Restoration of Natural Resources in the
Spring River and Neosho River Watersheds.***

While articulating this management goal represents a key step in the ecosystem-management process, it is too general to support the development of meaningful planning, research, and management initiatives for the study area. To be useful, this ecosystem goal must be further clarified and refined to establish *ecosystem objectives* that are more closely linked with

ecosystem science (Harris *et al.* 1987). In turn, the ecosystem objectives support the identification of indicators and metrics that provide direct information for assessing the health and integrity of the ecosystem. The following ecosystem objectives are proposed to support the development of remedial action objectives and restoration objectives for the Spring River and Neosho River watersheds:

- Maintain and, if necessary, restore aquatic environmental conditions in the Spring River and Neosho River watersheds that will support healthy and diverse warm-water aquatic life communities, including microbiota, aquatic plants, aquatic invertebrates (including freshwater mussels), fish, and amphibians;
- Maintain and, if necessary, restore cool-water fisheries in the applicable portions of the Spring River watershed (e.g., Center Creek, Shoal Creek);
- Maintain and, if necessary, restore aquatic, wetland, and riparian habitats that will support healthy, diverse, and self-sustaining populations of aquatic-dependent wildlife, including reptilian, avian, and mammalian species;
- Protect human health from adverse effects in association with consumption of fish and/or other aquatic organisms. In addition, reduce the incidence of, or eliminate, fish consumption advisories, which are indicative of a natural resource injury;
- Protect and, if necessary, restore other human uses of the Spring River and Neosho watersheds, including tribal cultural uses, public and private water supplies, primary contact recreation (i.e., swimming), secondary contact recreation (i.e., boating, fishing, etc.), livestock and wildlife watering, irrigation, and industrial water uses;
- Restore populations of any threatened or endangered species that were historically present in the assessment area, including freshwater mussels; and,
- Protect, enhance, and/or restore populations of Missouri’s species of conservation concern, which may be imperiled or vulnerable.

Such ecosystem goals and objectives inform the selection of the assessment and measurement endpoints that will be used to evaluate risks to ecological receptors utilizing aquatic habitats in the TSMD. In addition, these ecosystem goals and objectives support the selection of restoration goals for the TSMD.

Chapter 6 Overview of Problem Formulation for the Detailed Assessment of Risks to the Benthic Invertebrate Community

6.0 Introduction

The results of the SLERA of the TSMD demonstrated that exposure to contaminated surface water, sediment, and/or pore water posed potential risks to ecological receptors in the TSMD. Accordingly, a more thorough assessment of risks to ecological receptors utilizing aquatic and floodplain habitats in the TSMD was warranted. While potential risks to various ecological receptor groups are indicated by the SLERA results, USEPA and its partners have decided to focus near-term follow-up assessment activities on evaluating risks to the benthic invertebrate community posed by exposure to contaminated environmental media in the study area. This decision was taken because contaminated sediments represent long-term sources of COPCs to downstream areas and controlling these and other sources (such as mine water, tailings disposal areas, and floodplain soils) is likely to represent an important near-term priority. In addition, data and information from other sites indicates that benthic invertebrates are likely to be more sensitive to sediment-associated COPCs than are other aquatic receptors (such as microbiota, plants, and fish; MacDonald *et al.* 2002a; 2003). Accordingly, conditions that are protective of benthic invertebrate communities are likely to be protective of other aquatic receptor groups. Therefore, information from a DERA for benthic invertebrates communities is likely to support identification of source control and/or other risk management measures that would be protective of benthic invertebrates and other aquatic receptors.

As indicated previously, BERAs were previously completed for Cherokee County and Jasper County (Dames and Moore 1993; Black and Veatch Special Projects Corp. 1998). The results of these BERAs provide useful information for documenting risks to ecological receptors within these geographic areas and for supporting feasibility studies to identify appropriate actions for managing such risks. In the future, BERA(s) may be undertaken in Newton County and/or Ottawa County to provide additional information to support remedial action planning activities, should remedial measures be needed to mitigate risks to ecological

receptors in these portions of the study area. The DERA for the benthic invertebrate community is not intended to supplant the existing BERAs or obviate the need for additional assessments (e.g., evaluations of risks to ecological receptors associated with exposure to floodplain soils). Rather, it is intended to provide risk managers and others with a watershed-wide assessment of risks to benthic invertebrates that can be used to develop coordinated source control activities in the near-term and to better integrate remedial measures and restoration efforts in the future.

In accordance with USEPA guidance, the problem formulation for the DERA for benthic invertebrate communities is intended to provide three main products, including: assessment endpoints, conceptual models, and a risk analysis plan (USEPA 1997a; 1998). The problem formulation for the DERA is presented in Appendix 1 of this document. The following sections of this chapter provide an overview of the DERA problem formation, including summaries of the information on the sources and releases of COPCs, the transport and fate of these substances, the pathways by which ecological receptors are exposed to the COPCs, and the potential effects of these substances on the ecological receptors that occur in the TSMD. In addition, a series of hypotheses were developed that provide predictions regarding how ecological receptors will be exposed to and respond to the COPCs. Finally, the assessment endpoints, risk questions, and measurement endpoints that were selected for evaluation in the DERA of benthic invertebrate communities are presented.

6.1 Refinement of the Preliminary Chemicals of Potential Concern

As part of the problem formulation for the SLERA, an evaluation of potential sources of COPCs was conducted. This evaluation involved description of potential sources and identification of the substances that may have been released to the environment from each source (see Chapter 3 of Appendix 1). Subsequently, the available data on the concentrations of each of these preliminary COPCs in surface water, sediment and pore water was assembled and compiled. The maximum concentration of each substance was then compared to the corresponding TSV for that media type (e.g., surface water) to identify the substances that pose potential risks to one or more ecological receptor groups (see Chapter 4 of this

document for more information). The results of the SLERA showed that numerous substances posed potential or uncertain risks to ecological receptors utilizing aquatic habitats in the TSMD (i.e., using the data and information on surface-water chemistry, sediment chemistry, and pore-water chemistry). However, it may not be necessary to evaluate all of the COPCs in the DERA (i.e., some of the preliminary COPCs may pose negligible risks to ecological receptors or may not pose incremental risks compared to those that exist at reference locations in the watershed). To focus the assessment on the substances that are most likely to be risk drivers or contribute significantly to risk, COPC refinement typically represents the first step in the problem formulation process.

For the TSMD DERA, COPC refinement was conducted by comparing the 95th percentile concentration of each COPC in each environmental medium (i.e., for the study area as a whole) to the 95th percentile concentration calculated using the data for the selected reference samples. A COPC was considered to pose incremental risks to benthic invertebrates if the ratio of the concentrations in TSMD surface water, sediment or pore water to reference surface water, sediment or pore water exceeded 2.0 (MacDonald *et al.* 2002a). Such substances were retained as COPCs.

Surface Water: The results of the COPC refinement for surface water indicate that aluminum, cadmium, copper, iron, lead, nickel, and zinc should be retained as COPCs (Table 14). In addition ammonia, mercury (dissolved), and chlorine should be retained as uncertain COPCs. Because PAHs, PCBs, organochlorine pesticides, and many SVOCs tend to partition into sediment, soil, and biological tissues upon release into the environment and because specific sources of these COPCs were not identified in the TSMD, metals, nutrients, and chlorine should be considered the primary COPCs in surface water.

Sediment: The results of the COPC refinement for sediment indicated that aluminum, arsenic, barium, cadmium, chromium, copper, iron, lead, mercury, molybdenum, nickel, and zinc should be retained as COPCs (Table 15). One metal was identified as an uncertain COPC, molybdenum, because there were no data for the reference samples. Eleven individual PAHs, total high molecular weight PAHs, total low molecular weight PAHs, and total PAHs were also retained as COPCs. All of the PCBs, organochlorine pesticides, and SVOCs [with the exception of butylbenzyl phthalate (BBP)] had similar

concentrations in TSMD sediments and reference sediments (Table 15), indicating that they likely posed little or no incremental risks to benthic invertebrates in the study area. Accordingly, these substances were not retained as COPCs. Therefore, metals, PAHs, and BBP were identified as the COPCs in sediment.

Pore Water: The results of COPC refinement for pore water indicate that cadmium, cobalt, lead, and zinc should be retained as COPCs (Table 16; i.e., based on the reported results for dissolved metals). In addition, all total metals and dissolved mercury were retained as uncertain COPCs because they were not measured in the reference samples. Several metals that were identified previously as preliminary or uncertain COPCs were not retained as COPCs, including dissolved aluminum, dissolved iron, and dissolved silver. Although no data were located on the levels of organic compounds in pore water, the results of COPC refinement for sediment suggest that PCBs, organochlorine pesticides, and most SVOCs are unlikely to occur in pore water at concentrations that pose incremental risks to benthic invertebrates. Furthermore, pore-water zinc and pore-water divalent metal concentrations explained more than 80% of the variability in the amphipod survival data, suggesting that metals are the primary COPCs in pore water. The refined list of COPCs that were addressed in the DERA for benthic invertebrates is provided in Table 17.

6.2 Environmental Transport and Fate of Chemicals of Potential Concern

Upon release into aquatic ecosystems, COPCs partition into environmental media (i.e., water, sediment, and/or biota) in accordance with their physical and chemical properties and the characteristics of the receiving water body. As a result of such partitioning, elevated levels of COPCs can occur in surface water (including the water column, pore water, and/or surface microlayer), bottom sediments, and/or the tissues of aquatic organisms. Accordingly, information on the environmental fate can be used to classify the COPCs into three groups, including:

- Bioaccumulative substances (i.e., substances that accumulate in the tissues of aquatic organisms);
- Toxic substances that partition into sediment and/or soil; and,
- Toxic substances that partition into waters (including surface water, pore water, and the surface microlayer).

Detailed information on the environmental transport and fate of the COPCs is provided in Appendices 1 and 2.

6.3 Potential Exposure Pathways

Once released to the environment, there are three pathways through which ecological receptors can be exposed to COPCs. These routes of exposure include direct contact with contaminated environmental media, ingestion of contaminated environmental media, and inhalation of contaminated air. For bioaccumulative substances, the ingestion of contaminated prey species represents the most important route of exposure for the majority of aquatic organisms and aquatic-dependent wildlife species. Direct contact with contaminated water and/or contaminated sediment and ingestion of contaminated sediment represent important routes of exposure to bioaccumulative COPCs for many aquatic organisms, including benthic invertebrates.

For toxic substances that partition into sediments, direct contact with contaminated sediments and pore water represents the most important route of exposure for most aquatic organisms. However, ingestion of contaminated sediments and/or soil can also represent an important exposure pathway for certain aquatic organisms (e.g., oligochaetes that process sediments to obtain food) and aquatic-dependent wildlife species (e.g., sediment-probing birds, such as sandpipers).

For toxic substances that partition into surface water, direct contact with contaminated water represents the most important route of exposure for aquatic organisms (i.e., uptake through the gills and/or through the skin). For aquatic-dependent wildlife species, ingestion of

contaminated water represents the principal route of exposure to toxic substances that partition into surface water.

For toxic substances that partition into the surface microlayer, direct contact with the contaminated surface microlayer represents the most important route of exposure for aquatic organisms (i.e., uptake through the gills and/or through the skin). However, aquatic-dependent wildlife species can be exposed to substances that volatilize from the surface microlayer through inhalation. This route of exposure could become important during and following accidental spills of VOCs, when such substances are present as slicks on the water surface. Such spills of VOCs are not expected to occur in the study area, however. A more detailed description of the pathways through which ecological receptors can be exposed to environmental contaminants is presented in Appendix 1.

For benthic invertebrates, potentially complete exposure pathways include direct contact with surface water, direct contact with sediment and pore water, and ingestion of contaminated prey species.

6.4 Ecological Receptors at Risk

There are a wide variety of ecological receptors that could be exposed to contaminated environmental media in the TSMD. The receptor groups for which potentially complete exposure pathways exist in aquatic ecosystems within the TSMD can be classified into ten main receptor groups, including:

- Microbiota (e.g., bacteria, fungi and protozoa);
- Aquatic plants (including phytoplankton, periphyton, and aquatic macrophytes);
- Aquatic invertebrates (including zooplankton and benthic invertebrates);
- Fish (including benthic and pelagic fish);
- Amphibians;

- Terrestrial plants (including riparian plants and other terrestrial plants that inhabit floodplain areas);
- Terrestrial invertebrates;
- Aquatic-dependent reptiles (e.g., turtles, water snakes);
- Aquatic-dependent birds (including a number of feeding guilds); and,
- Aquatic-dependent mammals (including a number of feeding guilds).

The COPCs in the TSMD were classified into four categories based on their predicted environmental fate (MESL and CH2M Hill 2007). By considering this information, in conjunction with the exposure pathways that apply to these groups of COPCs, it is possible to identify the receptors that are potentially at risk due to exposure to contaminated environmental media. For bioaccumulative substances, the groups of aquatic organisms that are most likely to be exposed to tissue-associated contaminants include benthic invertebrates, carnivorous fish, and amphibians.

Toxic substances that partition into sediments and soils pose a potential risk to a variety of aquatic organisms and aquatic-dependent wildlife species. The groups of aquatic organisms that are most likely to be exposed to sediment-associated contaminants include decomposers (i.e., microbiota), aquatic plants (i.e., rooted aquatic macrophytes), benthic invertebrates, benthic fish, and amphibians. Although reptiles can come in contact with contaminated sediments, it is unlikely that significant dermal uptake would occur.

For toxic substances that partition into surface water, aquatic plants, aquatic invertebrates, fish, and amphibians represent the principal groups of exposed aquatic organisms. By comparison, aquatic invertebrates and pelagic fish, are likely to have the highest potential for exposure to toxic substances that partition into the surface microlayer.

The DERA will focus on evaluating risks to benthic invertebrate communities associated with exposure to contaminated environmental media in the TSMD. The existing BERAs provide evaluations of risks to selected receptor groups for portions of the study area (i.e., Cherokee County and Jasper County; Dames and Moore 1993; Black and Veatch Special Projects Corp. 1998). Additional ERAs may be needed in the future to evaluate risks to other receptor

groups, to evaluate risks to such receptors in other geographic areas, and/or to evaluate risks based on contemporary exposure scenarios.

6.5 Hypotheses Regarding the Potential Fate and Effects of Chemicals of Potential Concern

Exposure to environmental contaminants has the potential to adversely affect aquatic organisms utilizing habitats within the study area. The nature and severity of such effects are dependent on the substance under consideration, its bioavailability, the characteristics of the exposure medium, the duration of exposure, the species and life stage of the exposed biota, and several other factors. Evaluation of the environmental fate of COPCs and identification of the types of effects that could occur in the various groups of organisms found in the TSMD provides a basis for developing fate and effects hypotheses (i.e., using the information presented in Appendix 2). In turn, these hypotheses provide a basis for evaluating the logical consequences of exposing ecological receptors to environmental contaminants (i.e., predicting the responses of assessment endpoints when exposed to chemical stressors; USEPA 1998).

Certain metals (cadmium, copper, lead, mercury, and zinc), certain PAHs [e.g., benzo(a)pyrene], PCBs, organochlorine pesticides, and various SVOCs (i.e., those with $\log K_{ow,s} > 4.0$) are the bioaccumulative substances of greatest concern in the TSMD. Short- and long-term exposure to these substances have been demonstrated to adversely affect the survival, growth, and/or reproduction of aquatic invertebrates, fish, and amphibians. Extended exposure to some of these substances can also result in tumor induction and/or immune system suppression (see Chapter 4 of Appendix 1 and Appendix 2 for more information). The following fate and effects hypothesis was developed to identify the key stressor-effect relationships that need to be evaluated during the analysis phase of the assessment:

- Based on the physical-chemical properties (e.g., $K_{ow,s}$) of the bioaccumulative substances of concern, the nature of food web in the TSMD, and the effects that have been documented in field and laboratory studies, cadmium, copper, lead, mercury, selenium, zinc, certain PAHs, PCBs, organochlorine pesticides, and/or

various SVOCs that are released into surface waters will accumulate in the tissues of aquatic organisms to levels that will adversely affect the survival, growth, and/or reproduction of benthic invertebrates. Although not addressed in the DERA, the survival, growth, and/or reproduction of fish, amphibians, and aquatic-dependent wildlife will also be adversely affected by food web transfer of bioaccumulative substances.

Many of the COPCs in the TSMD were classified as toxic substances that partition into sediments, including metals (aluminum, arsenic, barium, cadmium, chromium, copper, iron, lead, mercury, nickel, zinc), PAHs (13 individual PAHs and total PAHs), and BBP. Adverse effects on the survival, growth, and/or reproduction have been observed in aquatic plants, aquatic invertebrates, fish, and amphibians exposed to one or more of these substances in sediments (see Chapter 4 and Appendix 1 for more information). Exposure to sediment-associated contaminants also has the potential to adversely affect the microbial community (i.e., decomposers). The following fate and effect hypothesis was developed to identify the key stressor-effect relationships that need to be evaluated during the analysis phase of the assessment:

- Based on the environmental fate of the toxic substances that partition into sediments and the effects that have been documented in laboratory studies, metals (aluminum, arsenic, cadmium, chromium, copper, iron, lead, mercury, molybdenum, nickel, zinc), PAHs (13 individual PAHs and total PAHs), and BBP will accumulate in sediments and/or pore water, to levels that will adversely affect the survival, growth, and/or reproduction of benthic invertebrates. Although not addressed in the DERA the activity of the microbial community (e.g., reduced rate of carbon processing by decomposers), the survival, growth, and/or reproduction of aquatic plants, terrestrial plants, terrestrial invertebrates, fish, amphibians, reptiles, birds, and/or mammals will also be adversely affected by exposure to toxic substances that partition into floodplain soils.

The toxic substances of greatest concern (i.e., COPCs) that partition into water in the TSMD include metals (aluminum, cadmium, copper, iron, lead, mercury, nickel, zinc), nutrients and chlorine. Adverse effects on survival, growth, and/or reproduction have been observed in aquatic plants, aquatic invertebrates, and fish exposed to one or more of these substances in

water (see Chapter 4 of Appendix 1 for more information). The following fate and effect hypothesis was developed to identify the key stressor-effect relationships that need to be evaluated during the analysis phase of the assessment:

- Based on the environmental fate of the toxic substances that partition into water (including pore water and the surface microlayer) and the effects that have been documented in laboratory studies, metals (aluminum, cadmium, copper, iron, lead, mercury, nickel, zinc), nutrients, and chlorine will occur in surface water at levels that will adversely affect the survival, growth, and/or reproduction of aquatic invertebrates. Although not addressed in the DERA, the survival, growth, and/or reproduction of aquatic plants, fish, and amphibians will also be adversely affected by exposure to toxic substances in surface water.

Integration of these fate and effects hypotheses results in the following that is directly applicable to benthic invertebrates in the TSMD:

- Based on the environmental fate of the toxic substances that partition into sediments and the effects that have been documented in laboratory studies, metals, PAHs and/or BBP will accumulate in surface water, sediment, and/or pore water to levels that will adversely affect the survival, growth, and/or reproduction of benthic invertebrates.

6.6 Conceptual Site Model Diagrams

As indicated previously, the conceptual modeling process for hazardous waste sites is intended to culminate in the development of:

- A series of hypotheses that describe the predicted relationships between stressors, exposures, and assessment endpoint responses (along with the rationale for their selection); and,
- Diagrams that illustrate the relationships presented in the risk hypotheses.

Accordingly, conceptual model diagrams were developed to illustrate the linkages between sources and releases of COPCs and the potential responses of ecological receptors for all three categories of COPCs (i.e., bioaccumulative COPCs, COPCs that partition in sediments; and COPCs that partition in water). A CSM for the TSMD is presented in Figure 9, while various food web models and CSM diagrams are presented in Appendix 1.

6.7 Selection of Assessment and Measurement Endpoints for Evaluating Risks to the Benthic Invertebrate Community

In the environment, a variety of plant and animal species can be exposed to COPCs (these species are referred to as receptors potentially at risk). Each of these receptors can be exposed to a chemical through different exposure routes and have the potential to exhibit different types and severities of effects. While information on the effects of each COPC on each component of the ecosystem would provide comprehensive information for evaluating ecological risks, it is not feasible to directly evaluate risks to all of the individual components of the ecosystem that could be adversely affected by environmental contamination at a site (USEPA 1997a). For this reason, risk assessment activities should focus on the receptors that represent valued ecosystem components (e.g., sportfish species) and on the receptors that support valued ecosystem functions (e.g., carbon processing by the microbial community, which is needed to support healthy fish populations). Of particular interest are those receptors that are most likely to be adversely affected by the presence of COPCs at the site (USEPA 1998). The process that was used to select assessment and measurement endpoints for evaluating risks to the benthic invertebrate community in the TSMD is described in the following sections of this document.

6.7.1 Considerations for Selecting Assessment Endpoints

An assessment endpoint is an ‘explicit expression of the environmental value that is to be protected’ (USEPA 1997a). The selection of assessment endpoints is an essential element of the overall ERA process because it provides a means of focusing assessment activities on the key environmental values (e.g., reproduction of sediment-probing birds) that could be

adversely affected by exposure to environmental contaminants. Assessment endpoints must be selected based on the ecosystems, communities, and species that occur, have historically occurred, or could potentially occur at the site (USEPA 1997a). The following factors need to be considered during the selection of assessment endpoints (USEPA 1997a):

- The COPCs that occur in environmental media and their concentrations;
- The mechanisms of toxicity of the COPCs to various groups of organisms;
- The ecologically-relevant receptor groups that are potentially sensitive or highly exposed to the contaminant, based upon their natural history attributes; and,
- The presence of potentially complete exposure pathways.

Thus, the fate, transport, and mechanisms of ecotoxicity for each contaminant or group of contaminants must be considered to determine which receptors are likely to be most at risk. This information must include an understanding of how the adverse effects of the contaminant could be expressed (e.g., eggshell thinning in birds) and how the form of the chemical in the environment could influence its bioavailability and toxicity.

6.7.2 Assessment Endpoints

As part of the preliminary problem formulation, a number of candidate assessment endpoints were considered for potential use in the advanced SLERA of the TSMD. In addition, development of the CSM for the TSMD supported the identification of a variety of candidate assessment endpoints that could be considered for the DERA [Note: the candidate assessment endpoints, risk questions, and measurement endpoints for the DERA were presented in MESL and CH2M Hill (2007) to provide a perspective on those that are recommended for the SLERA]. Importantly, the scope of the DERA has been limited to benthic invertebrates because these receptors represent key elements of aquatic food webs and because the results of studies at other sites have shown that benthic invertebrates tend to be more sensitive to sediment-associated COPCs than are other aquatic receptors (e.g., plants, fish, or microbes; MacDonald *et al.* 2002a; 2003). Accordingly, microbiota, aquatic plants, fish, amphibians, reptiles, birds, mammals, and all terrestrial receptor groups have been excluded from the assessment. The of assessment endpoints for the DERA include:

- Survival, growth, and reproduction of benthic invertebrates.

6.7.3 Risk Questions

Selection of assessment endpoints represents an essential element of the overall problem formulation process. While such assessment endpoints are essential for defining the environmental values that need to be protected at the TSMD, it is difficult or impossible to measure the effects on all of the members of a receptor group that are associated with exposure to COPCs at the site. For this reason, it is necessary to articulate specific risk questions (i.e., testable hypotheses) that can be answered through the collection and evaluation of focused data and information at the site. The preliminary list of risk questions that should be considered in the DERA for the TSMD includes:

- Are the concentrations of COPCs in surface-water from the TSMD greater than toxicity thresholds for benthic invertebrates?
- Are the concentrations of COPCs in sediment samples from the TSMD greater than toxicity thresholds for benthic invertebrates?
- Are the concentrations of COPCs in pore-water samples from the TSMD greater than toxicity thresholds for benthic invertebrates?
- Are the concentrations of COPCs in the tissues of benthic invertebrates from the TSMD greater than toxicity thresholds for benthic invertebrates?
- Is the survival or biomass of benthic invertebrates exposed to sediments from the TSMD significantly lower than that for benthic invertebrates exposed to reference sediments?
- Are the concentrations of COPCs in sediment greater than the toxicity thresholds for freshwater mussels (i.e., based on taxa richness, as evaluated in field surveys)?

6.7.4 Selection of Measurement Endpoints

A measurement endpoint is defined as ‘a measurable ecological characteristic that is related to the valued characteristic that is selected as the assessment endpoint’ and it is a measure of

biological effects (e.g., mortality, reproduction, growth; USEPA 1997a). Measurement endpoints are frequently numerical expressions of observations (e.g., toxicity test results, community diversity measures) that can be compared to similar observations at a control and/or reference site. Such statistical comparisons provide a basis for evaluating the effects that are associated with exposure to a COPC or group of COPCs at the site under consideration. Measurement endpoints can include measures of exposure (e.g., COPC concentrations in water or sediments) or measures of effects (e.g., survival or biomass of amphipods in 28-d toxicity tests). The relationship between an assessment endpoint, a risk question, and a measurement endpoint must be clearly described within the conceptual model and must be based on scientific evidence (USEPA 1997a).

After identifying receptors of concern and selecting assessment endpoints, it is helpful to describe the linkages that are likely to exist between exposure media (i.e., stressors) and receptors within the TSMD. The results of this process provide a basis for identifying measurement endpoints that could be used to evaluate the status of each assessment endpoint. As it would not be practical nor possible to incorporate all of the possible measurement endpoints into the DERA, it is necessary to identify the measurement endpoints that would provide the most useful information for evaluating the potential ecological risks associated with exposure to COPCs in the study area. Accordingly, the risk questions and the highest priority measurement endpoints for evaluating the status of the candidate assessment endpoints include (see Appendix 1 for additional information):

Assessment Endpoint: Survival, growth, and reproduction of benthic invertebrates.

RQ-1: Are the concentrations of COPCs in surface-water samples from the TSMD greater than toxicity thresholds for benthic invertebrates?

ME-1: The concentrations of COPCs in surface-water samples collected from the TSMD, compared to the site-specific TRVs for divalent metals in water.

RQ-2: Are the concentrations of COPCs in sediment samples from the TSMD greater than toxicity thresholds for benthic invertebrates?

ME-2: The concentrations of COPCs in sediment samples collected from the TSMD, compared to the site-specific TRVs for cadmium, lead, and zinc in sediment.

RQ-3: Are the concentrations of COPCs in pore-water samples from the TSMD greater than toxicity thresholds for benthic invertebrates?

ME-3: The concentrations of COPCs in pore-water samples collected from the TSMD, compared to the site-specific TRVs for zinc in pore water.

RQ-4: Are the concentrations of COPCs in the tissues of benthic invertebrates from the TSMD greater than toxicity thresholds for benthic invertebrates?

ME-4: The concentrations of COPCs in invertebrate-tissue samples collected from the TSMD, compared to the selected TRVs for cadmium, copper, lead, mercury, and zinc in invertebrate tissues.

RQ-5: Is the survival or biomass of benthic invertebrates exposed to sediments from the TSMD significantly lower than that for benthic invertebrates exposed to reference sediments?

ME-5: Survival and/or biomass of aquatic invertebrates in laboratory toxicity tests, compared to SSTTs established using the reference envelope approach.

RQ-6: Are the concentrations of COPCs in sediment greater than the toxicity thresholds for freshwater mussels (i.e., based on taxa richness as evaluated in field surveys or survival in laboratory toxicity tests)?

ME-6: The concentrations of COPCs in sediment samples collected from the TSMD, compared to the site-specific TRVs for freshwater mussels.

For each of the above listed MEs, toxicity thresholds (e.g., TRVs) have been selected to support risk characterization. The rationale for selection of these toxicity thresholds is provided in Section 7.3.5.

Chapter 7 Approach to the Assessment of Risks to the Benthic Invertebrate Community

7.1 Introduction

A number of sites within the TSMD have been listed on the NPL and, hence, require investigation under CERCLA. The largest of these NPL sites include Oronogo-Duenweg Mining Belt site (Jasper County, MO), Newton County Mine Tailings site (Newton, County, MO), Cherokee County site (Cherokee County, KS), and Tar Creek site (Ottawa County, OK). Following listing, a Remedial Investigation (RI) is typically conducted to characterize site conditions, to determine the nature of the wastes, to assess risk to human health and the environment, and to conduct treatability testing to evaluate the potential performance and cost of the treatment technologies that are being considered. Subsequently, a Feasibility Study (FS) may be conducted to support development, screening, and detailed evaluation of alternative remedial actions.

One of the objectives of an investigation of a hazardous waste site is to determine the risks to ecological receptors posed by exposure to environmental contamination. To meet this objective, one or more ecological risk assessments need to be conducted in accordance with the procedures laid out by the USEPA in the *Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessment* (USEPA 1997a). Under the eight-step process described by the USEPA for conducting ecological risk assessments, a SLERA must first be conducted to determine preliminary estimates of exposure and risk. The results of the SLERA indicated that exposure to surface water, sediment, pore water, and floodplain soil posed potential risks to ecological receptors utilizing habitats within the TSMD (see Chapter 4 for more information). Accordingly, a more thorough assessment of risks to ecological receptors was required.

In response to concerns regarding the risks posed to ecological receptors associated with exposure to contaminated media, two BERAs have already been completed in the TSMD. More specifically, Dames and Moore (1993; Hattemer-Frey *et al.* 1995) evaluated risks to aquatic receptors, terrestrial receptors, terrestrial plants, and threatened and endangered

species in the Cherokee County portion of the study area in 1993. Five years later, Black and Veatch Special Projects Corp. (1998) completed an evaluation of risks to the biological function of aquatic systems and terrestrial systems in the Jasper County portion of the site. While these BERAs provide useful information for characterizing risks to ecological receptors utilizing habitats in Cherokee County and Jasper County, they do not address the other two major geographic areas within the TSMD (i.e., Newton County and Ottawa County). Furthermore, the results of various studies conducted recently provide a great deal of additional information that is relevant for evaluating risks to ecological receptors, particularly those that are exposed to sediment and pore water under contemporary exposure scenarios. As such, it is beneficial to update the results of the earlier risk assessments and to document risks to ecological receptors in the Newton County and Ottawa County portions of the site.

This chapter describes the approach that was used to assess risks to benthic invertebrates in the TSMD. The evaluation relies on the data that have been collected during the period 2002 to 2009 to facilitate documentation of risks to the benthic invertebrate communities under current conditions. Due to its limited scope (i.e., evaluating risks to the benthic invertebrate community), it is understood that additional ERAs may be required to fully document risks to ecological receptors in the study area. Nevertheless, it is anticipated that the results of the DERA will provide risk managers with relevant information for identifying the need for further source control measures, for further investigations to evaluate risks to ecological receptors, and for developing preliminary remediation goals (PRGs) to support source control and/or remedial measures. Information on multiple lines-of-evidence was used in the DERA to address the various exposure routes identified in the CSM and to help risk managers focus further investigations to support remedial action planning.

7.2 Purpose of Detailed Ecological Risk Assessment for Benthic Invertebrate Communities

Benthic invertebrates are the animals that live in and on the sediments in freshwater ecosystems. Benthic animals are extremely diverse and are represented by nearly all taxonomic groups from protozoa to large invertebrates. The groups of organisms that are commonly associated with benthic communities include protozoa, sponges (i.e., Porifera),

coelenterates (such as *Hydra* sp.), flatworms (i.e., Platyhelminthes), bryozoans, aquatic worms (i.e., oligochaetes), crustaceans [such as ostracods, mysids, isopods, decapods (e.g. crayfish), and amphipods], mollusks (such as mussels and clams), and aquatic insects (such as dragonflies, mayflies, stoneflies, true flies, caddisflies, and aquatic beetles). Because benthic invertebrate communities are difficult to study in a comprehensive manner, benthic ecologists often focus on the relatively large members of benthic invertebrate communities, which are known as benthic macroinvertebrates. These organisms are usually operationally defined, for example, as those that are retained on a 0.5 mm sieve.

Benthic invertebrates represent key elements of aquatic food webs because they consume aquatic plants (such as algae and aquatic macrophytes) and detritus. In this way, these organisms facilitate energy transfer to fish, birds, and other organisms that consume aquatic invertebrates. The risk hypotheses laid out in the problem formulation indicate that many COPCs pose potential risks to the benthic invertebrate community from direct contact with contaminated sediments and/or pore water (see Chapter 6 for more information). The purpose of this assessment is to provide detailed information on the risks posed to the benthic invertebrate community associated with exposure to the COPCs in the TSMD.

7.3 Methods

A step-wise approach was used to assess the risks to the benthic invertebrate community posed by the COPCs in the TSMD. The six main steps in this process included:

- Identification of assessment endpoints, risk questions and testable hypotheses, and measurement endpoints;
- Collection, evaluation, and compilation of the relevant information on sediment quality conditions in the TSMD;
- Refinement of the preliminary list of COPCs;
- Assessment of the exposure of benthic invertebrates to COPCs (i.e., exposure assessment);

- Assessment of the effects of COPCs on benthic invertebrates (i.e., effects assessment); and,
- Characterization of risks to the benthic invertebrate community (i.e., risk characterization).

Each of these steps is described in the following sections of this report.

7.3.1 Identification of Assessment Endpoints, Risk Questions, and Measurement Endpoints

The assessment endpoints, risk questions, and measurement endpoints that were selected for evaluation in the DERA are presented in Chapter 6. These risk questions were developed using a combination of professional judgement and information on the potential sources of stressors, stressor characteristics, and actual and predicted ecological effects on the selected assessment endpoints (USEPA 1998). The conceptual model diagrams presented in the problem formulation provide a visual representation of the risk hypotheses (Chapter 6).

7.3.2 Collection, Evaluation, and Compilation of Relevant Information on Environmental Quality Conditions in the Tri-State Mining District

A total of six lines-of-evidence were selected for evaluating risks to the benthic invertebrate community associated with exposure to COPCs in the TSMD, including surface-water chemistry, sediment toxicity, sediment chemistry, pore-water chemistry, invertebrate-tissue chemistry (i.e., oligochaetes, mussels, and crayfish), and freshwater mussel species richness. Relevant data and information on the selected indicators of environmental quality conditions were acquired in several ways. First, all of the data that have been collected by USEPA over the past eight years (i.e., 2002 to 2009) were identified. Next, the members of the TSMD Ecological Risk Assessment Advisory Group were asked to identify any studies that they had conducted or were aware of that provided information on the status of the selected indicators. Finally, focused literature searches were conducted to identify any other information that

might be relevant to the DERA. Subsequently, hard and/or electronic copies of the relevant data were requested from the applicable sources.

All of the data sets that were compiled during the course of the study were critically reviewed to determine their applicability to the assessment of risks to the benthic invertebrate community in the TSMD. For those data sets that were considered to be relevant to the DERA, the applicable data were translated into MS Access format. Following translation, the data were further evaluated to assure the quality of the data used in the risk assessment. This database auditing process involved analyses of outliers (i.e., to identify inconsistencies with units) and completeness (i.e., to identify missing samples or missing data); examination of data qualifier fields (i.e., to assure internal consistency in the DERA database), checking of sample identification numbers (i.e., to ensure that data were not duplicated). Finally, the data were verified against the original data source. A listing of the data sets that were compiled in the project database is presented in Table 18.

To support the compilation and subsequent analysis of the information on sediment quality conditions in the TSMD, a relational project database was developed in MS Access format. All of the surface-water chemistry, sediment chemistry, pore-water chemistry, sediment toxicity, invertebrate-tissue chemistry, and mussel distribution data compiled in the database were georeferenced to facilitate mapping and spatial analysis using GIS-based applications (i.e., ESRI's ArcView and Spatial Analyst programs). The database structure made it possible to retrieve data in several ways, including by data type (i.e., chemistry vs. toxicity), by sediment horizon (i.e., surficial vs. sub-surface sediments), and AoI (i.e., Center Creek vs. Turkey Creek). As such, the database facilitated a variety of data analyses.

7.3.3 Refinement of the Preliminary List of Chemicals of Potential Concern

The preliminary list of COIs for the TSMD was not developed based on a comprehensive assessment of all possible sources and releases of contaminants within the study area. Rather, the members of the TSMD Ecological Risk Assessment Advisory Group were asked to identify key sources of contaminants in the study area and the classes of contaminants that were likely to be released into the environment from each source. Then, analytes that are

typically measured for each of the chemical classes were identified. This approach resulted in an inclusive list of substances that may have been released into surface waters within the TSMD.

The DERA is being conducted to evaluate the nature, severity, and areal extent of risks to benthic invertebrates utilizing aquatic habitats in the TSMD. In addition the DERA is being conducted to identify the substances that are causing or substantially contributing to any risks to the benthic invertebrate community that are identified (i.e., risk drivers). Several steps were taken to support identification of the potential risk drivers for the benthic invertebrate community, including:

- Conduct a SLERA to identify the substances that pose potential risks to ecological receptors (i.e., substances were retained as COPCs if the maximum concentrations measured in surface-water, sediment, or pore-water samples from the TSMD exceeded the corresponded TSVs);
- Conduct Spearman-Rank correlation analysis and/or regression analysis to identify the physical and/or chemical characteristics of sediment or pore water that are significantly correlated with sediment chemistry (i.e., substances were retained as COPCs if the measured concentrations explained more than 40% of the variability of the data for one or more toxicity test endpoint and the relationship was statistically significant (i.e., $r^2 > 0.40$; $p < 0.05$; see MacDonald *et al.* 2009 for the results of this analysis; Table 19); and,
- Compare the concentrations of preliminary COPCs in surface-water, sediment, and pore-water samples from the TSMD to those in the selected reference samples [i.e., substances were retained as COPCs if the upper limit of their concentrations in TSMD surface water, sediment, or pore water (i.e., 95th percentile concentrations) exceeded the upper limit of their concentrations in the selected reference samples by a factor of two or more].

The substances that were retained following the completion of all three steps in the COPC refinement process were further evaluated in the DERA. These substances are listed in Table 17. In addition, several chemical mixture models were retained for further evaluation in the DERA, including sum probable effect concentration quotients (PEC-Qs) for cadmium (Cd),

lead (Pb), and zinc (Zn; $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$; i.e., the Dudding Model), sum pore-water toxic units for zinc ($\sum \text{PW-TU}_{\text{Zn}}$), and sum surface-water toxic units for divalent metals (cadmium, copper, lead, nickel, silver, zinc; $\sum \text{SW-TU}_{\text{DIVALENT METALS}}$).

7.3.4 Assessment of Exposure of Benthic Invertebrates to Chemicals of Potential Concern

Risks to ecological receptors are estimated by combining the exposure profile with the effects profile that are developed for each stressor (USEPA 1998). For an exposure profile to be useful, it should be compatible with the stressor-response relationships that are generated in the effects characterization. In the SLERA, the potential effects associated with exposure to COPCs in surface water, sediment, and pore water were evaluated. To support that assessment, estimates of the maximum concentration of each COPC in each media type were developed for the study area as a whole. This approach to assessing maximum exposure to COPCs provided a conservative basis for evaluating potential risks to ecological receptors in the TSMD.

In the DERA, however, it is desirable to establish more realistic estimates of exposure that provide a basis for better understanding the spatial and temporal extent of co-occurrence of stressors with receptors. For the benthic invertebrate community, exposure point concentrations calculated for individual AoIs or the study area as a whole are informative, but are not the most relevant for characterizing risks because these receptors are not mobile. Rather, they are exposed to COPCs at the specific location where they occur. For this reason, exposure to COPCs was evaluated on a sampling station-by-sampling station basis. This point-by-point analysis provides spatially-relevant information for assessing risks to benthic invertebrates in the TSMD.

7.3.5 Assessment of Effects of Chemicals of Potential Concern on Benthic Invertebrates

In this assessment, exposure of the benthic invertebrate community to COPCs was evaluated using information on the concentrations of contaminants in surface water, sediment, pore water, and invertebrate tissues. As such, it was necessary to compile information on the

effects on benthic invertebrate communities associated with exposure to COPCs in these environmental media. Evaluation of the potential effects on benthic invertebrate communities associated with exposure to COPCs necessitated the selection and/or development of five types of chemical benchmarks, including:

- Toxicity thresholds for surface water;
- Toxicity thresholds for sediment;
- Toxicity thresholds for pore water;
- Toxicity thresholds for invertebrate tissue; and,
- Toxicity thresholds for mussel.

The chemical benchmarks that were selected for use in the DERA are described in the following sections of this report.

Toxicity Thresholds for Surface Water - Ambient water quality standards and/or criteria are commonly used to identify the concentrations of COPCs in surface water that pose tolerable risks to aquatic organisms. As such, ambient WQC or functionally-equivalent values were used to evaluate the potential effects on aquatic organisms associated with exposure to COPCs in surface water from the TSMD (i.e., for the SLERA). However, the results of site-specific evaluations of the relationships between the concentrations of metals in water and the responses of benthic invertebrates were used to establish the toxicity thresholds for surface water used in the DERA. More specifically, MacDonald *et al.* (2009) developed SSTTs for several individual COPCs and various COPC mixtures. These toxicity thresholds were then evaluated to determine their reliability and predictive ability. The results of this evaluation showed that the concentrations of divalent metals in pore water (i.e., expressed as toxic units of divalent metals, calculated as the measured concentrations of cadmium, copper, lead, nickel, silver and zinc divided by their respective hardness-adjusted CCCs) explained more than 80% of the variability in the data for 28-d amphipod survival. In addition, the SSTTs based on pore-water toxic units of divalent metals provided a reliable basis for classifying sediment samples as toxic or not toxic to amphipods, midges, and mussels. Because these results are also likely to be relevant for evaluating surface-water (SW) quality, the T_{10} - and T_{20} -values [i.e., the concentrations of COPCs or COPC mixtures that correspond to a 10% (T_{10}) or 20% (T_{20})

reduction in control-adjusted survival or biomass of the toxicity-test organisms relative to the average response rate observed for the selected reference samples] for SW-TU_{DIVALENT METALS} were selected for use in evaluating surface-water chemistry data in the DERA (i.e., 1.03 as the low risk toxicity threshold and 1.41 as the high risk toxicity threshold).

Toxicity Thresholds for Sediment - Numerical benchmarks [including sediment quality guidelines (SQGs), sediment quality criteria, sediment quality objectives, and sediment quality standards] represent useful tools for assessing the quality of freshwater sediments (USEPA 1992; Adams *et al.* 1992; USEPA 1996; USEPA 1997b; Ingersoll and MacDonald 1999; MacDonald *et al.* 2000a; 2000b). Such benchmarks have been developed by various jurisdictions in North America using a variety of approaches. The approaches for deriving SQGs that have been selected by individual jurisdictions depend on the geographic area evaluated, on the receptors that are considered (e.g., benthic invertebrates, fish, and/or aquatic-dependent wildlife), and on their intended uses (e.g., screening tools, injury thresholds, remediation objectives).

To support the SLERA, TSVs were established for each of the COPCs that were identified in the TSMD [i.e., threshold effect concentrations from MacDonald *et al.* (2000a) or functionally equivalent values]. While such conservative TSVs provide useful tools for evaluating potential effects on the benthic invertebrate community, they have the potential to over-estimate toxicity due to their conservative nature. For this reason, MacDonald *et al.* (2009) evaluated the predictive ability of the consensus-based sediment effect concentrations (i.e., PECs) in the TSMD. The results of this evaluation indicated that the PECs may over-estimate toxicity to amphipods, midges, and/or freshwater mussels exposed to sediment samples from the study area. MacDonald *et al.* (2009) developed site-specific toxicity thresholds (SSTTs) for individual COPCs and various COPC mixtures using matching sediment chemistry and sediment toxicity data from the TSMD.

The SSTTs for the TSMD were derived using a step-wise approach. First, the matching sediment chemistry and sediment toxicity data were compiled and evaluated. Next, sediment samples were designated as toxic or not toxic for each toxicity test endpoint using the reference envelope approach. Reference sediment samples were identified using

both chemical and biological criteria (as described in MacDonald *et al.* 2009). For each toxicity test endpoint, the reference envelope was calculated as the 5th percentile to the maximum control-adjusted response rate. Samples with control-adjusted response rates outside the reference envelope were designated as toxic for the endpoint under consideration. Subsequently, concentration-response models were developed for each of the COPCs and COPC mixtures that met the selection criteria (i.e., $r^2 > 0.4$; $p < 0.05$; Table 19).

The SSTTs were then derived by determining the concentration of each COPC or COPC mixture that corresponded to a 10% or 20% reduction in survival or biomass compared to the lower limit of the reference envelope. These SSTTs were then evaluated to determine which one would provide the most reliable basis for classifying sediment samples from the study area as toxic or not toxic.

Since the original SSTTs were derived, additional alternatives for evaluating the results of toxicity tests and deriving SSTTs have been proposed. More specifically, reviewers recommended alternative approaches for calculating the reference envelope and for estimating the toxicity thresholds. In addition, an additional chemical mixture model (i.e., $\sum \text{PEC}_{\text{Cd,Cu,Pb,Hg,Ni,Zn}}$) was recommended for possible use in classifying sediment samples from the study area. The alternate reference envelope approach involved calculation of the reference envelope as the full range of responses for the sediment samples that met the selection criteria for reference samples. The proposed procedures for calculating SSTTs (i.e., T_{10} and T_{20}) values included the following:

- **Scenario 1:** Establishing the T_{10} and T_{20} values by determining the concentrations of COPCs/COPC mixtures that corresponded to the response rates at the lower limit of the reference envelope and 10% below the lower limit of the reference envelope, respectively (Table 20);
- **Scenario 2:** Establishing the T_{10} and T_{20} values by determining the concentrations of COPCs/COPC mixtures that corresponded to response rates that are 10% and 20% below the lower limit of the reference envelope, respectively (Table 20); and,

- **Scenario 3:** Establishing the T_{10} and T_{20} values by determining the concentrations of COPCs/COPC mixtures that corresponded to response rates that are 10% and 20% below the mean response rate for the reference samples, respectively (Table 20).

The SSTTs derived using the three procedures described above for both chemical-mixture models were evaluated. In the predictive ability evaluation, the incidence of toxicity above and below the toxicity threshold was determined for all six of the toxicity test endpoints (*Chironomus dilutus* biomass and survival, *Hyaella azteca* biomass and survival, and *Lampsilis siliquodea* biomass and survival). Toxicity thresholds were considered to have high predictive ability if the incidence of toxicity was < 20% below the T_{10} or T_{20} value, if the incidence of toxicity was > 50% above the T_{10} or T_{20} value, and the overall correct classification rate was $\geq 80\%$. These criteria were applied across all six toxicity test endpoints to support comparison of the relative predictive ability of the toxicity thresholds (Table 20). In addition, each sediment sample was assigned an overall toxicity designation based on the results of the observed toxicity for all six toxicity test endpoints. That is, the sample was designated as toxic if toxicity was observed for any one of the six endpoints measured for the sample. Examination of the results indicated that toxicity to midges frequently caused the incidence of toxicity to be elevated at concentrations below the T_{10} or T_{20} values (Table 20). In addition, the results of previous analyses showed that the responses of midges in 10-d toxicity tests were not well correlated with either sediment or pore-water chemistry (MacDonald *et al.* 2009). As midge appear to be responding to factors other than the principal COPCs in the TSMD, a second overall toxicity designation was established to exclude the midge results. The second overall toxicity designation considered only the results of the amphipod and mussel toxicity tests (overall HaLs; Table 20). This latter overall toxicity designation provides an important tool for evaluating the predictive ability the various SSTTs.

The results of the evaluation for the sediment toxicity thresholds show that many of the SSTTs generated using the two models under the three scenarios met all of the above criteria for predictive ability for one or more endpoints. However, none of the T_{10} or T_{20} values met all three criteria for either of the overall toxicity designations. Therefore, none of the SSTTs provide infallible tools for classifying sediment samples from the TSMD as toxic or not toxic. Nevertheless, many of the SSTTs provide useful tools for accurately

classifying sediment samples as toxic or not toxic for multiple species and toxicity test endpoints. Based on the evaluation, SSTTs derived under Scenario 1 (Table 20) provide the most reliable tools for predicting toxicity to *Hyalella azteca* and *Lampsilis siliquoidea* (i.e., using the overall toxicity designations; overall HaLs). The incidence of toxicity below all T-values was $\leq 25\%$, the incidence of toxicity above all T-values was $\geq 75\%$, and the overall correct classification rate was $\geq 75\%$ for all of the SSTTs. Therefore, the probability of making Type I errors (incorrectly classifying a not toxic sample as toxic; i.e., false positive) and Type II errors (incorrectly classifying a toxic sample as not toxic; i.e., false negative) is expected to be $\leq 25\%$ for this set of SSTTs. Predictive ability was lower for the SSTTs derived using the two alternative methods applied to the two chemical-mixture models. The underlying models used for T-value generation explained similar levels of variability in the *Hyalella azteca* survival data ($\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$, $r^2 = 0.53$, $p < 0.001$; Figure 15; $\text{PEC-Q}_{\text{Cd,Cu,Pb,Hg,Ni,Zn}}$, $r^2 = 0.53$, $p < 0.001$; Figure 16); therefore, the simpler model was selected (i.e., $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$).

Based on the results of the predictive ability evaluation, the T_{10} and T_{20} SSTTs of 6.47 and 10.04, respectively, were selected to evaluate the risks to benthic invertebrates posed by exposure to sediments from the TSMD study area (Figure 17). Therefore, the selected T_{10} and T_{20} SSTTs correspond to the minimum survival of amphipods and 10% below the minimum value of the reference envelope, respectively. More specifically, sediment samples with $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ below 6.47 were considered to pose low risks to benthic invertebrates. Nine percent of the samples with mean $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ less than this SSTT were toxic to amphipods or mussels, considering the survival or biomass endpoints. Moderate risks to the benthic community were considered to exist if $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ was between 6.47 and 10.04 (50%). High risks to the benthic invertebrate community were considered to exist if $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ exceeded 10.04. Eighty-four percent of the sediment samples from the TSMD were toxic to amphipods or mussels at mean $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ above this level. These toxicity thresholds apply directly to the < 2.00 mm fraction. Sediment chemistry data used in the DERA were converted to < 2.00 mm equivalent values using the procedures described in Appendix 3.

Toxicity Thresholds for Pore Water - Pore water is the water that occupies the spaces between sediment particles and usually accounts for over 50% of the volume of surficial sediments. Because sediment-associated contaminants tend to partition into pore water,

this medium can represent an important source of exposure to contaminants for sediment-dwelling organisms (Ingersoll *et al.* 1997). For this reason, pore-water assessments can provide useful information on the potential effects of sediment-associated contaminants, particularly on infaunal species (i.e., those species that routinely reside within the sediment matrix). While such assessments can include several components, pore-water toxicity tests and evaluations of pore-water chemistry represent the central elements of most pore-water assessments (ASTM 2009a). Importantly, interpretation of the pore-water chemistry data that is collected in such assessments is dependent on the availability of suitable benchmarks for assessing pore-water quality.

A variety of benchmarks for assessing pore-water chemistry are available in the published literature. However, none were identified that were explicitly intended for assessing effects on the benthic invertebrate community in the TSMD. For this reason, MacDonald *et al.* (2009) developed site-specific pore-water toxicity thresholds for several individual COPCs and various COPC mixtures. These pore-water toxicity thresholds were then evaluated to determine their reliability and predictive ability. The results of this evaluation showed that pore-water zinc concentrations (i.e., expressed as pore-water toxic units of zinc, calculated as the measured concentration of zinc in pore water divided by the hardness-adjusted CCC for zinc) explained more than 80% of the variability in the data for 28-d amphipod survival. In addition, the site-specific pore-water toxicity thresholds based on pore-water toxic units of zinc provided a reliable basis for classifying sediment samples as toxic or not toxic to amphipods, midges, and mussels. Therefore, the T_{10} - and T_{20} -values for $PW-TU_{Zinc}$ (0.581 and 0.867) were selected as low risk and high risk toxicity thresholds for pore water, respectively.

Toxicity Thresholds for Invertebrate Tissues - Data on the concentrations of COPCs in invertebrate tissues can provide important information for evaluating effects on benthic invertebrates. Toxicity thresholds for invertebrate tissues were summarized from reviews on the linkages between biological effects and tissue residues (Jarvinen and Ankley 1999; USEPA 2000). While the toxicity tests from the original studies sourced in the databases were rarely designed to determine the critical body residues (CBR), the matching tissue residue and biological effects data can provide relevant information for estimating the concentrations of selected COPCs in invertebrate tissues that are associated with adverse effects on survival, growth and/or reproduction. While this type of data can provide

information for establishing CBRs for invertebrates, it can also lead to incorrect conclusions. For example, many COPCs require 28 days or longer to reach equilibrium in biological tissues (ASTM 2009b). Therefore, data from short-term toxicity tests can under-estimate CBRs in aquatic invertebrates. In addition, compilation of such tissue residue and biological data ignores the mode of toxicity of the COPCs under consideration (e.g., certain COPCs can exert their toxicity at the gills, causing toxicity without achieving equilibrium with the exposure medium). Furthermore, some COPCs preferentially partition into certain tissue types, making whole-body tissue residue levels less relevant than the concentrations in the target tissues. These and other factors make selection of toxicity thresholds for invertebrate tissues challenging and suggest that invertebrate-tissue chemistry should be used as a secondary line-of-evidence in a benthic risk assessment.

Information was compiled from Jarvinen and Ankley (1999) and USEPA (2000) to support the selection of toxicity thresholds for cadmium, copper, lead, mercury and zinc in invertebrate tissues. The compiled information consisted of studies that determined both NOELs and lowest observed effect levels (LOELs) of COPCs for the survival of both freshwater and marine invertebrates, based on whole-body tissue analyses. For each NOEL/LOEL pair, an apparent toxicity threshold was estimated by calculating the geometric mean of these values. Subsequently, the 20th percentile of the distribution of apparent toxicity threshold values was determined for each COPC. This analysis method was chosen to estimate thresholds that would protect approximately 80% of the invertebrate population (Table 21).

The toxicity threshold for cadmium was estimated to be 6.02 mg/kg WW; data from 19 studies were compiled, with NOELs ranging from 0.9 to 310 mg/kg WW and LOELs ranging from 2.4 to 670 mg/kg WW (Table 21). The toxicity threshold for copper was estimated to be 17.6 mg/kg WW. There were eight studies compiled for copper with NOELs ranging from 6.32 to 95.5 mg/kg WW and LOELs ranging from 5 to 107 mg/kg WW (Table 21). The toxicity threshold for lead was estimated from one study in the Jarvinen and Ankley database. The geometric mean of the observed NOEL and LOEL from this study for lead was 84.9 mg/kg WW (Table 21). The toxicity threshold for mercury was estimated to be 13.6 mg/kg WW. Data from two studies on mercury in the Jarvinen and Ankley (1999) database were compiled, with NOELs ranging from 6.00 to

7.57 mg/kg WW and LOELs ranging from 18.4 to 73.1 mg/kg WW (Table 21). The toxicity threshold for zinc was estimated to be 23.8 mg/kg WW; data from nine studies in the Jarvinen and Ankley (1999) database met the selection criteria. The NOELs in the database ranged from 12.7 to 150 mg/kg WW, while the LOELs ranged from 24 to 600 mg/kg WW (Table 21).

Because the toxicity of these metals may be approximately additive, a toxic units approach was used to evaluate invertebrate-tissue chemistry data. More specifically, the results of 28-d toxicity tests with the amphipod, *Hyaella azteca*, were integrated with the results of 28-d bioaccumulation tests with the oligochaete, *Lumbriculus variegatus*. In this analysis, the concentrations of COPCs in oligochaete tissues were not measured directly. While exposure conditions and durations were similar for the two species, it is uncertain if oligochaete-tissue concentrations reflect those in amphipods. Additionally, the oligochaetes tested were not fully depurated prior to chemical analysis. Therefore, toxicity thresholds derived using these data may under-estimate toxicity to benthic invertebrates. Nevertheless, these data were used to calibrate a toxic units model for selected COPCs in invertebrate tissues (Figure 18) using the resultant toxicity thresholds. Toxic units were converted from DW chemistry values using a WW conversion factor of 0.2 (estimated based on median DW:WW ratio reported by Ricciardi and Bourget 1998). Risks to the benthic invertebrate community were considered to be low if $\sum TU_{\text{METALS}} < 6.01$, moderate if $\sum TU_{\text{METALS}} = 6.01$ to 7.45, and high if $\sum TU_{\text{METALS}} > 7.45$ (Figure 15).

Toxicity Thresholds for Laboratory Toxicity Tests - The results of sediment toxicity tests were used directly to evaluate effects on the survival of benthic invertebrates associated with exposure to contaminated sediments. More specifically, the results of 28-day sediment-toxicity tests with the epibenthic amphipod, *Hyaella azteca*, 10-d sediment-toxicity tests with the midge, *Chironomus dilutus*, and 28-d sediment-toxicity tests with the freshwater mussel, *Lampsilis siliquoidea*, were used to evaluate effects on benthic invertebrates associated with exposure to TSMD sediments (ASTM 2009a; 2009c; USEPA 2000b). The survival and biomass of amphipods, midges, and mussels exposed to TSMD sediments were compared with that of animals exposed to reference sediment samples from the study area. Sediment samples were designated as toxic if survival or biomass in TSMD sediments was lower than the lower limit of the normal range for the reference sediments. The normal range of responses of amphipods exposed to reference

sediments was determined by calculating the minimum of the data for each endpoint (i.e., following data transformation to achieve normality). The lower limits of the normal range of responses for survival and biomass of amphipods were 92.3% and 60.0%, respectively (expressed on a control-adjusted basis). For midges, the toxicity thresholds for survival and biomass were 94.7% and 73.8%. The toxicity thresholds for mussel survival and biomass were 95% and 62.7%. Although several other procedures could have been used to designate samples as toxic or not toxic (e.g., ANOVA compared to control, paired T-tests with control results, minimum significant difference from control; Thursby *et al.* 1997), the reference envelope approach was utilized because it provides a means of evaluating incremental toxicity at test sites when compared to reference sites (Hunt *et al.* 2001). In this way, only the toxicity that is attributable to differences in the characteristics of test and reference samples is considered for the purposes of the DERA. That is, the reference envelope approach provides a basis of determining the toxicity that is attributable primarily to COPC-related factors (see Appendix 4 for additional information on the interpretation of toxicity tests results).

Toxicity Thresholds for Mussel Species Richness - Information on the species richness of freshwater mussels was used to evaluate risks to the benthic invertebrate community associated with exposure to COPCs in the TSMD. More specifically, matching sediment chemistry and species richness data were used to estimate toxicity thresholds for sediment that were directly relevant to freshwater mussels (Angelo *et al.* 2007). Evaluation of these data indicate that the number of live mussel taxa (LMT), number of threatened and endangered mussel taxa (TEMT), and total number of mussel taxa (TMT) tend to decrease with increasing concentrations of metals in sediment (< 63 μm in diameter). While there was substantial variability in the underlying data, sediment samples with the lowest metal concentrations (i.e., $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}} < 0.6$; $n = 2$) had the highest LMT (averaging 14.5 taxa/station), TEMT (averaging 5.5 taxa/station), and TMT (averaging 20.0 taxa/station) counts. By comparison, moderate LMT (averaging 7.0 taxa/station), TEMT (averaging 2.8 taxa/station), and TMT (averaging 9.9 taxa/station) counts were observed at the stations with $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 0.6 to 3.0 ($n = 9$). The lowest LMT (averaging 4.2 taxa/station), TEMT (averaging 0.8 taxa/station), and TMT (averaging 6.0 taxa/station) counts were observed at the stations with $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}} > 3.0$ ($n = 5$; Table 22). Accordingly, low risk and high risk toxicity thresholds for freshwater mussels were established at $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 0.6 and 3.0, respectively. It is important to recognize

that the preceding data analysis is preliminary in nature and may not provide the robust basis for estimating toxicity thresholds from the results of these field surveys. Nevertheless, these toxicity thresholds are generally consistent with the PECs established by MacDonald *et al.* (2000a), suggesting that the PECs accurately predicted effects on freshwater mussels in the study area).

The sediment toxicity thresholds that were established using data from field surveys of mussel species richness (i.e., $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 0.6 and 3.0) are substantially lower than the toxicity thresholds that were established using the results of 28-d laboratory toxicity tests with freshwater mussels (i.e., $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 39.7 and 72.6; See MacDonald *et al.* 2009). There are several possible reasons for these differences. First and foremost, the freshwater mussel toxicity tests were conducted under controlled laboratory conditions. Under such conditions, water quality is maintained at levels that are unlikely to adversely affect the survival or growth of the species tested. Under field conditions, water quality can vary substantially. In some cases, such variations can be sufficient to stress aquatic organisms and make them more susceptible to sediment-associated contaminants or other stressors. In addition, exceedances of water quality standards in surface water and/or pore water can adversely affect freshwater mussels utilizing aquatic habitats. Dietary exposure to COPCs can also result in adverse effects on mussels in the field. Furthermore, mussels in the field may consume food with various levels of contaminants whereas the mussels used in laboratory toxicity tests are fed contaminant-free diets. As a result, toxicity thresholds derived from field-collected data can be lower than those developed from the results of laboratory studies. Similar results were reported for field and laboratory studies conducted in the Southeast Missouri Lead Mining District (i.e., Big River; Besser *et al.* 2009). The endpoints measured and durations of exposure in the field and laboratory studies were also different, with the results of field studies integrating effects on multiple life stages and endpoints over extended periods and routes of exposure. Finally, recruitment of freshwater mussels is dependent on the availability of suitable hosts, whose distribution and abundance can also be influenced by water quality and/or sediment quality conditions. The results of laboratory toxicity tests with mussels or other species may under-estimate toxicity thresholds for benthic invertebrates. For these reasons, the results of field studies on freshwater mussels provide an additional perspective for evaluating risks to benthic invertebrates and should be considered during prioritization of areas for further study or source control measures. The results of such

field studies may be important to the Natural Resources Trustees as they work towards definition of restoration goals for aquatic ecosystems in the TSMD.

7.3.6 Characterization of Risks to the Benthic Invertebrate Community

Characterization of risks to the benthic invertebrate community associated with exposure to COPCs in the TSMD consisted of two main steps. First, the nature, severity, and areal extent of risks to the benthic community were evaluated using one or more lines-of-evidence. Next, the substances that are causing or substantially contributing to effects on the benthic community were identified (i.e., contaminants of concern; COCs). The methods that were used in each of these steps of the process are described in the following sections.

Evaluation of the Nature, Severity and Areal Extent of Risks - In this assessment, six measurement endpoints were used to evaluate the risks posed to the benthic invertebrate community by exposure to COPCs in the TSMD. These lines-of-evidence included surface-water chemistry, sediment chemistry, sediment toxicity, pore-water chemistry, invertebrate-tissue chemistry, and freshwater mussel species richness. More specifically, the results of sediment toxicity tests and field surveys of freshwater mussel distribution were used to evaluate the nature of the risks to benthic invertebrates. All six lines-of-evidence were used to evaluate the severity of effects (i.e., as indicated by the incidence of observed and/or predicted effects) on benthic invertebrates. By comparison, sediment chemistry data (i.e., $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$, which was used to estimate the predicted magnitude of toxicity to freshwater amphipods) were used primarily to evaluate the areal extent of risks to benthic invertebrate communities. For all six lines-of-evidence, the available data were evaluated on a sample-by-sample basis and the sample-specific results were summed to provide information on risks within each AoI.

To facilitate characterization of the magnitude and areal extent of risks to the benthic macroinvertebrate community, risks were classified into three categories, for each sample and AoI. More specifically, risks to benthic invertebrates were characterized as low, moderate, or high, based on the observed and predicted incidence or magnitude of sediment toxicity, as follows:

Low Risks - Risks to benthic invertebrates were classified as low if the effects that were observed or predicted to occur within a sample or an AoI were similar to those for selected reference samples. Such effects were considered to be negligible relative to the maintenance of the structure and/or function of the benthic invertebrate community within a reach or an area of concern. Nevertheless, conditions that require attention may exist within portions of an AoI that were classified as having low risks to the benthic invertebrate community. Low risks were indicated by:

- For surface-water chemistry, low risks to the benthic invertebrate community were indicated by $\sum \text{SW-TU}_{\text{DIVALENT METALS}} < 1.03$;
- For sediment toxicity, low risks to the benthic invertebrate community were indicated by the following control-adjusted results:

<i>Species Tested</i>	<i>Endpoint</i>	<i>Duration</i>	<i>Low Risk</i>
<i>H. azteca</i>	Survival	28-days	$\geq 92.3 \%$
<i>H. azteca</i>	Biomass	28-days	$\geq 60.0 \%$
<i>C. dilutus</i>	Survival	10-days	$\geq 94.7 \%$
<i>C. dilutus</i>	Biomass	10-days	$\geq 73.8 \%$
<i>L. siliquoidea</i>	Survival	28-days	$\geq 95.0 \%$
<i>L. siliquoidea</i>	Biomass	28-days	$\geq 62.7 \%$

- For sediment chemistry, low risks to the benthic invertebrate community were indicated by $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of < 6.47 ;
- For pore-water chemistry, low risks to the benthic invertebrate community were indicated by PW-TU_{Zn} of < 0.581 ;
- For invertebrate-tissue (IT) chemistry, low risks to the benthic invertebrate community were indicated by $\sum \text{IT-TU}_{\text{METALS}} < 6.01$; and,
- For freshwater mussel species richness, low risks to the benthic invertebrate community were indicated by mean $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of < 0.6 .

Moderate Risks - Risks to benthic invertebrates were classified as moderate if the effects that were observed or predicted to occur within a sample or an AoI were moderately higher in frequency and/or magnitude than those for selected reference areas. Such effects were considered to be of concern relative to the maintenance of the structure

and/or function of the benthic invertebrate community within an AoI. Although such risks are nontrivial, decisions regarding remediation at individual locations should consider the costs and ecological effects of remedial actions, the potential for natural recovery, and other relevant factors (such as the presence of viable benthic communities). It is important to note that low or high risks to the benthic invertebrate community could exist within portions of an AoI that was classified as posing moderate risks. Moderate risks are indicated by:

- For surface-water chemistry, moderate risks to the benthic invertebrate community were indicated by $\sum\text{SW-TU}_{\text{Divalent Metals}}$ of 1.03 to 1.41;
- For sediment toxicity, moderate risks to the benthic invertebrate community were indicated by the following control-adjusted results:

<i>Species Tested</i>	<i>Endpoint</i>	<i>Duration</i>	<i>Low Risk</i>
<i>H. azteca</i>	Survival	28-days	83.1 to < 92.3 %
<i>H. azteca</i>	Biomass	28-days	54.0 to < 60.0 %
<i>C. dilutus</i>	Survival	10-days	85.2 to < 94.7 %
<i>C. dilutus</i>	Biomass	10-days	66.4 to < 73.8 %
<i>L. siliquoidea</i>	Survival	28-days	85.5 to < 95.0 %
<i>L. siliquoidea</i>	Biomass	28-days	56.4 to < 62.7 %

- For sediment chemistry, moderate risks to the benthic invertebrate community were indicated by $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 6.47 to 10.04;
- For pore-water chemistry, moderate risks to the benthic invertebrate community were indicated by PW-TU_{Zn} of 0.581 to 0.867;
- For invertebrate-tissue chemistry, moderate risks to the benthic invertebrate community were indicated by $\sum\text{IT-TU}_{\text{Metals}}$ 6.01 to 7.45; and,
- For freshwater mussel species richness, moderate risks to the benthic invertebrate community were indicated by $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 0.6 to 3.0.

High Risks - Risks to benthic invertebrates were classified as high if the effects that were observed or predicted to occur within a sample or an AoI were substantially higher than those for selected reference areas. Such effects were considered to be the highest concern relative to the maintenance of the structure and/or function of the benthic invertebrate

community within an AoI. AoIs so designated represent the highest priority areas for source control measures in the near term and for remedial action planning in the longer term. It is important to note that low or moderate risks to the benthic invertebrate community could exist within portions of an AoI that were classified as posing high risks. Therefore, any source control measures or remedial actions that are contemplated within such AoIs should consider the severity and areal extent of the observed and predicted effects. High risks are indicated by:

- For surface-water chemistry, high risks to the benthic invertebrate community were indicated by $\sum \text{SW-TU}_{\text{DIVALENT METALS}}$ of > 1.41 ;
- For sediment toxicity, high risks to the benthic invertebrate community were indicated by the following control-adjusted results:

<i>Species Tested</i>	<i>Endpoint</i>	<i>Duration</i>	<i>Low Risk</i>
<i>H. azteca</i>	Survival	28-days	< 83.1 %
<i>H. azteca</i>	Biomass	28-days	< 54.0 %
<i>C. dilutus</i>	Survival	10-days	< 85.2 %
<i>C. dilutus</i>	Biomass	10-days	< 66.4 %
<i>L. siliquoidea</i>	Survival	28-days	< 85.5 %
<i>L. siliquoidea</i>	Biomass	28-days	< 56.4 %

- For sediment chemistry, high risks to the benthic invertebrate community were indicated by $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of > 10.04 ;
- For pore-water chemistry, high risks to the benthic invertebrate community were indicated by PW-TU_{Zn} of > 0.867 ;
- For invertebrate-tissue chemistry, high risks to the benthic invertebrate community were indicated by $\sum \text{IT-TU}_{\text{METALS}} > 7.45$; and,
- For freshwater mussel species richness, high risks to the benthic invertebrate community were indicated by $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of > 3.0 .

Identification of Contaminants of Concern - The COCs in the TSMD (i.e., primary risk drivers) were identified using a step-wise approach. In the first step of this process, the 95th percentile concentrations of COPCs in surface water, sediment, or pore water in each AoI were compared to the 95th percentile concentrations of COPCs in surface water,

sediment, or pore water from the reference areas (i.e., the upper limit of background levels; Tables 14 to 16). The substances that occurred in the TSMD at concentrations that were a factor of two or greater than the upper limit of background concentrations in the reference areas were retained as preliminary COCs in surface water, sediment, or pore water. Substances were also retained for further assessment if the 95th percentile concentration could not be calculated for the reference area or if the 95th percentile concentration could not be calculated for an AoI. In both cases, the substance was designated as an uncertain COC. The substances that were designated as preliminary or uncertain COCs were considered to pose potential incremental risks to the benthic invertebrate community.

In the second step of the process, the estimates of the upper limit of the concentrations of preliminary COCs in surface water (Tables 23 to 25), sediment (Tables 26 to 28), or pore water (Tables 29 to 31; i.e., 95th percentile concentrations) in each AoI of the study area were compared to both the 95th percentile concentration in the reference area and to the corresponding chemical benchmark (Table 4 for sediment, Table 3 for surface water and pore water). More specifically, the concentrations of preliminary COCs in sediments were compared to the sediment chemistry benchmarks (Tables 26 to 28), while the concentrations of preliminary COCs in surface water or pore water were compared to the chronic toxicity thresholds summarized in (Table 23 to 25; 29 to 31). Substances for which the 95th percentile concentration in surface-water, sediment, or pore-water samples, exceeded both the 95th percentile concentration in the reference area by a factor of two or more and exceeded the selected benchmark, were retained as COCs relative to the benthic invertebrate community (i.e., the substances for which hazard quotients of > 1.0 were calculated, where $HQ = \text{concentration} \div \text{benchmark}$). A substance was designated as an uncertain COC if there was no benchmark available for the substance or if the 95th percentile concentration could not be determined for either the reference area, or for the AoI (i.e., due to high detection limits or lack of analytical data). The COC's for surface water, pore water, and sediment for each sub-basin are shown in Tables 33 to 35, respectively.

Evaluation of Risks to Benthic Invertebrates using Multiple Lines-of-Evidence - In this assessment, data from chemical analyses, toxicity tests, and biological surveys were used to characterize risks to benthic invertebrates associated with exposure to COCs in

the TSMD. More specifically, the data on six lines-of-evidence were used to estimate risks to benthic invertebrates exposed to surface water, sediment, and/or pore water in the study area. However, four or more lines-of-evidence were available for only a small proportion of the sampling locations in the study area. Three or more lines-of-evidence were available for a total of 76 sampling locations. By comparison, sediment chemistry data were compiled for a total of 1162 locations in the study area. For this reason, the risk designations for more than 90% of the sampling locations were assigned using a single line-of-evidence (i.e., typically sediment chemistry). For this reason, a weight-of-evidence evaluation was not conducted to evaluate risks to benthic invertebrates exposed to COPCs in the TSMD. Rather, an evaluation was conducted to assess concordance between risk designations that were made using sediment chemistry data only and those made using other lines-of-evidence. The results of this evaluation provide a basis for determining the level of confidence that can be placed in risk designations made using sediment chemistry data alone.

The evaluation of the reliability of the risk designation procedures were evaluated in two ways. First, all of the sampling locations for which sediment chemistry and sediment toxicity data were available were identified. For all of these sampling stations, the risk designations that were assigned for each line-of-evidence were compiled and reviewed to determine the degree of concordance between sediment chemistry and the other lines-of-evidence. Frequent concordance between the abiotic measures of risk and the biological indicators of risk was considered to increase the confidence that can be placed in the results of the DERA. Next, sediment samples were sorted into three categories based on the risk designations (i.e., low, moderate, and high risks that were assigned using the various lines-of-evidence; sediment chemistry, pore-water chemistry). Then, the average response rates (\pm standard deviation) for each toxicity test endpoint were calculated for each risk category. Consistent and marked increases in the magnitude of response across risk categories was considered to increase the confidence that can be placed in the results of the DERA. Together, these two evaluations provide useful information for evaluating uncertainty in the results of the DERA.

Chapter 8 Detailed Assessment of Risks to the Benthic Invertebrate Community

8.0 Introduction

The assessment of the risks to the benthic invertebrate community posed by exposure to the COPCs in the TSMD involved several steps. In the first step of the process, the assessment endpoints, risk questions and testable hypotheses, and measurement endpoints were identified (i.e., in the problem formulation; See Chapter 6). Next, the relevant information on sediment quality conditions in the study area were collected, evaluated, and compiled. Subsequently, the chemical benchmarks for assessing sediment quality conditions were selected, including toxicity thresholds for sediment and for pore water. Finally, the risks to the benthic invertebrate community associated with exposure to sediment and to pore-water samples from the TSMD were assessed. The results of these evaluations are presented in the following sections of this report.

8.1 Assessment Endpoints

Benthic invertebrates are the animals that live in and on the sediments in freshwater ecosystems. The groups of organisms that are commonly associated with benthic communities include protozoa, sponges (i.e., Porifera), coelenterates (such as *Hydra* sp.), flatworms (i.e., Platyhelminthes), bryozoans, aquatic worms (i.e., oligochaetes), crustaceans (such as ostracods, isopods, and amphipods), mollusks (such as freshwater mussels and clams), and aquatic insects (such as dragonflies, mayflies, stoneflies, true flies, caddisflies, and aquatic beetles). Because benthic invertebrate communities are difficult to study in a comprehensive manner, benthic ecologists often focus on the relatively large members of benthic invertebrate communities, which are known as benthic macroinvertebrates. These organisms are usually operationally defined, for example, as those that are retained on a 0.5 mm sieve.

Benthic invertebrates represent key elements of aquatic food webs because they consume aquatic plants (such as algae and aquatic macrophytes) and detritus. In this way, these organisms facilitate energy transfer to fish, birds, and other organisms that consume aquatic invertebrates. As the goal of this assessment is to determine if exposure to contaminated surface water, sediment, and/or pore water, are likely to adversely affect the key functions that are provided by the benthic invertebrate community, the survival, growth, and reproduction of benthic invertebrates was identified as the assessment endpoint for the DERA.

8.2 Risk Questions and Testable Hypotheses

To provide a valid basis for assessing ecological effects, the assessment endpoint needs to be linked to the measurement endpoints by a series of risk questions and/or testable hypotheses. In this study, the investigations to assess the effects of environmental contaminants on the benthic invertebrate community were designed to answer the following risk questions:

- Are the concentrations of COPCs in surface-water from the TSMD greater than the toxicity thresholds for benthic invertebrates?
- Are the concentrations of COPCs in sediment samples from the TSMD greater than the toxicity thresholds for benthic invertebrates?
- Are the concentrations of COPCs in pore-water samples from the TSMD greater than the toxicity thresholds for benthic invertebrates?
- Are the concentrations of COPCs in the tissues of benthic invertebrates exposed to TSMD sediments greater than the toxicity thresholds for benthic invertebrates?
- Is the survival or biomass of benthic invertebrates exposed to sediments from the TSMD significantly lower than that for benthic invertebrates exposed to reference sediments?
- Are the concentrations of COPCs in sediment greater than the toxicity thresholds for freshwater mussels (i.e., based on taxa richness, evaluated in field surveys)?

8.3 Measurement Endpoints

The benthic invertebrate community represents an essential component of aquatic food webs, providing an important source of food for many species of fish, birds, and mammals. As such, it is important to evaluate the effects of environmental contaminants on this group of ecological receptors. Benthic invertebrates can be exposed to environmental contaminants through direct contact with contaminated surface water, through contact with sediments, and through contact with contaminated pore water. For this reason, it is important to evaluate the effects of exposure to surface water, sediment, and pore water on the survival, growth, and reproduction of benthic invertebrates. In this way, it is possible to determine if exposure to surface water, sediment, and/or pore water is likely to adversely affect the key ecosystem functions that are provided by the invertebrate community. A suite of measurement endpoints was selected to provide the information needed to determine if the benthic invertebrate community is being or is likely to be adversely affected due to exposure to COCs, including:

- Surface-water chemistry data (i.e., concentrations of divalent metals in surface water; Figures 10 and 11);
- Sediment chemistry data (i.e., the concentrations of cadmium, lead, and zinc in surficial sediments; Figures 12 and 13);
- Pore-water chemistry data (i.e., the concentrations of zinc in pore water; Figures 13 and 14);
- Invertebrate-tissue chemistry data (i.e., the concentrations of cadmium, copper, lead, mercury, and zinc in invertebrate tissues; Figure 19);
- Sediment toxicity data [i.e., the results of toxicity tests with amphipods, *Hyaella azteca* (Endpoints: survival and biomass), midges, *Chironomus dilutus* (Endpoints: survival and biomass), and freshwater mussels, *Lampsilis siliquoidea* (Endpoints: survival and biomass); Figure 20]; and,
- Species richness of freshwater mussels (i.e., as evaluated using data on the concentrations of COPCs in sediment samples from the TSMD; Figure 21).

8.4 Exposure of the Benthic Invertebrate Community to Chemicals of Potential Concern

Exposure is the contact or co-occurrence of a contaminant and a receptor (Suter *et al.* 2000). The exposure assessment is intended to provide an estimate of the magnitude of exposure of receptors to COPCs, over time and space. Both current exposure and potential future exposure need to be evaluated during the exposure analysis. For the benthic invertebrate community, contaminated surface water, sediment, and pore water were considered to be the principal routes of exposure requiring analysis. Invertebrate-tissue chemistry data integrate the exposures from all three of the exposure routes and provide additional information for evaluating total exposure to COPCs. The data that were collected between 2002 and 2009 were considered to be equivalent and were used to assess both current and near-term future exposure to COPCs. Summaries of the available data on the concentrations of COPCs in surface water (Tables 5 and 6), sediment (Tables 7 and 8), pore water (Tables 9 and 10), and invertebrate tissue (Table 36) were prepared to provide an overview of the distributions of these data. However, actual exposure of benthic invertebrates to site-related COPCs was evaluated on a station-by-station basis.

8.5 Effects of Chemicals of Potential Concern on Benthic Invertebrates

In the analysis of effects, risk assessors determine the nature of toxic effects that are associated with exposure to contaminants and their magnitude as a function of exposure (Suter *et al.* 2000). Information on the effects of environmental contaminants may be acquired from the results of single chemical toxicity tests (e.g., spiked sediment toxicity tests), ambient media toxicity tests (e.g., the results of toxicity tests conducted using sediments collected from the site under investigation), and/or biological surveys (e.g., benthic invertebrate community assessments). Importantly, the data that are collected during this phase of the assessment should be directly related to the exposure estimates (e.g., if the exposure estimates are based on dry weight concentrations of COPCs, the effects data should

describe the responses of receptors to changing dry weight concentrations of that COPC), thereby facilitating characterization of risks to each assessment endpoint.

In this assessment, exposure of the benthic invertebrate community to COPCs was evaluated using information on the concentrations of contaminants in surface water, sediment, pore water, and invertebrate tissues. As such, it was necessary to compile information on the effects on benthic invertebrate communities associated with exposure to COPCs in these environmental media. The TSVs compiled to support the SLERA provide conservative toxicity thresholds for all of the COPCs that were identified (see Chapter 3 for further information). While these TSVs are directly relevant for conducting the SLERA, their use has the potential to over-estimate toxicity to benthic invertebrates. For this reason, MacDonald *et al.* (2009) evaluated the matching chemistry and toxicity data that have been generated for the TSMD to support the derivation of SSTTs for sediment and pore water. More specifically, the SSTTs in pore water were selected for evaluating surface-water chemistry (i.e., $\sum \text{SW-TU}_{\text{DIVALENT METALS}}$) and the pore-water chemistry data (i.e., $\sum \text{PW-TU}_{\text{Zn}}$). Similarly, the SSTTs for sediment were selected for evaluating the sediment chemistry data for the TSMD (i.e., $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$). Toxicity thresholds for invertebrate tissues were selected from the database of CBRs that were compiled by Jarvinen and Ankley (1999). The toxicity thresholds that were selected for use in the DERA are presented in Section 7.3.5 of this document.

8.6 Characterization of Risks to Benthic Invertebrates

The purpose of risk characterization is to determine if significant effects are occurring or are likely to occur at the site under investigation. In addition, this step of the process is intended to provide the information needed to describe the nature, magnitude, and areal extent of effects on the selected assessment endpoints. Finally, the substances that are causing or substantially contributing to such effects (termed COCs) are identified from the COPCs. This information is generated by integrating the results of the exposure assessment with the results of the effects assessment for each line-of-evidence that was considered. An evaluation of the uncertainty in the analysis provides a basis for determining the level of confidence that can be placed on these results. In this assessment, a total of six lines-of-evidence were examined to

determine if environmental conditions in the TSMD pose significant risks to the benthic invertebrate community. Four of these data types were considered to provide primary lines-of-evidence for assessing benthic risk, including: surface-water chemistry, sediment chemistry, pore-water chemistry, and sediment toxicity. By comparison, invertebrate-tissue chemistry and freshwater mussel species richness were considered to provide secondary lines-of-evidence due to the higher level of uncertainty associated with these data.

Evaluation of the available primary data on the condition of aquatic habitats indicated that the survival, growth, and/or reproduction of benthic invertebrates are likely being adversely affected within the TSMD. First, the concentrations of divalent metals (expressed as $\sum SW-TU_{\text{DIVALENT METALS}}$) exceeded the SSTT of 1.03 in 50% (268 of 537) of the surface-water samples collected from the study area (compared with 6% for reference surface-water samples; n = 18; Table 37). Second, comparison of the concentrations of sediment-associated cadmium, lead, and zinc (expressed as $\sum PEC-Q_{\text{Cd,Pb,Zn}}$) to the SSTT of 6.47 indicated that toxicity to amphipods is predicted to occur for 49% (566 of 1162) of the sediment samples included in the project database (compared with 0% for reference sediment samples; n = 10; Table 38). Similarly, 30% (29 of 96) of pore-water samples had concentrations of zinc sufficient to be toxic to amphipods in 28-d toxicity tests (compared with 0% of reference sediment samples; n = 8; Table 39). By comparison, 29% of the sediment samples (22 of 76 samples) collected from the study area were found to be toxic to amphipods (endpoint: survival or biomass, compared with 0% for reference sediment samples; n = 10; Table 40). A higher incidence of toxicity was observed for both midges (50%; 35 of 70 samples) and mussels (33%; 16 of 48 samples), when the survival or biomass endpoints were considered [compared with 0% for reference sediment samples for midges (n = 8) and 0% for reference samples for mussels (n = 5; Table 40)]. The concentrations of zinc or divalent metals in pore water explained over 80% of the variability in the amphipod survival data, indicating that other COPCs, hydrogen sulfide, and/or ammonia likely do not represent primary risk drivers in TSMD sediments (Table 19).

Invertebrate-tissue chemistry and mussel taxa abundance provide secondary lines-of-evidence for characterizing risks to benthic invertebrates in the TSMD. Evaluation of the available invertebrate-tissue chemistry data indicated that metals are biologically available in TSMD sediments and that cadmium, copper, lead, mercury, and/or zinc can accumulate to levels that are toxic to sediment-dwelling organisms (Table 41). Finally, Angelo *et al.* (2007) reported

that live mussels were absent at 26% (5 of 19) of the stream reaches surveyed, while live threatened or endangered species or species in need of conservation were absent at 42% (8 of 19) stream reaches. The field- and laboratory-derived toxicity thresholds for invertebrate-tissue chemistry were exceeded in 92% (1064 of 1162) and 15% (169 of 1162), respectively, of the sediment samples from the TSMD (Tables 42 and 43). Therefore, both of these secondary lines-of-evidence further support the conclusion that benthic invertebrates in the TSMD are being adversely affected by exposure to contaminants. Collectively, the four primary lines-of-evidence confirm that exposure to contaminated surface water and/or sediments is adversely affecting the survival, growth, and/or reproduction of benthic invertebrates in the TSMD.

8.6.1 Upper and Middle Spring River Sub-Basin

The Upper and Middle Spring River Sub-Basin (UMSR) encompasses the northern portion of the Spring River watershed from the headwater areas to the inlet of Empire Lake. This portion of the watershed has been divided into eight AoIs, including the North Fork Spring River, Upper Spring River, Center Creek, Cow Creek, Middle Spring River, Turkey Creek, Short Creek, and Shawnee Creek AoIs (Figure 4). The risks to the benthic invertebrate community posed by exposure to contaminated surface water, sediment, and pore water were evaluated for each of these AoIs. Additionally, hotspots with respect to contaminated surface water, sediment, and/or pore water were identified whenever possible.

8.6.1.1 Nature of Effects on the Benthic Invertebrate Community in the Upper and Middle Spring River Sub-Basin

In total, data on six lines-of-evidence were used to determine if adverse effects on the benthic invertebrate community were occurring in the UMSR in response to exposure to COPCs, including surface-water chemistry, sediment chemistry, pore-water chemistry, sediment toxicity, invertebrate-tissue chemistry, and mussel species richness. These data also provided a basis for assessing the nature of the effects that are occurring or are likely to be occurring to benthic invertebrate communities. Both the presence of conditions sufficient to cause or substantially contribute to effects (i.e., predicted incidence of toxicity) and occurrence of

specific types of effects (i.e., observed incidence of toxicity) were used to determine if effects are occurring within the study area and to determine the nature of those effects.

Surface-water chemistry data were used to determine if conditions sufficient to adversely affect benthic invertebrates have occurred within the UMSR. More specifically, the available data on the concentrations of divalent metals in surface water were evaluated using sample-specific, hardness-adjusted final chronic values (i.e., CCCs; i.e., by calculating $\sum SW-TU_{\text{DIVALENT METALS}}$). The results of this evaluation indicated that 45% (48 of 106) surface-water samples had concentrations of divalent metals sufficient to adversely affect the survival of amphipods (Table 37). Evaluation of the matching chemistry and toxicity data from the study area indicated that adverse effects on midges and mussels, including reduced survival and biomass, could also be expected with prolonged exposure (i.e., 10 to 28 days) to surface water with these chemical characteristics (Table 44). Therefore, these data demonstrated that surface-water quality conditions were sufficient to reduce the survival and biomass of sediment-dwelling organisms in portions of the UMSR.

When considered in conjunction with numerical SQGs, sediment-chemistry data provided a basis for evaluating the effects of contaminated sediments on benthic invertebrates. The sediment-chemistry data compiled for the period 2002 to 2009 were evaluated using SSTTs for sediment that were developed using the matching sediment chemistry and amphipod survival data. The results of this evaluation indicated that roughly 40% (156 of 394; Table 38) of the sediment samples from the UMSR had concentrations of cadmium, lead, and zinc (expressed as $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}}$) that were sufficient to cause or substantially contribute to toxicity to freshwater amphipods (i.e., reduced survival and biomass). Evaluation of the matching chemistry and toxicity data from the study area indicated that adverse effects on midges and mussels, including reduced survival and biomass, could also be expected with prolonged exposure (i.e., 10 to 28 days) to sediments with these chemical characteristics (Table 45). As amphipod reproduction is strongly correlated with amphipod growth (Swartz *et al.* 1994; USEPA 2000a), it is likely that the reproduction of benthic invertebrates would also be impaired when exposed to contaminated sediments from the UMSR (i.e., $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}} > 10.04$). Therefore, these data demonstrated that sediment quality conditions in portions of the UMSR were sufficient to reduce the survival and biomass of sediment-dwelling organisms.

The pore-water chemistry data for the UMSR were compared to the SSTTs for pore water that were developed for the TSMD (i.e., \sum PW-TU_{Zn}). The results of this evaluation indicated that the selected toxicity threshold (0.581) was exceeded in 38% (20 of 53) of pore-water samples from the UMSR (Table 39). Pore-water samples with these characteristics had reduced survival of amphipods (Table 46). At PW-TU_{Zn} > 0.867, the survival and biomass of all three species was substantially reduced. About 32% (17 of 53) of the pore-water samples from the UMSR had PW-TU_{Zn} greater than the high risk threshold (0.867; Table 39). Therefore, these data demonstrated that pore-water quality conditions in portions of the UMSR were sufficient to reduce the survival and biomass of sediment-dwelling organisms.

Based on the results of acute and chronic toxicity tests, it is apparent that sediments from in the UMSR were adversely affecting the survival and/or biomass of benthic invertebrates. Of the 39 sediment samples that were collected from the UMSR, a total of 20 (51%) were found to be acutely toxic to midges (i.e., survival and/or biomass was reduced relative to the lower limit of responses for samples from reference areas; Table 40; Figures 22 and 23). By comparison, 13 of the 45 sediment samples (29%) from the UMSR were found to be toxic to freshwater amphipods in 28-d toxicity tests (Table 40; Figures 24 and 25). Similarly, toxicity to freshwater mussels was observed in 36% (12 of 33) of sediment samples from the UMSR (Figures 26 and 27). Because reductions in the survival and/or growth of amphipods has been linked to impaired reproductive success (Swartz *et al.* 1994; USEPA 2000a), it is likely that reproduction of sediment-dwelling species would also be impaired in response to exposure to high risk sediments from the UMSR. These data demonstrated that sediment quality conditions in portions of the UMSR were sufficient to adversely affect the survival and/or biomass of benthic invertebrates.

Invertebrate-tissue chemistry data were also evaluated to determine if sediment quality conditions in the UMSR were sufficient to adversely affect sediment-dwelling organisms. The results of this evaluation indicated that 23% (45 of 195) of invertebrate-tissue samples had concentrations of cadmium, copper, lead, mercury, and/or zinc sufficient to adversely affect the survival, growth, or physiology of benthic invertebrates (Table 41; Jarvinen and Ankley 1999). As embryonic development can be adversely affected at lower tissue residue levels than is the case for survival (Salazar 2006), it is likely that reproduction would be impaired in benthic invertebrates that accumulated these metals to levels in exceedance of the selected toxicity thresholds (i.e., \sum TUs > 6.01; Figure 18). Evaluation of matching invertebrate-tissue

chemistry and sediment toxicity data from the study area indicates that adverse effects on amphipods, midges, and mussels, including survival and/or biomass, can be expected when benthic invertebrates accumulate metals in their tissues beyond the selected toxicity thresholds (Table 47). Therefore, it is likely that body residues of metals were sufficient to adversely affect the survival, growth, and/or biomass of benthic invertebrates in portions of the UMSR.

Species richness of freshwater mussels was evaluated at 10 locations in the UMSR (Angelo *et al.* 2007). The results of these field surveys showed that live mussel taxa were observed at 90% (9 of 10) of these locations, with the number of live mussel taxa ranging from 0 to 18 overall. Threatened or endangered mussel species or mussel species in need of conservation were absent at 30% of these locations. This portion of the study area supported the highest densities of clams and mussels (Angelo *et al.* 2007). Adverse effects on mussel species richness and density in the UMSR were limited to the areas located downstream of major disturbance activities (i.e., mining, municipal development; Angelo *et al.* 2007). Evaluation of matching mussel species richness and sediment chemistry data from the study area indicates that the number of live mussel taxa, live mussel taxa classified as threatened endangered, or of special concern, and total mussel taxa can be expected to be reduced when the concentrations of metals in sediment exceed the toxicity thresholds of 0.6 or 3.0 for \sum PEC- $Q_{Cd,Pb,Zn}$ (Table 22).

When considered together, the six lines-of-evidence examined indicated that contaminated sediments in the UMSR posed risks to the benthic invertebrate community. More specifically, it is likely that the survival, biomass, and reproduction of benthic invertebrates are being adversely affected by exposure to contaminated sediments in portions of the UMSR. Therefore, it is concluded that significant effects on the benthic invertebrate community are occurring in portions of the UMSR (i.e., primarily in Short Creek, Turkey Creek, Center Creek, and the Middle Spring River AoIs).

8.6.1.2 Magnitude of Effects on the Benthic Invertebrate Community in the Upper and Middle Spring River Sub-Basin

The magnitude of the effects on benthic invertebrates exposed to contaminated sediments was evaluated using two lines-of-evidence, including sediment toxicity and sediment chemistry. Based on the results of three toxicity tests, it is apparent that exposure to sediment samples

from the UMSR is associated with a range of responses in sediment-dwelling organisms. Of the 45 sediment samples that were collected from the UMSR, a total of 32 (71%) were found to pose a low risk to amphipods based on the results of 28-d toxicity tests (i.e., survival of *H. azteca* was similar to those observed for samples from reference areas; Table 48). Similar results were observed for amphipod biomass (Table 49). By comparison, moderate (i.e., up to 10% reduction in survival) or high (i.e., > 10% reduction in survival) risks to amphipods was observed in two (4%) and 11 (24%) of the samples from the UMSR, respectively (Table 48; Figures 28 and 29). For midges, 29 of 39 sediment samples (74%) from the UMSR had survival rates that were consistent within those observed for reference sediment samples (i.e., low risk; Table 50; Figures 30 and 31). By comparison, 6 (15%) of the sediment samples posed moderate risks and 4 (10%) posed high risks to the benthic invertebrate community, based on midge survival. Higher risks to midges were indicated by the biomass endpoint (Table 51). Using survival of mussels in 28-d toxicity tests, 21 of the 33 samples (64%) were classified as posing low risk, 7 of the 33 samples (21%) were classified as posing moderate risk, and 5 of the 33 samples (15%) were classified as posing high risk to benthic invertebrate communities (Table 52; Figures 32 and 33). Lower risks to mussels were indicated by the biomass endpoint (Table 53). Overall, the available sediment toxicity data indicated that the magnitude of toxicity to benthic invertebrates ranged from low to high within the UMSR.

The magnitude of toxicity to benthic invertebrate communities was also evaluated using the sediment chemistry data that were compiled for the period 2002 to 2009. More specifically, the predicted magnitude of toxicity was determined for each sediment sample using a site-specific concentration-response model (i.e., $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}}$) for amphipod survival (samples were classified as low risk if $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}} < 6.47$, moderate risk if $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}}$ was 6.47 to 10.04, and high risk if $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}} > 10.04$). A total of 238 of 394 sediment samples (60%) were classified as posing low risk to the benthic invertebrate community (Table 38). By comparison, 34 of the 394 sediment samples (9%) had concentrations of cadmium, lead, and zinc sufficient to pose moderate risks to benthic invertebrates. The high risk designation was assigned to 122 of the 394 sediment samples (31%) from the UMSR (Table 38). Therefore, the predicted magnitude of toxicity is low for the majority of the sediment samples from the UMSR. Nevertheless, risks to the benthic community in the UMSR were rated as high because the predicted frequency of toxicity exceeded that in reference sediment samples by more than 20%.

Overall, the information on the observed and predicted magnitude of toxicity to freshwater amphipods indicated that exposure to sediments from the UMSR generally posed low risks to the benthic invertebrate community (Table 37 to 46; 48 to 53). Nevertheless, the concentrations of COPCs were sufficient to cause or substantially contribute to sediment toxicity in 40% of the sediment samples (i.e., 156 of 394) collected from this portion of the Spring River watershed. Importantly, the survival of amphipods, midges, or mussels was reduced relative to the lower limit for reference samples in 58% (26 of 45) of the sediment samples tested (Figure 34; Table 40). These results demonstrated that this portion of the watershed had a number of hot spots with respect to sediment contamination and/or toxicity that may benefit from source control measures and/or other risk management actions.

8.6.1.3 Areal Extent of Effects on the Benthic Invertebrate Community in the Upper and Middle Spring River Sub-Basin

The areal extent of adverse effects on benthic invertebrate communities in the UMSR was assessed using the sediment chemistry data that were compiled for the period 2002 to 2009. To support this evaluation of the spatial distribution of chemical contamination, the $\sum\text{PEC}-Q_{\text{Cd,Pb,Zn}}$ was calculated for each of the sediment samples ($n = 394$) that were collected from the UMSR. Subsequently, each sediment sample was classified into one of three categories (i.e., low, moderate, or high), based on the risk that it posed to amphipod survival (i.e., samples were classified as low, moderate, or high risk if $\sum\text{PEC}-Q_{\text{Cd,Pb,Zn}} < 6.47$, 6.47 to 10.04 , and > 10.04 , respectively). Then, these data were compiled on an AoI by AoI basis and mapped using ArcMap/Spatial Analyst software (Figures 35 to 42). The AoIs that were considered in this analysis included the North Fork Spring River, Upper Spring River, Center Creek, Cow Creek, Middle Spring River, Turkey Creek, Short Creek, and Shawnee Creek AoIs.

North Fork Spring River AoI - Sediment chemistry data were available for a total of 27 samples from the North Fork Spring River AoI. The geometric mean of the $\sum\text{PEC}-Q_{\text{Cd,Pb,Zn}}$ for these samples was 0.54, suggesting that, on average, sediment-associated contaminants posed relatively low risks to sediment-dwelling organisms in this reach of the study area (Table 38). Importantly, $\sum\text{PEC}-Q_{\text{Cd,Pb,Zn}}$ sufficient to pose moderate or high risks to the benthic community were not observed in sediment samples from this AoI (Table 38). The results of sediment toxicity tests confirmed that 0% ($n = 2$ to 5) of

sediment samples from this AoI were toxic to the selected indicator species of benthic invertebrates (Table 40).

Upper Spring River AoI - For the Upper Spring River AoI, sediment chemistry data were available for a total of 18 sediment samples. The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ for these samples was 1.07 (Table 38), suggesting that sediment-associated contaminants generally pose relatively low risks to sediment-dwelling organisms in this portion of the watershed. Only one of the sediment samples collected from this AoI had $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ sufficient to adversely affect the survival of freshwater amphipods (Table 38). The results of sediment toxicity tests confirm that sediment samples from this AoI were not toxic to amphipods (Table 40). While some toxicity to midges was observed in this AoI, the concentrations of metals in sediment or pore water were not sufficient to explain this toxicity.

Center Creek AoI - Based on the results of chemical analysis of 81 sediment samples, it was apparent that, on average, sediment-associated contaminants posed a low risk to benthic invertebrates in the Center Creek AoI. A geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 5.39 was calculated for the AoI (Table 38). Application of the concentration-response relationship for amphipod survival to the sediment chemistry data suggested that 37 of the 81 samples (46%) collected in this AoI posed moderate or high risks to benthic invertebrates (Table 38). The samples with elevated $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ were generally collected within the lower 20 km of the creek (Figure 39). Samples with elevated levels of zinc in pore water were also collected from this portion of Center Creek (Figure 43). Thirty-six percent of the samples (4 of 11) tested from Center Creek were found to be toxic to amphipods. The incidence of toxicity was higher for midges (44%; n = 9; Figure 44) and freshwater mussels (40%; n = 10; Figure 34) exposed to sediment from Center Creek, considering the survival or biomass endpoints (Table 39). Concordance between sediment chemistry and sediment toxicity suggested that metals are the primary risk drivers in Center Creek.

Cow Creek AoI - The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ was 1.87 for the 34 sediment samples from the Cow Creek AoI (Table 38). As such, risks to the benthic invertebrate community were generally classified as low within this AoI. Nevertheless, the sediment chemistry data that were available for this AoI indicated that the

concentrations of COPCs were sufficient to pose moderate or high risks to benthic invertebrates in 5 of the 34 sediment samples (15%; Table 38). The results of toxicity tests conducted with amphipods, midges, and/or freshwater mussels confirmed that neither of the sediment samples tested were toxic to amphipods or mussels, considering survival or biomass (Table 40). However, both samples were toxic to midges. As midge toxicity was not strongly correlated with any of the COPCs measured in this study (MacDonald *et al.* 2009), the results of the amphipod and mussel toxicity tests should be given more weight.

Middle Spring River AoI - For the Middle Spring River AoI, sediment chemistry data were available for a total of 115 sediment samples. Evaluation of the data on the concentrations of cadmium, lead, and zinc in these sediment samples (i.e., expressed as the geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$; 2.29) indicated that sediment-associated contaminants posed relatively low risks to sediment-dwelling organisms in this AoI (Table 38). Nevertheless, $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ exceeded the moderate and high risk thresholds in 13% (15 of 115) and 10% (12 of 115) sediment samples, respectively, from this portion of the study area (Table 38). The samples with the highest levels of contamination by these metals were collected in the vicinity of Empire Lake (Figure 37). The results of sediment toxicity tests confirm that none of the sediment samples ($n = 7$) from this AoI were toxic to freshwater amphipods. However, about one-third of the samples from this AoI were toxic to midges and amphipods (Table 40).

Turkey Creek AoI - Sediment chemistry data are available for a total of 48 sediment samples from the Turkey Creek AoI. The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ for these samples was 18.1 (Table 38), suggesting that sediment-associated contaminants generally posed relatively high risks to sediment-dwelling organisms in this portion of the watershed. Five of the sediment samples (10%) from this reach had $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ sufficient to reduce the survival of freshwater amphipods by up to 10% relative to reference areas (Table 38). Even lower survival (i.e., > 10% reduction relative to reference) of freshwater amphipods was predicted for 35 of the 48 sediment samples (73%) from this reach (Table 38). Most of the samples that posed moderate or high risks to sediment-dwelling organisms were located in the lower 15 km of this creek (Figure 40). The results of sediment toxicity tests confirmed that sediment samples from the Turkey Creek AoI were toxic to amphipods (6 of 10 samples), midges (8 of 10 samples), and

freshwater mussels (4 of 7 samples), with toxicity observed throughout the creek (Figure 45; Table 40).

Short Creek AoI - It is apparent that sediment-associated contaminants posed a high risk to benthic invertebrates in the Short Creek AoI, based on the results of chemical analysis of 44 sediment samples. More specifically, a geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 74.2 was calculated for this AoI (Table 38). Application of the SSTs for amphipod survival to the available sediment chemistry data suggested that all of the 44 samples (100%) collected in this AoI posed moderate or high risks to benthic invertebrates (Table 38). In addition, all of the samples collected from Short Creek were found to be toxic to amphipods, midges, or freshwater mussels, considering the survival or biomass endpoints (Table 40; Figure 45).

Shawnee Creek AoI -Using the available data on the concentrations of cadmium, lead, and zinc, $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ was calculated for all of the sediment samples that were collected in Shawnee Creek ($n = 27$). A geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 1.37 was calculated for these samples (Table 38). As such, risks to the benthic invertebrate community were generally classified as low within this AoI. Nevertheless, the available sediment chemistry data indicated that the concentrations of COPCs were sufficient to pose moderate risks to benthic invertebrates in 2 of the 27 sediment samples (7%) collected from Shawnee Creek (Table 38). The results of toxicity tests conducted with amphipods, midges, or freshwater mussels showed that sediment samples from neither of the two locations tested were toxic, considering survival or biomass (Table 40; Figure 45).

The distribution of samples that were classified as posing low, moderate, and high risks to benthic invertebrates based on surface-water chemistry, sediment chemistry, pore-water chemistry, invertebrate-tissue chemistry, and predicted effects on freshwater mussels are presented in Figures 35 to 42. Overall, the geometric means of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ calculated for the sediment samples collected from eight reaches within this portion of the study area ranged from 0.54 to 74.2. These results showed that the concentrations of cadmium, lead, and zinc were frequently (40% of samples) sufficient to cause sediment toxicity (Table 38). The incidence of toxicity to amphipods was 29% for sediment samples from the UMSR (Table 40). Therefore, risks to benthic invertebrates were classified as high in this portion of

the study area. A number of hot spots with respect to sediment contamination were identified within the UMSR, with the highest risks to benthic invertebrates occurring in the Short Creek AoI, Turkey Creek AoI, Center Creek AoI, and Middle Spring River AoI (Table 38).

8.6.1.4 Contaminants of Concern in the Upper and Middle Spring River Sub-Basin

Following the assessment of risks to the benthic invertebrate community, it is useful to identify the factors that are causing or substantially contributing to adverse effects on sediment-dwelling organisms. In this document, the substances that occur in UMSR sediments at concentrations sufficient to cause or substantially contribute to adverse effects on the survival, growth, or reproduction of benthic invertebrates are termed COCs. The COCs in the UMSR, relative to the potential for adversely affecting benthic invertebrate communities, were identified by comparing the concentrations of COPCs in surface water, sediment, or pore water to the concentrations of those substances in reference sediments and to the selected benchmarks for those substances.

Based on the results of the exposure assessment, a total of 26 substances or groups of substances occurred in sediments from the TSMD (i.e., 95th percentile concentrations) at levels a factor of two or more higher than the corresponding 95th percentile concentrations for reference sediment samples (Table 26). Subsequent screening against the selected benchmarks for sediment chemistry (i.e., probable effect concentrations; MacDonald *et al.* 2000a) revealed that the substances that represented COCs relative to the benthic invertebrate community in the UMSR included: aluminum, arsenic, barium, cadmium, chromium, copper, iron, lead, mercury, nickel, zinc, benzo(g,h,i)perylene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, total high molecular weight PAHs, and total low molecular weight PAHs (Table 35). Historical and/or ongoing sources of these substances are known to occur in the study area (see the problem formulation for more information on the sources of these COCs; Appendix 1). Insufficient information was available to determine if several other substances represented COCs, including molybdenum, various individual PAHs, and BBP. It is possible that PAHs contributed to sediment toxicity in one or more samples from Turkey Creek (Table 26). Correlations between sediment chemistry and sediment toxicity indicated that cadmium, copper, lead, and zinc are likely the primary risk drivers in the study area. The results of 28-d bioaccumulation tests with the

oligochaete, *Lumbriculus variegatus*, confirmed that cadmium, copper, lead, mercury, and/or zinc have accumulated in the tissues of benthic invertebrates to levels sufficient to pose elevated risks to this receptor group.

8.6.2 Lower Spring River Sub-Basin

The Lower Spring River Sub-Basin (LSR) encompasses the southern portion of the Spring River watershed from the inlet of Empire Lake to the Grand Lake of the Cherokees (i.e., Grand Lake). This portion of the watershed has been divided into nine AoIs, including the Empire Lake, Lower Spring River, Shoal Creek, Brush Creek, Willow Creek, Spring Brook, Beaver Creek, Warren Branch, and Lost Creek AoIs (Figure 4). The risks to the benthic invertebrate community posed by exposure to contaminated surface water, sediment, and pore water were evaluated for each of these AoIs. Additionally, hotspots with respect to contaminated surface water, sediment, and/or pore water were identified when possible.

8.6.2.1 Nature of Effects on the Benthic Invertebrate Community in the Lower Spring River Sub-Basin

In total, data on six lines-of-evidence were used to determine if adverse effects on the benthic invertebrate community were occurring in the LSR in response to exposure to COPCs, including surface-water chemistry, sediment chemistry, pore-water chemistry, sediment toxicity, invertebrate-tissue chemistry, and mussel species richness. These data also provided a basis for assessing the nature of the effects that are occurring or are likely to be occurring to benthic invertebrate communities. Both the presence of conditions sufficient to cause or substantially contribute to effects (i.e., predicted incidence of toxicity) and occurrence of specific types of effects (i.e., observed incidence of toxicity) were used to determine if effects are occurring within the study area and to determine the nature of those effects.

Surface-water chemistry data were used to determine if conditions sufficient to adversely affect benthic invertebrates have occurred within the LSR. More specifically, the available data on the concentrations of divalent metals in surface water were evaluated using sample-specific, hardness-adjusted final chronic values (i.e., CCCs; by calculating $\sum SW-TU_{\text{DIVALENT METALS}}$). The results of this evaluation indicated that 29% (61 of 208) of surface-water

samples had concentrations of divalent metals sufficient to adversely affect the survival of amphipods (Table 37). Evaluation of the matching chemistry and toxicity data from the study area indicated that adverse effects on midges and mussels, including reduced survival and biomass, could also be expected with prolonged exposure (i.e., 10 to 28 days) to surface water with these chemical characteristics (Table 44). Therefore, these data demonstrated that surface-water quality conditions were sufficient to reduce the survival and biomass of sediment-dwelling organisms in portions of the LSR.

The sediment-chemistry data compiled for the period 2002 to 2009 were evaluated using SSTTs for sediment developed using the matching sediment chemistry and amphipod survival data. The results of this evaluation indicated that roughly 50% (192 of 385; Table 38) of the sediment samples from the LSR had concentrations of cadmium, lead, and zinc (expressed as $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$) that were sufficient to cause or substantially contribute to toxicity to freshwater amphipods (i.e., reduced survival or biomass). Evaluation of the matching chemistry and toxicity data from the study area indicated that adverse effects on midges and mussels, including reduced survival and biomass, could also be expected with prolonged exposure (i.e., 10 to 28 days) to sediments with these chemical characteristics (Table 45). As amphipod reproduction is strongly correlated with amphipod growth (Swartz *et al.* 1994; USEPA 2000a), it is likely that the reproduction of benthic invertebrates would also be impaired when exposed to contaminated sediments from the LSR (i.e., $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}} > 10.04$). Therefore, these data demonstrated that sediment quality conditions in portions of the LSR were sufficient to reduce the survival and biomass of sediment-dwelling organisms.

The pore-water chemistry data for the LSR were compared to the SSTTs for pore water that were developed for the TSMD (i.e., $\sum\text{PW-TU}_{\text{Zn}}$). The results of this evaluation indicated that the selected toxicity threshold (0.581) was exceeded in 13% (3 of 23) of pore-water samples from the LSR. Pore-water samples with these characteristics had reduced survival and/or biomass of amphipods, midges, and/or mussels (Table 39). Therefore, these data demonstrated that pore-water quality conditions in portions of the LSR were sufficient to reduce the survival and biomass of sediment-dwelling organisms.

Based on the results of acute and chronic toxicity tests, it is apparent that sediments from the LSR are adversely affecting the survival and/or biomass of benthic invertebrates. Of the 16 sediment samples collected from the LSR, a total of 6 (38%) were found to be acutely toxic

to midges (i.e., survival and/or biomass was reduced relative to the lower limit of responses for samples from reference areas; Table 40). By comparison, 1 of the 16 sediment samples (6%) from the LSR were found to be toxic to freshwater amphipods in 28-d toxicity tests (Table 40; Figures 24 and 25). Similarly, toxicity to freshwater mussels was observed in 14% (1 of 7) of the sediment samples from the LSR (Figures 26 and 27). Because reductions in the survival and/or growth of amphipods has been linked to impaired reproductive success (Swartz *et al.* 1994; USEPA 2000a), it is likely that reproduction of sediment-dwelling species would also be impaired in response to exposure to high risk sediments in the LSR. These data demonstrated that sediment quality conditions in portions of the LSR are sufficient to adversely affect the survival and/or biomass of benthic invertebrates.

Invertebrate-tissue chemistry data were also evaluated to determine if sediment quality conditions in the LSR were sufficient to adversely affect sediment-dwelling organisms. The results of this evaluation indicated that 20% (8 of 40) of the invertebrate-tissue samples had concentrations of cadmium, copper, lead, mercury, and/or zinc sufficient to adversely affect the survival, growth, or physiology of benthic invertebrates (Table 41; Jarvinen and Ankley 1999). As embryonic development can be adversely affected at lower tissue residue levels than is the case for survival (Salazar 2006), it is likely that reproduction would be impaired in benthic invertebrates that accumulated these metals to levels in exceedance of the selected toxicity thresholds (i.e., \sum TUs > 6.01; Figure 18). Evaluation of matching invertebrate-tissue chemistry and sediment toxicity data from the study area indicated that adverse effects on amphipods, midges, and mussels, including survival and/or biomass, could be expected when benthic invertebrates accumulated metals in their tissues beyond the selected toxicity thresholds (Table 47). Therefore, it is likely that body residues of metals are sufficient to adversely affect the survival and/or biomass of benthic invertebrates in portions of the LSR.

Species richness of freshwater mussels was evaluated at nine locations in the LSR, including four stations on the Spring River mainstem, three stations on Shoal Creek, one station on Brush Creek, and one Station on Willow Creek (Angelo *et al.* 2007). The results of these field surveys showed that live mussel taxa were observed at 56% (5 of 9) of these locations, with the number of live mussel taxa ranging from 0 to 8 overall. Threatened or endangered mussel species or mussel species in need of conservation were absent at 56% of these locations. The lowest number of taxa and lowest densities of mussels were observed at the downstream station on Shoal Creek, in Willow Creek, and the four stations on the Spring

River mainstem (Angelo *et al.* 2007). Evaluation of matching mussel species richness and sediment chemistry data from the study area indicated that the number of live mussel taxa, live mussel taxa classified as threatened, endangered, or of special concern, and total mussel taxa can be expected to be reduced when the concentrations of metals in sediment exceed the toxicity thresholds of 0.6 or 3.0 for \sum PEC-Q_{Cd,Pb,Zn} (Table 47).

When considered together, the six lines-of-evidence examined indicated that contaminated sediments in the LSR pose risks to the benthic invertebrate community. More specifically, it is likely that the survival and biomass (and likely reproduction) of benthic invertebrates are being adversely affected by exposure to contaminated sediments in portions of the LSR. Therefore, it is concluded that significant effects on the benthic invertebrate community are occurring in portions of the LSR (including the Empire Lake, Lower Spring River, Shoal Creek, Willow Creek, Spring Brook, and Beaver Creek AoIs).

8.6.2.2 Magnitude of Effects on the Benthic Invertebrate Community in the Lower Spring River Sub-Basin

The magnitude of the effects on benthic invertebrates exposed to contaminated sediments was evaluated using two lines-of-evidence, including sediment toxicity and sediment chemistry. Based on the results of three toxicity tests, it is apparent that exposure to sediment samples from the LSR is associated with a range of responses in sediment-dwelling organisms. Of the 16 sediment samples that were collected from the LSR, a total of 15 (94%) were found to pose a low risk to amphipods based on the results of 28-d toxicity tests (i.e., the survival of *H. azteca* was similar to that observed for samples from reference areas; Table 48; Figure 28). By comparison, moderate (i.e., < 10% reduction in survival compared to the lower limit of the reference envelope) risk to amphipods was observed in 1 (6%) of the samples from the LSR (Table 48). Similar results were observed for amphipod biomass (Table 49). For midges, 12 of 16 sediment samples (75%) from the LSR had survival rates that were consistent within those observed for reference sediment samples (i.e., low risk; Table 50; Figure 30). By comparison, three of the sediment samples were considered to pose moderate (19%) risks and one was considered to pose high (6%) risk to the benthic invertebrate community, based on midge survival; the biomass endpoint exhibited a similar pattern of toxicity (Table 51). Using survival of mussels in 28-d toxicity tests, 6 of the 7 samples (86%) were classified as posing low risk, and 1 of the 7 samples (14%) was classified as posing

moderate risk to benthic invertebrates (Table 52; Figure 32). None of the samples were classified as posing high risks to benthic invertebrate communities based on the results of mussel toxicity tests (Table 52). Overall, the available sediment toxicity data indicated that the magnitude of toxicity to benthic invertebrates ranges from low to high within the LSR.

The magnitude of toxicity to benthic invertebrate communities was also evaluated using the sediment chemistry data that were compiled for the period 2002 to 2009. More specifically, the predicted magnitude of toxicity was determined for each sediment sample using a site-specific concentration-response model (i.e., $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}}$) for amphipod survival. Samples were classified as low risk if $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}} < 6.47$, moderate risk if $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}}$ was 6.47 to 10.04, and high risk if $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}} > 10.04$. A total of 193 of 385 sediment samples (50%) were classified as posing low risk to the benthic invertebrate community (Table 38). By comparison, 63 of the 385 sediment samples (16%) had concentrations of cadmium, lead, and zinc sufficient to pose moderate risks to benthic invertebrates. The high risk designation was assigned to 129 of the 385 sediment samples (34%) from the LSR (Table 38). Therefore, the predicted magnitude of toxicity is low to high for the majority of the sediment samples from the LSR.

Overall, the information on the observed and predicted magnitude of toxicity to freshwater amphipods indicated that exposure to sediments from the LSR generally posed low risks to the benthic invertebrate community (Table 40). Nevertheless, the concentrations of COPCs were sufficient to cause or substantially contribute to sediment toxicity in 50% of the sediment samples (i.e., 192 of 385, Table 38) collected from this portion of the Spring River watershed. Importantly, the survival or biomass of amphipods, midges, or mussels was reduced relative to the lower limit for the reference envelope in 38% (6 of 16) of the sediment samples tested (Table 40; Figure 45). These results demonstrated that this portion of the watershed had a number of hot spots with respect to sediment contamination and/or toxicity that may benefit from source control measures and/or other risk management actions.

8.6.2.3 Areal Extent of Effects on the Benthic Invertebrate Community in the Lower Spring River Sub-Basin

The areal extent of adverse effects on benthic invertebrate communities in the LSR was assessed using the sediment chemistry data that were compiled for the period 2002 to 2009.

To support this evaluation of the spatial distribution of chemical contamination, $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ were calculated for each of the sediment samples ($n = 385$) that were collected from the LSR. Subsequently, each sediment sample was classified into one of three categories (i.e., low, moderate, or high), based on the risk that it posed to amphipod survival (i.e., samples were classified as low, moderate, or high risk if $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}} < 6.47$, 6.47 to 10.04 , and > 10.04 , respectively). These data were then compiled on an AoI by AoI basis and mapped using ArcMap/Spatial Analyst software (Figures 46 to 54). The AoIs that were considered in this analysis included the Empire Lake, Lower Spring River, Shoal Creek, Brush Creek, Willow Creek, Spring Brook, Beaver Creek, Warren Branch, and Lost Creek AoIs.

Empire Lake AoI - Sediment chemistry data were available for a total of 41 samples from the Empire Lake AoI. The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ for these samples was 20.9, suggesting that on average sediment-associated contaminants posed relatively high risks to sediment-dwelling organisms in this reach of the study area (Table 38). Concentrations of cadmium, lead, and zinc ($\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$) sufficient to reduce the survival of amphipods by up to 10% relative to the lower limit of survival rates for reference samples were observed in 3 of the 41 sediment samples (7%) from this AoI (Table 38). By comparison, 38 of the 41 sediment samples (93%) collected from this AoI had $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ sufficient to reduce the survival of freshwater amphipods by $> 10\%$, relative to the lower limit for reference conditions (Table 38). Contaminated sediments pose a moderate or high risk to sediment-dwelling organisms throughout Empire Lake (Figure 46). Only one sample was collected to evaluate sediment toxicity in this AoI; this sample was not toxic to either midges or amphipods.

Lower Spring River AoI - For the Lower Spring River AoI, sediment chemistry data were available for a total of 66 sediment samples. The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ for these samples was 5.04 (Table 38), suggesting that, on average, sediment-associated contaminants posed relatively low risks to sediment-dwelling organisms in this portion of the watershed. However, 20 of the sediment samples (30%) from this reach had $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ sufficient to reduce the survival of freshwater amphipods by up to 10% relative to reference areas (i.e., posed moderate risk to benthic invertebrates; Table 38). Even lower survival (i.e., $> 10\%$ reduction relative to reference; high risk) of freshwater amphipods was predicted for 12 of the 66 sediment samples (18%) from this reach (Table 38). Contaminated sediments posing moderate or high risks (32 of 66; 48%)

to sediment-dwelling organisms were primarily collected downstream of Empire Lake and downstream of Willow Creek (Figure 47). The results of sediment toxicity tests indicate that sediment samples from this AoI were infrequently toxic to amphipods, midges, or freshwater mussels (Table 40; Figures 28 to 34, 44, 45, 55).

Shoal Creek AoI - Based on the results of chemical analysis of 112 sediment samples, it is apparent that, on average, sediment-associated contaminants posed a low risk to benthic invertebrates in the Shoal Creek AoI. A geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 5.56 was calculated for this AoI (Table 38). Application of the concentration-response relationship for amphipod survival to the sediment chemistry data suggested that 55 of the 112 samples (49%) collected in this AoI posed moderate or high risks to benthic invertebrates (Table 38). The samples with elevated mean PEC-Qs were primarily collected from the lower sections of Shoal Creek (Figure 48). While none of the sediment samples tested from Shoal Creek were found to be toxic to amphipods or freshwater mussels (considering the survival or biomass endpoints; Figures 22 to 27, 45), 29% of the 7 samples that were tested were found to be toxic to midges (Table 40).

Brush Creek AoI - The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ was 1.47 for the 14 sediment samples from the Brush Creek AoI (Table 38). As such, risks to the benthic invertebrate community were generally classified as low within this AoI. Nevertheless, the sediment chemistry data that are available indicated that the concentrations of COPCs were sufficient to pose high risks to benthic invertebrates in one of the 14 sediment samples from this AoI (7%; Table 38). No toxicity tests were conducted on sediment samples from Brush Creek.

Willow Creek AoI - For the Willow Creek AoI, sediment chemistry data were available for a total of 30 sediment samples. Evaluation of the data on the concentrations of cadmium, lead, and zinc in these sediment samples (i.e., expressed as the geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$; 6.79) indicated that, on average, sediment-associated contaminants posed relatively low risks to sediment-dwelling organisms in this AoI (Table 38). Nevertheless, $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ exceeded the moderate and high risk thresholds in 27% (8 of 30) and 20% (6 of 30) of the sediment samples, respectively, from this portion of the study area (Table 38). The results of sediment toxicity tests confirmed that one of the

two sediment samples from this AoI was toxic to midges. No toxicity to freshwater amphipods or mussels was observed, however (Table 40).

Spring Brook AoI - Sediment chemistry data were available for a total of 15 sediment samples from the Spring Brook AoI. The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ for these samples was 27.3 (Table 38), suggesting that, on average, sediment-associated contaminants posed relatively high risks to sediment-dwelling organisms in this portion of the watershed. Fourteen of the 15 sediment samples (93%) were predicted to pose high risks to benthic invertebrates; based on the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ that were calculated using the sediment chemistry data (Table 38). No sediment toxicity data were available for this AoI.

Beaver Creek AoI - On average, sediment-associated contaminants posed a moderate risks to benthic invertebrates in the Beaver Creek AoI, based on the a geometric mean $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 7.51 (Table 38). Application of the SSTTs for amphipod survival to the available sediment chemistry data suggested that 33 of the 65 samples (51%) collected in this AoI posed moderate or high risks to benthic invertebrates (Table 38). The only sediment sample from Beaver Creek that was submitted for toxicity testing was found to be toxic to amphipods, midges, and freshwater mussels, considering the survival or biomass endpoints (Table 40; Figures 22 to 27, 45).

Warren Branch AoI - Using the available data on the concentrations of cadmium, lead, and zinc, a $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ was calculated for all of the sediment samples that were collected in Warren Branch (n = 9). A geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 1.23 was calculated for these samples (Table 38). As such, risks to the benthic invertebrate community were, on average, classified as low within this AoI. In addition, the available sediment chemistry data indicated that concentrations of COPCs sufficient to pose moderate or high risks to benthic invertebrates were not observed in any of the sediment samples collected from Warren Branch (Table 38). None of the sediment samples from this AoI were tested to evaluate toxicity to benthic invertebrates.

Lost Creek AoI - For the Lost Creek AoI, sediment chemistry data are available for a total of 33 sediment samples. Evaluation of the data on the concentrations of cadmium, lead, and zinc in these sediment samples (i.e., expressed as the geometric mean of the

$\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 1.49) indicated that, on average, sediment-associated contaminants pose relatively low risks to sediment-dwelling organisms in this AoI (Table 38). Nevertheless, the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ exceeded the high risk thresholds in 9% (3 of 33) of the sediment samples, from this portion of the study area (Table 38). One-third of the sediment samples (n = 3) from this AoI were found to be toxic to midges, considering survival or biomass (Table 40; Figures 22 to 27, 45). No toxicity to freshwater amphipods or mussels were observed, however.

The distributions of samples that were classified as posing low, moderate, and high risks to benthic invertebrates based on surface-water chemistry, sediment chemistry, pore-water chemistry, invertebrate-tissue chemistry, and predicted effects on freshwater mussels are presented in Figures 46 to 54. Overall, the geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ calculated for the sediment samples collected from the nine AoIs within the LSR averaged 5.87 and ranged from 1.23 to 27.3. The concentrations of cadmium, lead, and zinc were sufficient to be toxic to amphipods in 28-d toxicity tests (endpoint: survival) in 192 of the 385 sediment samples (50%) from the LSR. Additionally, the incidence of toxicity to amphipods (6%; n = 16), midges (38%; n = 16), and freshwater mussels (14%; n = 7; Table 40) was lower than that in the UMSR. Nevertheless, a number of hot spots with respect to sediment contamination were identified within the LSR, with the highest risks to benthic invertebrates occurring in the Empire Lake, Lower Spring River, Shoal Creek, Willow Creek, Spring Brook, and Beaver Creek AoIs.

8.6.2.4 Contaminants of Concern in the Lower Spring River Sub-Basin

Following the assessment of risks to the benthic invertebrate community, it is useful to identify the factors that are causing or substantially contributing to adverse effects on sediment-dwelling organisms. In this document, the substances that occur in LSR sediments at concentrations that are sufficient to cause or substantially contribute to adverse effects on the survival, growth, or reproduction of benthic invertebrates are termed COCs. The COCs in the LSR, relative to the potential for adversely affecting benthic invertebrate communities, were identified by comparing the concentrations of COPCs in surface water, sediment, or pore water to the concentrations of those substances in reference sediments, and to the selected benchmarks for those substances.

Based on the results of the exposure assessment, a total of 26 substances or groups of substances occurred in sediments from the TSMD (i.e., 95th percentile concentrations) at levels a factor of two or more higher than the corresponding 95th percentile concentrations for reference sediment samples (Table 27). Subsequent screening of the LSR sediments against reference sediment samples, and against selected benchmarks for sediment chemistry revealed that nine metals (aluminum, arsenic, barium, cadmium, chromium, lead, mercury, nickel, and zinc) represent COCs relative to the benthic invertebrate community (Tables 34 and 41). Historical and/or ongoing sources of these substances are known to occur in the study area (see the problem formulation for more information on the sources of these COCs). Insufficient information was available to determine if several other substances represented COCs, including various individual PAHs and BBP. Based on the correlations between sediment chemistry and sediment toxicity, it is likely that cadmium, copper, lead, and zinc represent the primary risk drivers in the study area. The results of 28-d bioaccumulation tests with the oligochaete, *Lumbriculus variegatus*, confirmed that cadmium, copper, lead, mercury, and/or zinc have accumulated in the tissues of benthic invertebrates to levels sufficient to pose risks to this receptor group.

8.6.3 Neosho River Sub-Basin

The Neosho River Sub-Basin (NR) encompasses the southern portion of the Neosho River watershed from roughly Oswego to the Grand Lake of the Cherokees (i.e., Grand Lake). This portion of the watershed has been divided into six AoIs, including the Neosho River, Upper Tar Creek, Middle Tar Creek, Lytle Creek, Lower Tar Creek, and Elm Creek AoIs (Figure 4). The risks to the benthic invertebrate community posed by exposure to contaminated surface water, sediment, and pore water were evaluated for each of these AoIs. Additionally, hotspots with respect to contaminated surface water, sediment, and/or pore water were identified when possible.

8.6.3.1 *Nature of Effects on the Benthic Invertebrate Community in the Neosho River Sub-Basin*

In total, data on six lines-of-evidence were used to determine if adverse effects on the benthic invertebrate community have occurred in the NR in response to exposure to COPCs,

including surface-water chemistry, sediment chemistry, pore-water chemistry, sediment toxicity, invertebrate-tissue chemistry, and mussel species richness. These data also provided a basis for assessing the nature of the effects that have occurred or are likely to have occurred to benthic invertebrate communities. Both the presence of conditions sufficient to cause or substantially contribute to effects (i.e., predicted incidence of toxicity) and the occurrence of specific types of effects (i.e., observed incidence of toxicity) were used to determine if effects are occurring within the study area and to determine the nature of those effects.

Surface-water chemistry data were used to determine if conditions sufficient to adversely affect benthic invertebrates have occurred within the NR. More specifically, the available data on the concentrations of divalent metals in surface water were evaluated using sample-specific, hardness-adjusted final chronic values (i.e., CCCs; by calculating $\sum \text{SW-TU}_{\text{DIVALENT METALS}}$). The results of this evaluation indicated that 71% (159 of 223) surface-water samples had concentrations of divalent metals sufficient to adversely affect the survival of amphipods (Table 37). Evaluation of the matching chemistry and toxicity data from the study area indicated that adverse effects on midges and mussels, including reduced survival and biomass, could also be expected with prolonged exposure (i.e., 10 to 28 days) to surface water with these chemical characteristics (Table 44). Therefore, these data demonstrated that surface-water quality conditions in portions of the NR are sufficient to reduce the survival and biomass of sediment-dwelling organisms.

Sediment-chemistry data were compiled for the period 2002 to 2009 to facilitate evaluation of risks to the benthic invertebrate community, and evaluated using SSTTs for amphipod survival. The results of this evaluation indicated that roughly 57% (218 of 383; Table 38) of the sediment samples from the NR had concentrations of cadmium, lead, and zinc (expressed as $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$) sufficient to cause or substantially contribute to toxicity to freshwater amphipods (i.e., reduced survival and biomass). Evaluation of the matching chemistry and toxicity data from the study area indicated that adverse effects on midges and mussels, including reduced survival and biomass, could also be expected with prolonged exposure (i.e., 10 to 28 days) to sediments with these chemical characteristics (Table 45). As amphipod reproduction is strongly correlated with amphipod growth (Swartz *et al.* 1994; USEPA 2000a), it is likely that the reproduction of benthic invertebrates would also be impaired when exposed to contaminated sediments from the NR (i.e., $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}} > 10.04$). Therefore,

these data demonstrated that sediment quality conditions in portions of the NR are sufficient to reduce the survival and biomass of sediment-dwelling organisms.

The pore-water chemistry data for the NR were compared to the SSTTs for pore water that were developed for the TSMD (i.e., $\sum \text{PW-TU}_{\text{Zn}}$). The results of this evaluation indicated that the selected toxicity threshold (0.581) was exceeded in 30 % (6 of 20) of the pore-water samples from the NR (Table 39). Pore-water samples with these characteristics had reduced survival and biomass of amphipods, midges, and mussels (Table 46). Therefore, these data demonstrated that of the pore-water quality conditions in portions of the NR are sufficient to reduce the survival and biomass of sediment-dwelling organisms.

Based on the results of acute and chronic toxicity tests, it is apparent that sediments from the NR have adversely affected the survival and/or biomass of benthic invertebrates. Of the 15 sediment samples that were collected from the NR, a total of 9 (60%) were found to be acutely toxic to midges (i.e., survival and/or biomass was reduced relative to the lower limit of responses for samples from reference areas; Table 40). Similarly, 8 of the 15 sediment samples (53%) from the NR were found to be toxic to freshwater amphipods in 28-d toxicity tests (Table 40; Figures 24 and 25). By comparison, toxicity to freshwater mussels was observed in 38% (3 of 8) of the sediment samples from the NR (Figures 26 and 27). Because reductions in the survival and/or growth of amphipods have been linked to impaired reproductive success (Swartz *et al.* 1994; USEPA 2000a), it is likely that reproduction of sediment-dwelling species would also be impaired in response to exposure to sediments in the NR. These data demonstrated that sediment quality conditions in portions of the NR are sufficient to adversely affect the survival and/or biomass of benthic invertebrates.

Invertebrate-tissue chemistry data were also evaluated to determine if sediment quality conditions in the NR were sufficient to adversely affect sediment-dwelling organisms. The results of this evaluation indicated that 100% (4 of 4) of the invertebrate-tissue samples had concentrations of cadmium, copper, lead, mercury, and/or zinc sufficient to adversely affect the survival, growth, or physiology of benthic invertebrates (Table 41; Jarvinen and Ankley 1999). As embryonic development can be adversely affected at lower tissue residue levels than is the case for survival (Salazar 2006), it is likely that reproduction would be impaired in benthic invertebrates that accumulate these metals to levels in exceedance of the selected toxicity thresholds (i.e., $\sum \text{TUs} > 6.01$; Figure 18). Evaluation of matching invertebrate-tissue

chemistry and sediment toxicity data from the study area indicates that adverse effects on amphipods, midges, and mussels, including survival and/or biomass, can be expected when benthic invertebrates accumulate metals in their tissues beyond the selected toxicity thresholds (Table 47). Therefore, it is likely that body residues of metals are sufficient to adversely affect the survival and/or biomass of benthic invertebrates in portions of the NR.

No data were located on freshwater mussel species richness in the NR (Angelo *et al.* 2007). Therefore, it is not possible to determine if adverse effects on mussel species richness or density have occurred within this portion of the study area.

When considered together, the five lines-of-evidence examined indicated that contaminated sediments in the NR posed risks to the benthic invertebrate community. More specifically, it is likely that the survival and/or biomass (and likely reproduction) of benthic invertebrates have been adversely affected by exposure to contaminated sediments in portions of the NR. Therefore, it is concluded that significant effects on the benthic invertebrate community are occurring in portions of the NR, primarily including the Upper Tar Creek, Middle Tar Creek, Lytle Creek, Lower Tar Creek, and Elm Creek AoIs.

8.6.3.2 Magnitude of Effects on the Benthic Invertebrate Community in the Neosho River Sub-Basin

The magnitude of the effects on benthic invertebrates exposed to contaminated sediments was evaluated using two lines-of-evidence, including sediment toxicity and sediment chemistry. Based on the results of three toxicity tests, it is apparent that exposure to sediment samples from the NR is associated with a range of responses in sediment-dwelling organisms. Of the 15 sediment samples that were collected from the NR, a total of 7 (47%) were found to pose a low risk to amphipods based on the results of 28-d toxicity tests (i.e., survival and biomass of *H. azteca* were similar to those observed for samples from reference areas; Table 48). By comparison, moderate (i.e., up to 10% reduction in survival compared to the lower limit of the reference envelope) or high (i.e., > 10% reduction in survival compared to the lower limit of the reference envelope) risks to amphipods was observed in 3 (20%) and 5 (33%) of the samples from the NR, respectively (Table 48). The incidence of toxicity (i.e., moderate and high risk samples) was lower when the biomass endpoint was considered for amphipods (Tables 49). For midges, 9 of 15 sediment samples (60%) from the NR had survival rates that

were consistent with those observed for reference sediment samples (i.e., low risk; Table 50; Figures 28 to 30). By comparison, 1 (7%) and 5 (33%) of the sediment samples were considered to pose moderate and high risks, respectively, to the benthic invertebrate community, based on midge survival (Table 50; Figure 30). Consideration of the biomass endpoint resulted in a higher proportion of the samples being designated as moderate or high risk (i.e., 47%; Table 51). Using survival of mussels in 28-d toxicity tests, 5 of the 8 samples (63%) were classified as posing low risk, 2 of the 8 samples (25%) were classified as posing moderate risk, and 1 of the 8 samples (12%) were classified as posing high risk to benthic invertebrate communities (Table 52; Figure 32). The biomass endpoint was less sensitive for mussels (Table 53). Overall, the available sediment toxicity data indicated that the magnitude of toxicity to benthic invertebrates is low to high within the NR.

The magnitude of toxicity to benthic invertebrate communities was also evaluated using the sediment chemistry data that were compiled for the period 2002 to 2009. More specifically, the predicted magnitude of toxicity was determined for each sediment sample using the site-specific concentration-response model (i.e., $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}}$) for amphipod survival. Samples were classified as low risk if $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}} < 6.47$, moderate risk if $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}}$ was 6.47 to 10.04, and high risk if $\sum \text{PEC}-Q_{\text{Cd,Pb,Zn}} > 10.04$. A total of 165 of 383 sediment samples (43%) were classified as posing low risk to the benthic invertebrate community (Table 38). By comparison, 13 of the 383 sediment samples (3%) had concentrations of cadmium, lead, and zinc sufficient to pose moderate risks to benthic invertebrates (Table 38). The high risk designation was assigned to 205 of the 383 sediment samples (54%) from the NR. Therefore, the predicted magnitude of toxicity is high for the majority of the sediment samples from the NR (Table 38).

Overall, the information on the observed and predicted magnitude of toxicity to freshwater amphipods indicated that exposure to sediments from the NR generally posed a high risk to the benthic invertebrate community (Table 40). The concentrations of COPCs were sufficient to cause or substantially contribute to sediment toxicity in 57% of the sediment samples (i.e., 218 of 383) collected from this portion of the Spring River watershed (Table 38). Importantly, the survival of amphipods, midges, or mussels was reduced relative to the lower limit of reference samples in 67% (10 of 15) of the sediment samples tested (Table 40). These results demonstrated that this portion of the watershed had a number of hot spots with respect

to sediment contamination and/or toxicity that may benefit from source control measures and/or other risk management actions.

8.6.3.3 Areal Extent of Effects on the Benthic Invertebrate Community in the Neosho River Sub-Basin

The areal extent of adverse effects on benthic invertebrate communities in the NR was assessed using the sediment chemistry data that were compiled for the period 2002 to 2009. To support this evaluation of the spatial distribution of chemical contamination, $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ were calculated for each of the sediment samples ($n = 383$) that were collected from the NR. Subsequently, each sediment sample was classified into one of three categories (i.e., low, moderate, or high), based on the risk that it posed to amphipod survival (i.e., samples were classified as low, moderate, or high risk if $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}} < 6.47$, 6.47 to 10.04 , and > 10.04 , respectively). These data were then compiled on an AoI by AoI basis and mapped using ArcMap/Spatial Analyst software (Figures 56 to 61). The AoIs that were considered in this analysis included the Neosho River, Upper Tar Creek, Middle Tar Creek, Lytle Creek, Lower Tar Creek, and Elm Creek AoIs.

Neosho River AoI - Sediment chemistry data are available for a total of 117 samples from the Neosho River AoI. The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ for these samples was 1.26, suggesting that on average sediment-associated contaminants posed relatively low risks to sediment-dwelling organisms in this reach of the study area (Table 38). Nevertheless, $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ sufficient to reduce the survival of amphipods by up to 10% relative to the lower limit of survival rates for reference samples were observed in 5 of the 117 sediment samples (4%) from this AoI (Table 38). In addition, 4 of the 117 sediment samples (3%) collected from this AoI had $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ sufficient to reduce the survival of freshwater amphipods by $> 10\%$, relative to reference conditions (Table 38). Of the four samples that were collected in this AoI, one was toxic to amphipods and to midges and none were toxic to mussels (Table 40). These results showed that some portions of the Neosho River AoI had conditions sufficient to pose moderate or high risks to benthic invertebrates.

Upper Tar Creek AoI - For the Upper Tar Creek AoI, sediment chemistry data were available for a total of 39 sediment samples. The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$

for these samples was 3.12 (Table 38), suggesting that sediment-associated contaminants generally posed relatively low risks to sediment-dwelling organisms in this portion of the watershed. However, 8 of the sediment samples (21%) from this reach had $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ sufficient to reduce the survival of freshwater amphipods by $> 10\%$ relative to reference areas (Table 38; Figure 57). The results of sediment toxicity tests confirmed that sediment samples from this AoI were not toxic to amphipods (i.e., 0 of 2 samples; 0%), midges (i.e., 1 of 2 samples; 50%), or freshwater mussels (1 of 2 samples; 50%; Table 40; Figure 45).

Middle Tar Creek AoI - Based on the results of chemical analysis of 52 sediment samples, it is apparent that on average sediment-associated contaminants pose a high risk to benthic invertebrates in the Middle Tar Creek AoI. A geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ of 79.9 was calculated for this AoI (Table 38). Application of the concentration-response relationship for amphipod survival to the sediment chemistry data suggests that all of the samples collected in this AoI pose moderate ($n = 1$) or high ($n = 51$) risks to benthic invertebrates (Table 38). Samples from Middle Tar Creek were always toxic to amphipods ($n = 2$) and midges ($n = 2$), considering the survival or biomass endpoints (Table 40; Figure 45). No freshwater mussel toxicity data were available for this AoI.

Lytle Creek AoI - The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ was 62.5 for the 41 sediment samples from the Lytle Creek AoI (Table 38). As such, risks to the benthic invertebrate community were generally classified as high within this AoI. The sediment chemistry data that are available for this AoI also indicated that concentrations of COPCs were sufficient to pose moderate or high risks to benthic invertebrates in 39 of the 41 sediment samples (95%; Table 38). The results of toxicity tests conducted with amphipods and midges indicated that sediment samples from one of the two locations tested (50%) were toxic, considering survival or biomass (Table 40; Figures 43, 45, 62, 63). No samples were found to be toxic to freshwater mussels.

Lower Tar Creek AoI - For the Lower Tar Creek AoI, sediment chemistry data were available for a total of 108 sediment samples. Evaluation of the data on the concentrations of cadmium, lead, and zinc in these sediment samples (i.e., expressed as the geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$; 13.6) indicated that sediment-associated contaminants posed high risks to sediment-dwelling organisms in this AoI (Table 38).

The $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ exceeded the moderate and high risk thresholds in 3% (3 of 108) and 79% (85 of 108) sediment samples, respectively, from this portion of the study area (Table 38). Sediment samples from this AoI were toxic to amphipods (3 of 4 samples; 75%), midges (3 of 4 samples; 75%), or mussels (2 of 2 samples; 100%; Table 40; Figure 45).

Elm Creek AoI - Sediment chemistry data are available for a total of 26 sediment samples from the Elm Creek AoI. The geometric mean of the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ for these samples was 34.1 (Table 38), suggesting that sediment-associated contaminants generally posed high risks to sediment-dwelling organisms in this portion of the watershed. Two of the 26 sediment samples (8%) from this reach had $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ sufficient to reduce the survival of freshwater amphipods by up to 10% relative to reference areas (Table 38). Even lower survival (i.e., > 10% reduction relative to reference) of freshwater amphipods was predicted for 20 of the 26 sediment samples (77%) from this reach (Table 38). The sediment samples from this AoI were found to be toxic to amphipods and midges (Table 40; Figure 45).

The distribution of samples that were classified as posing low, moderate, and high risks to benthic invertebrates based on surface-water chemistry, sediment chemistry, pore-water chemistry, invertebrate-tissue chemistry, and predicted effects on freshwater mussels are presented in Figures 56 to 61. Overall, the $\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ calculated for the sediment samples (geometric mean of 8.41) collected from this portion of the study area indicated that concentrations of cadmium, lead, and zinc sufficient to pose high risks to benthic invertebrates are frequently encountered (i.e., 57%; 218 of 383 samples; Table 38). Additionally, the incidence of toxicity to amphipods (53%; n = 15), midges (60%; n = 15), and freshwater mussels (38%; n = 8) demonstrated that exposure to NR sediments posed high risks to benthic invertebrates (Table 40). The highest risks to benthic invertebrates were estimated for the Upper Tar Creek, Middle Tar Creek, Lytle Creek, Lower Tar Creek, and Elm Creek AoIs.

8.6.3.4 Contaminants of Concern in the Neosho River Sub-Basin

Following the assessment of risks to the benthic invertebrate community, it is useful to identify the factors that are causing or substantially contributing to adverse effects on

sediment-dwelling organisms. In this document, the substances that occurred in NR sediments at concentrations sufficient to cause or substantially contribute adverse effects on the survival, growth, or reproduction of benthic invertebrates are termed COCs. The COCs in the NR, relative to the potential for adversely affecting benthic invertebrate communities, were identified by comparing the concentrations of COPCs in surface water, sediment, or pore water to the concentrations of those substances in reference sediments and to the selected benchmarks for those substances.

Based on the results of the exposure assessment, a total of 26 substances or groups of substances occurred in sediments from the TSMD (i.e., 95th percentile concentrations) at levels a factor of two or more higher than the corresponding 95th percentile concentrations for reference sediment samples (Table 28). Subsequent screening of the NR sediments against reference sediments, and against the selected benchmarks for sediment chemistry revealed that 11 substances represent COCs relative to the benthic invertebrate community including arsenic, barium, cadmium, chromium, copper, iron, lead, mercury, nickel, zinc, and benzo(k)fluoranthene (Table 35). Historical and/or ongoing sources of these substances are known to occur in the study area (see the problem formulation for more information on the sources of these COCs; Appendix 1). Insufficient information was available to determine if many other substances represented COCs, including molybdenum, various individual PAHs and BBP. Correlations between sediment chemistry and sediment toxicity suggest that cadmium, copper, lead, and zinc are likely the primary risk drivers in the study area. The results of 28-d bioaccumulation tests with the oligochaete, *Lumbriculus variegatus*, confirmed that cadmium, copper, lead, mercury, and/or zinc have accumulated to elevated levels in the tissues of benthic invertebrates sufficient to pose elevated risks to this receptor group.

Chapter 9 Uncertainty Analysis

9.0 Introduction

There are a number of sources of uncertainty in assessments of risk to the benthic invertebrate community, including uncertainties in the conceptual model, in the exposure assessment, and in the effects assessment. As each of these sources of uncertainty can influence the estimations of risk, it is important to describe and, when possible, quantify the magnitude and direction of such uncertainties. The purpose of this section is to evaluate uncertainty in a manner that facilitates attribution of the level of confidence that can be placed in the assessments conducted using the various lines-of-evidence. Accordingly, the uncertainties associated with the assessment of risks to benthic invertebrate communities are described in the following sections.

9.1 Uncertainties Associated with the Conceptual Model

The conceptual model is intended to define the linkages between stressors, potential exposure, and predicted effects on ecological receptors. As such, the conceptual model provides the scientific basis for selecting assessment and measurement endpoints to support the risk assessment process. Potential uncertainties arise from lack of knowledge regarding ecosystem functions, failure to adequately address spatial and temporal variability in the evaluations of sources, fate, and effects, omission of stressors, and overlooking secondary effects (USEPA 1998). The types of uncertainties that are associated with the conceptual model that links contaminant sources to effects on the benthic invertebrate community include those associated with the identification of COPCs, environmental transport and fate of COPCs, exposure pathways, receptors at risk, and ecological effects.

Identification of COPCs represents an important source of uncertainty in the conceptual model for the TSMD. In this study, the TSMD Ecological Risk Assessment Advisory Group represented the primary source of information on the sources and releases of COPCs in the study area. As this group is comprised of a large number of individuals with in-depth

knowledge of land and water uses in the TSMD, it is likely that the majority of potential sources of COPCs were documented and that the COPCs that may have been released from these sources were identified. Nevertheless, it is possible that additional sources contributed one or more COPCs to aquatic habitats within the study area. In particular, there is substantial uncertainty regarding the types and quantities of herbicides, fungicides, and insecticides that are currently being used within the Spring River and Neosho River sub-basins. To address this uncertainty, the 2007 Sediment Sampling Program was designed to evaluate the contamination of sediments by a broad range of chemical substances, including metals, PAHs, PCBs, organochlorine pesticides, and an extensive suite of SVOCs. As a result, the potential for missing possible risk drivers is relatively low.

Identification of exposure pathways also represents a potential source of uncertainty in the conceptual model. In this assessment, it was assumed that exposure to sediments and pore water represents the most important pathways for benthic invertebrate communities to COPCs (i.e., as the benthic invertebrates associated with benthic habitats likely play key ecological functions and contaminant concentrations are likely to be highest in these media types). However, benthic invertebrates may also be exposed to COPCs in the water column. While data were compiled on the concentrations of metals in surface water, data were unavailable on the concentrations of other COPCs in this medium. As such, risks to the benthic invertebrate community could be under-estimated if this pathway resulted in significant exposure of benthic invertebrates to COPCs other than metals or if the available data did not fully capture the range of surface water conditions in the study area.

9.2 Uncertainties Associated with the Exposure Assessment

The exposure assessment is intended to describe the actual or potential co-occurrence of stressors with receptors. As such, the exposure assessment identifies the exposure pathways and the intensity and extent of contact with stressors for each receptor or group of receptors at risk. There are a number of potential sources of uncertainty in the exposure assessment, including measurement errors, extrapolation errors, and data gaps.

In this assessment, two types of measurements were used to evaluate exposure of benthic invertebrate communities to COPCs: chemical analyses of environmental media (i.e., surface water, sediment, pore water, and invertebrate tissues); and, toxicity tests conducted using indicator species. Relative to the surface-water, pore-water, sediment, and invertebrate-tissue chemistry data, analytical errors and descriptive errors represent potential sources of uncertainty. Three approaches were used to address concerns relative to these sources of uncertainty. First, analytical errors were evaluated using information on the accuracy, precision, and detection limits that were generated to support each of the studies represented in the project database. The results of this analysis indicated that most of the data used in this assessment met the project data quality objectives. Second, all data entry, data translation, and data manipulations were audited to assure their accuracy. Data auditing involved 10% number-for-number checks against the primary data source initially, increasing to 100% number-for-number checks if significant errors were detected in the initial auditing step. Finally, statistical analyses of resultant data were conducted to evaluate data distributions, identify the appropriate summary statistics to generate, and evaluate the variability in the observations. As such, measurement errors in the surface-water, pore-water, sediment, and invertebrate-tissue chemistry data are considered to be of minor importance and are unlikely to substantially influence the results of the risk assessment.

Extrapolation errors have the potential to influence the results of the DERA. While most of the data that were used to evaluate exposure of ecological receptors to COPCs were used in their original form, the sediment chemistry data were adjusted prior to developing exposure point concentrations. More specifically, all of the sediment chemistry data that were reported for the < 63 μm , < 250 μm , and whole-sediment fractions for cadmium, lead, and zinc were converted to < 2.00 mm equivalent concentrations to provide data that were relevant for comparison to the SSTTs for sediment (which were explicitly developed for the < 2.00 mm fraction). The procedures that were used to perform these data conversions are described in Appendix 3. Given the variability in the underlying relationships between the chemical concentrations in the various size fractions, these data conversions may have introduced substantial extrapolation errors (i.e., possibly up to a factor of two) into the data. As a result, risks to ecological receptors may have been under-estimated or over-estimated for the samples for which such extrapolations were made.

The treatment of surface water, sediment, pore-water, or invertebrate-tissue chemistry data has the potential to influence the results of the DERA. In particular, the treatment of less than detection limit data can affect the results of the exposure assessment and the risk characterization. A number of investigators have evaluated the implications of applying various procedures for estimating the concentrations of COPCs from less than detection limit data (Gaskin *et al.* 1990; Porter and Ward 1991; El-Shaawari and Esterby 1992; Clarke and Brandon 1994). While there is no consensus on which data censoring method should be used in various applications, the simplest methods tend to be used most frequently, including deletion of non-detect values or substitution of a constant, such as zero, the detection limit, or one-half the detection limit (USACE 1995).

To address the need for guidelines for statistical treatment of less than detection limit data, the USACE (1995) conducted a simulation study to assess the performance of 10 methods for censoring data. The results of that investigation indicated that no single data censoring method works best in all situations. Accordingly, USACE recommended a variety of methods depending on the proportion of the data that requires censoring, the distribution and variance of the data, and the type of data transformation. For data sets for which a low to moderate proportion of the data require censoring, substitution of the detection limit is generally the preferred method (i.e., to optimize statistical power and control type I error rates). However, as the proportion of the data that requires censoring and the coefficient of variation of the data increase, statistical power is better maintained by substituting one-half the detection for the less than detection limit data, particularly for log-normally distributed and transformed data. Substitution of zero or other constants was also recommended for a variety of circumstances. Overall, it was concluded that simple substitution methods work best to maintain power and control error rates in statistical comparisons of chemical concentration data (USACE 1995).

In this analysis, decisions regarding the treatment of less than detection limit data were made by considering the recommendations that have emerged from previous investigations in the context of their potential effects on the results of the DERA. Including all of the surface-water, sediment, pore-water, and invertebrate-tissue chemistry data that were compiled in the project database, more than 50% of the data required censoring prior to data analysis. To minimize the potential effects of the less than detection limit data on the results of the DERA, none of the less than detection limit data for which the detection limits were greater than the

corresponding toxicity thresholds for surface-water, sediment, pore-water, or invertebrate-tissue chemistry (i.e., benchmarks) were used in the exposure analysis. Consistent with the guidance developed by USACE (1995), one-half of the detection limit was substituted for all of the other less than detection limit data. This procedure facilitated the estimation of distributions of the concentrations of COPCs and eliminated the potential for identifying significant risks based on less than detection limit data.

Selection of an alternate procedure for treating the less than detection limit data has the potential to influence the results of the DERA. For example, substitution of zero for less than detection limit data would have altered the distributions of the COPC concentration data for the 23 AoIs, for the study area as a whole, and for the reference samples (i.e., the estimated 5th, 10th, 25th, 50th, 75th, 90th, and 95th percentile concentrations would likely have been lower than the estimates developed for the exposure assessment). Likewise, substitution of the detection limit for the less than detection limit data would have altered the distributions of the COPC concentration data (i.e., the estimated 5th, 10th, 25th, 50th, 75th, 90th, and 95th percentile concentrations would likely have been higher than the estimates developed for the exposure assessment). Although the influence of these alternate methods on the estimate of the 75th or 95th percentile concentration would likely have been relatively minor, their selection could have influenced the identification of COCs. However, the nature, magnitude, nor areal distribution of risks to benthic invertebrate communities were unlikely to be affected by the selection of data treatment methods. As such, the potential impact of the methods that were selected for treating less than detection limit data on the results of the DERA are considered to be minor.

Data gaps also represent a source of uncertainty in the assessments of exposure for aquatic receptors. For example, the available data on the chemical composition of pore-water chemistry (n = 96; Table 39) and on sediment toxicity (n = 76; Table 40) were limited (i.e., compared to over 1000 samples for sediment chemistry). As such, it is difficult to assess exposure of benthic invertebrate communities to pore water in certain reaches of the TSMD. Similarly, the available surface-water chemistry and invertebrate-tissue chemistry data are somewhat limited. Although these data gaps are significant, they are mitigated to a large extent by the abundance of data on sediment chemistry.

In this study, exposure to site-related COPCs was evaluated by comparing concentrations of COPCs at the site (95th percentile) to the upper limit of background concentrations. Incremental exposure to COPCs was identified when the upper limit of the concentrations at the site exceeded the upper limit of background by a factor of two or more. This approach was selected to account for uncertainties associated with defining background concentrations of COPCs using data from numerous sites collected over an extended period of time (i.e., 2002-2009). In this way, only those COPCs that were likely elevated beyond background levels were included in the detailed exposure evaluation and in the identification of COCs. Finally, dietary exposure of benthic invertebrates to site-related COPCs was not evaluated in the DERA. As a result, risks to benthic invertebrates in the TSMD may have been underestimated. The extent to which such risks could have been understated could not be determined, however.

9.3 Uncertainties in the Effects Assessment

The effects assessment is intended to describe the effects that are caused by stressors, link them to the assessment endpoints, and evaluate how effects change with fluctuations in the levels (i.e., concentrations) of the various stressors. There are several sources of uncertainty in the assessment of effects on aquatic receptors, including measurement errors, extrapolation errors, and data gaps.

In this investigation, the effects on benthic invertebrate communities associated with exposure to sediment-associated COPCs were evaluated using several types of information, including toxicity thresholds for surface water, sediment chemistry, pore water, and invertebrate tissues, as well as the results of sediment toxicity tests. Although the toxicity thresholds are not directly subject to measurement errors, the toxicity tests are. The data on negative controls and positive controls were examined to identify potential measurement errors in the toxicity tests. In addition, the results obtained from samples collected in the reference areas were considered in this analysis. More specifically a reference envelope approach was used to classify sediment samples as toxic or not toxic. Because this approach facilitated the determination of the normal range of responses for reference samples and only samples for which the response was beyond the lower limit of the reference envelope (i.e., 5th percentile),

the probability of incorrectly classifying a not-toxic sample as toxic is roughly 0.05. However, the probability of incorrectly classifying a toxic sample as not-toxic is probably higher. Therefore, application of the reference envelope approach may tend to under-estimate risks to the benthic invertebrate community. Because the concentration-response relationships were developed using the sediment chemistry and toxicity data, these models are subject to the same measurement errors that were ascribed to the underlying data. Importantly, the steps that were taken to minimize the potential impacts of measurement errors on the results of the analyses conducted with the sediment chemistry or sediment toxicity data also reduce the uncertainties associated with concentration-response models.

There are several sources of extrapolation errors in the effects assessment for the DERA of the TSMD. The toxicity thresholds for surface water are based on matching pore-water chemistry and sediment chemistry data from the TSMD. While $\sum \text{PW-TU}_{\text{DIVALENT METALS}}$ explained more than 80% of the variability in the amphipod survival data, the applicability of this toxic units model for assessing surface-water quality in the study area is uncertain. However, the results of the reliability evaluation provide enhanced confidence that these toxicity thresholds are relevant for evaluating effects on benthic invertebrates associated with exposure to divalent metals in water (see MacDonald *et al.* 2009 for the results of the reliability evaluation). In addition, the TSVs for divalent metals that were used in the calculation of $\sum \text{TU}_{\text{DIVALENT METALS}}$ apply specifically to a water hardness of 100 mg/L. Accordingly, the $\sum \text{TU}_{\text{DIVALENT METALS}}$ would tend to over-predict toxicity at higher water hardnesses and under-predict toxicity at lower water hardnesses.

Second, the toxicity thresholds for sediments were primarily the concentrations that corresponded to a 10 or 20% increase in the magnitude of toxicity to amphipods, relative to the average responses of amphipods exposed to reference samples from the TSMD. While these toxicity thresholds were found to provide an accurate basis for predicting toxicity to amphipods, mussels, and, to a lesser extent, midges, it is possible that these benchmarks could under-estimate the effects of sediment-associated contaminants on more sensitive benthic species. Because these toxicity thresholds are based on the concentrations of cadmium, lead, and zinc in sediments, they would also under-estimate toxicity to benthic invertebrates for sediments that contained substantial amounts of other COPCs (e.g., PAHs, PCBs, organochlorine pesticides). This uncertainty is largely mitigated by the fact that other COPCs

are rarely present in TSMD sediments at concentrations in excess of PEC-type sediment quality guidelines (MacDonald *et al.* 2000a).

The selected pore-water toxicity thresholds were developed using matching pore-water chemistry and sediment chemistry data from the TSMD. Because these toxicity thresholds are based on PW-TU_{Zn}, they could under-estimate toxicity to benthic invertebrates if other COPCs were present at elevated concentrations in pore water. This uncertainty is mitigated, in part, by the fact that these toxicity thresholds explained more than 80% of the variability in the amphipod survival data for sediment samples from the TSMD and provided an accurate basis for classifying sediment samples as toxic or not toxic to amphipods, mussels, and midges (MacDonald *et al.* 2009).

The toxicity thresholds for invertebrate tissues were developed using matching invertebrate-tissue chemistry data and sediment toxicity data from the TSMD. While use of site-specific data increases confidence in the resultant toxicity thresholds, the tissue-chemistry data were for a different species (*Lumbriculus variegatus*) than the toxicity data (*Hyalella azteca*). As the amphipod is an epibenthic species, the tissue-chemistry data for the oligochaete could over-estimate tissue metal levels. As a result, toxicity thresholds based on amphipod tissue concentrations could be lower than those used in the DERA. This represents an uncertainty when the toxicity thresholds are applied to mussel tissues, possibly resulting in under-estimates of risks to benthic invertebrates using the tissue chemistry line-of-evidence.

Indicator species have been used in this investigation to assess the effects of contaminated sediments on the benthic invertebrate community. More specifically, the results of sediment toxicity tests were used to estimate risks to benthic invertebrates in the field. Uncertainties associated with the application of this approach were evaluated by reviewing the results of sediment quality assessments conducted at other sites. This review indicated that the results of whole-sediment toxicity tests are frequently well correlated with results of assessments of benthic invertebrate community structure (Ingersoll and MacDonald 2002; Swartz *et al.* 1994; MacDonald *et al.* 2002a; Hayward 2002). In some cases, adverse effects on the benthic community have been observed at lower levels of contamination than is the case for the whole-sediment toxicity tests (Hyland *et al.* 2002; MacDonald *et al.* 2002b), probably due to the combined effects of physical and chemical stressors. The results of the selected pore-water toxicity tests have also been correlated with adverse effects on sediment-dwelling

organisms (Carr *et al.* 1996). Finally, the concentration-response models that were included in the effects assessment were developed using site-specific data. In this way, the uncertainties associated with extrapolation of the models between areas was avoided. The use of multiple lines-of-evidence also minimizes the potential effects of extrapolation errors on the results of the DERA.

Uncertainty in the exposure and effects assessments for aquatic receptors is also increased by data gaps. To the extent possible, this source of uncertainty was mitigated by collecting detailed information on the effects of COPCs in the TSMD. In addition, the use of multiple lines-of-evidence provides a basis for minimizing the influence of data gaps on the effects assessment. Nevertheless, limitations on certain types of data, pore-water chemistry, invertebrate-tissue chemistry, and benthic invertebrate community structure, makes it difficult to fully evaluate the effects of COPC exposures on benthic invertebrate communities. For this reason, the present assessment could over-estimate or under-estimate risks to the benthic invertebrate community.

Chapter 10 Development of Preliminary Remedial Action Objectives for the Tri-State Mining District

10.0 Introduction

Remedial action objectives (RAOs) provide the foundation upon which remedial alternatives are developed and evaluated. More specifically, RAOs are needed to clearly articulate the intent of any remedial actions that may be undertaken to address risks to human health and/or ecological receptors within the TSMD. Preliminary remediation goals complement the RAOs by defining the concentrations of COPCs and COPC mixtures that need to be achieved in environmental media to reduce such risks to tolerable levels [see MacDonald *et al.* (2009) for information on the technical basis for establishing numerical PRGs for the TSMD; the information presented therein is also relevant for establishing numerical restoration goals for the study area]. Establishment of RAOs, and associated PRGs, represents an essential component of the overall RAP process. Importantly, these tools enable risk managers to evaluate the costs and benefits of pursuing the various remedial alternatives that are proposed for the TSMD. The development of RAOs requires a long-term vision for the future of the water body under consideration that reflects the interests and needs of stakeholders, as articulated in ecosystem goals and objectives. The following describes preliminary RAOs that are proposed for each of the environmental media that have been degraded in association with mining activities within the TSMD, including surface water, sediment, soil, and biological tissues.

10.1 Surface Water

The preliminary RAOs for surface water that address risks to aquatic receptors, aquatic-dependent wildlife, and human health associated with exposure to contaminated surface water are presented below:

- **RAO for aquatic receptors:** Minimize or prevent exposure to surface waters that are sufficiently contaminated to pose moderate or high risks, respectively, to microorganisms, aquatic plants, aquatic invertebrates, fish, or amphibians;
- **RAO for aquatic-dependent wildlife:** Minimize risks to avian, mammalian, or reptilian species associated with direct contact, with ingestion of surface waters, and/or with ingestion of aquatic organisms from the TSMD; and,
- **RAO for humans:** Minimize risks to human health associated with ingestion of surface water (i.e., obtained from public or private water supplies) and/or ingestion of fish from the TSMD. In addition, minimize risks to human health associated with incidental ingestion of surface waters during primary or secondary contact recreation.

10.2 Sediment and Pore Water

The preliminary RAOs for sediment and pore water that address risks to aquatic receptors, aquatic-dependent wildlife, and humans associated with exposure to contaminated sediments are presented below:

- **RAO for aquatic receptors:** Minimize or prevent exposure to sediments and/or pore water that are sufficiently contaminated to pose moderate or high risks, respectively, to microbial, aquatic plant, benthic invertebrate, or fish communities (particularly for fish species that use sediment substrates for spawning);
- **RAO for aquatic-dependent wildlife:** Minimize risks to sediment-probing birds or omnivorous mammals associated with incidental ingestion of sediments during feeding activities; and,
- **RAO for humans:** Minimize risks to human health associated with direct contact with sediments during primary contact recreation (swimming or wading) or maintenance activities (e.g., maintenance utility workers).

10.3 Riparian Soil

The preliminary RAOs for riparian soil that address risks to terrestrial receptors, terrestrial wildlife, and humans associated with direct exposure to contaminated floodplain soils are presented below:

- **RAO for terrestrial receptors:** Minimize or prevent exposure to riparian soils that are sufficiently contaminated to pose moderate or high risks, respectively, to the microbial, terrestrial plant, or terrestrial invertebrate communities;
- **RAO for aquatic-dependent wildlife:** Minimize risks to reptiles, amphibians, birds, or mammals associated with direct exposure to floodplain soils or incidental ingestion of riparian soils during feeding activities; and,
- **RAO for humans:** Minimize risks to human health associated with ingestion of riparian soil, direct contact with riparian soil, or inhalation of dust.

10.4 Biological Tissues

The preliminary RAOs for the tissues of aquatic organisms (i.e., invertebrates and fish) that address risks to fish, aquatic-dependent wildlife, and human health associated with the bioaccumulation of COPCs in the food web are presented below:

- **RAO for fish:** Reduce the concentrations of bioaccumulative COPCs in fish tissues to levels that are not associated with adverse effects on survival, growth, reproduction of fish, or on the incidence of lesions or tumors in fish;
- **RAO for aquatic-dependent wildlife:** Reduce the concentrations of bioaccumulative COPCs in the tissues of prey species (i.e., invertebrates and fish) to levels that do not pose unacceptable risks to insectivorous birds, sediment-probing birds, carnivorous-wading birds, piscivorous birds, omnivorous mammals, or piscivorous mammals; and,
- **RAO for humans:** Minimize or prevent exposure to fish tissues that are sufficiently contaminated to pose unacceptable excess lifetime cancer risks to humans engaging in traditional lifestyles. Additionally, prevent exposure to fish

tissues that are sufficiently contaminated to cause a non-cancer hazard index of greater than one for humans engaging in traditional lifestyles.

Chapter 11 Summary and Conclusions

11.0 Introduction

The Tri-State Mining District (TSMD) is a historical lead and zinc mining area that includes portions of Kansas, Missouri, and Oklahoma. The TSMD was one of the world's foremost lead and zinc mining areas, yielding about 460 million tons of ore between 1885 and 1970 (Black and Veatch Special Projects Corp. 2006). The lead and zinc deposits within the TSMD, an area of about 500 square miles, were associated with the geologic region known as the Ozark Plateau. The ore deposits were typically accessed using underground mining methods, with recovered ore typically crushed on site and concentrated using gravity separation and/or floatation. These two ore-concentration processes resulted in the production of sand- and gravel-sized particles called chat (i.e., coarse tailings) and sand- and silt-sized particles called tailings. Further smelting and refining of these ore concentrates was conducted at various locations within the study area or elsewhere. Historical mining activities in the TSMD have resulted in contamination of surface water, groundwater, sediments, and/or floodplain soils in the Neosho River and Spring River basins by lead, zinc, and other heavy metals.

In response to public concerns regarding the potential for adverse effects on human health and ecological receptors associated with exposure to site-related chemicals of interest (COIs), USEPA and its partners have conducted numerous investigations within the study area to provide the data and information needed to evaluate the nature and extent of contamination in the study area, to assess risks to human health associated with exposure to contaminants, and to evaluate risks to ecological receptors utilizing habitats within the TSMD. This document describes the results of two ecological risk assessments (ERAs) that were conducted to determine if exposure to contaminants in aquatic habitats within the TSMD posed potential risks to ecological receptors, including:

- A screening-level ERA (SLERA) to evaluate potential risks to aquatic organisms utilizing aquatic habitats in the study area; and,
- A detailed ERA (DERA) to assess risks to benthic invertebrates utilizing habitats within the study area.

Together, these two ERAs are referred to as the Advanced SLERA for the TSMD. The Advanced SLERA is not intended to obviate the need for baseline ERAs (BERAs) of the TSMD, but rather to provide risk managers with additional information for identifying in-stream sources of contaminants, evaluating candidate source control measures, and assessing other risk management options in the near term. In addition, the information contained in this document is intended to assist the Natural Resources Trustees in the development of restoration goals for aquatic habitats in the TSMD.

It is important to note that the SLERA and DERA were conducted in general accordance with USEPA (1997a) guidance. Accordingly, the results of these ERAs can be integrated into ongoing remedial investigations (RIs; e.g., those underway in Cherokee, Jasper, and/or Newton counties) and/or RIs that may be conducted in the future (e.g., OU-5 of the Tar Creek Site).

11.1 Study Objectives

The goal of this study was to assess the risks to ecological receptors exposed to environmental media in aquatic habitats within the TSMD. The primary objectives of this study were to:

- Evaluate the potential risks posed to ecological receptors exposed to abiotic media within aquatic habitats in the TSMD (i.e., conduct a SLERA for aquatic habitats);
- Evaluate risks to benthic invertebrates utilizing aquatic habitats in the TSMD (i.e., conduct a DERA for benthic invertebrates);
- Provide the information needed by risk managers to determine the need for additional source control measures and to establish candidate clean-up goals for the site; and,
- Provide the information needed by the Natural Resources Trustees to identify restoration goals for the site.

11.2 Study Approach

A step-wise approach was used to evaluate risks to ecological receptors utilizing aquatic habitats within the TSMD. More specifically, the study approach involved the following steps:

- Compiling information that describes current conditions within the watershed (i.e., data collected between 2002 and 2009; which is considered to represent current conditions);
- Conducting a screening-level problem formulation and ecological effects evaluation;
- Completing a screening-level exposure estimate and risk calculation;
- Developing a detailed problem formulation to support evaluation of risks to the benthic invertebrate community;
- Establishing assessment and measurement endpoints for evaluating risks to the benthic invertebrate community and refining the preliminary analysis plan to direct the risk assessment;
- Evaluating risks to benthic invertebrates using multiple lines-of-evidence; and,
- Formulating preliminary remedial action objectives to guide risk management activities.

These steps are in general accordance with the ERA framework and the eight-step process for conducting an ERA described in *Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessment* (USEPA 1997a). Detailed descriptions of the procedures used in the SLERA are described in Chapters 3 and 4 of this document. Chapters 5, 6, and 7 describe the general approach and detailed procedures that were used in the DERA to evaluate the nature, severity, and areal extent of risks to benthic invertebrates utilizing habitats in the study area. The results of the DERA are presented in Chapter 8, while uncertainties associated with the assessment are discussed in Chapter 9. Preliminary remedial action objectives for the TSMD are presented in Chapter 10. This data compilation and analysis may also be useful to the Natural Resources Trustees as they conduct natural resource damage assessments and evaluate restoration goals.

11.3 Screening-Level Ecological Risk Assessment

A SLERA was conducted to determine if exposure to contaminants in abiotic media poses potential risks to ecological receptors utilizing aquatic habitats in the TSMD. Screening-level problem formulation involved describing the environmental setting, identifying suspected contaminants, evaluating contaminant transport and fate, assessing ecotoxicology, identifying potential receptors and potentially-complete exposure pathways, and establishing assessment and measurement endpoints. Evaluation of the available information indicated that metals (e.g., cadmium, lead, and zinc) were the principal COIs in the study area and that several other substances could be identified as additional COIs [i.e., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides, and various semi-volatile organic compounds (SVOCs)]. The potentially-complete exposure pathways included direct exposure to surface water, sediment, and pore water. As the organisms that utilize aquatic habitats were identified as the receptors potentially at risk, the assessment endpoint that was evaluated in the SLERA included:

- Survival, growth, and reproduction of ecological receptors associated with exposure to contaminants in surface water, sediment, and/or pore water.

Toxicity screening values (TSVs) were identified for each of the three abiotic media types, as part of the screening level ecological effects evaluation. More specifically, ambient water quality criteria (i.e., criteria continuous concentrations; USEPA 1999; 2006a) or functionally-equivalent values (e.g., water quality guidelines; CCME 2002) were selected for evaluating surface-water and pore-water chemistry data. Consensus-based threshold effect concentrations (MacDonald *et al.* 2000a) or sediment quality benchmarks with similar narrative intent (MacDonald *et al.* 2008) were selected to evaluate sediment chemistry data. In all cases, the TSVs that were selected were intended to provide conservative estimates of no observed adverse effect levels (NOAELs) for the COIs.

To support this evaluation, data and information from multiple sources were acquired, reviewed, and evaluated. The data that met the evaluation criteria were compiled in a project database in MS Access format. Following translation into database format, the data were verified using a combination of electronic and manual procedures. Subsequently, the database was audited to identify potential outliers (which were further checked to determine if the data

were correct), assure data completeness, examine qualifier codes, and verify sample identification numbers. The audited watershed database was considered a reliable tool for evaluating risks to ecological receptors in the study area.

Potential exposure of ecological receptors to site-related contaminants was evaluated using data on the concentrations of suspected contaminants in three abiotic media, including surface water, sediment, and pore water. The surface-water chemistry data (n = up to 694, depending on the analyte) provided broad spatial coverage of the study area and were considered to be sufficient to support the SLERA. Similarly, the available sediment-chemistry data (n = up to 1156, depending on the analyte) were considered to provide an adequate basis for assessing the potential risk to ecological receptors. While the data set for pore-water chemistry was limited (n = up to 70, depending on the analyte), the spatial coverage was considered to be sufficient to support a screening-level assessment. For all media types, the exposure point concentration (EPC) was estimated using the highest concentration of each substance measured in the study area (i.e., maximum values; USEPA 1997).

The screening-level risk calculations involved determination of hazard quotients (HQs; where $HQ = EPC \div TSV$) for each contaminant in each environmental medium. An HQ of < 1.0 was considered to indicate that exposure to the measured concentrations of the contaminant or contaminant mixture [e.g., sum equilibrium partitioning-based sediment benchmarks-toxic units ($\sum ESB-TUs$); sum simultaneously extracted metals minus acid volatile sulfides ($\sum SEM-AVS$); USEPA 2003a; 2005] would not pose potential risks to ecological receptors. The results of this evaluation showed that the levels of one or more substances in surface water, sediment, and pore water exceeded the selected TSVs. Therefore, the available information indicated that there was a potential for adverse effects on ecological receptors (via all three of these exposure routes) and that a more thorough assessment was needed to evaluate risks to ecological receptors in the TSMD. The substances that were identified as chemicals of potential concern (COPCs) for further evaluation included metals, PAHs, PCBs, organochlorine pesticides, various SVOCs, and nutrients (i.e., ammonia, chlorine; Table 17).

11.4 Detailed Ecological Risk Assessment for the Benthic Invertebrate Community

The results of the SLERA indicated that the concentrations of contaminants in surface water, sediment, and/or pore water posed potential risks to ecological receptors utilizing aquatic habitats in the TSMD. For this reason, a DERA was undertaken to further evaluate risks to ecological receptors associated with exposure to site-related COPCs in the TSMD. The results of conceptual site modeling indicated that a variety of ecological receptor groups could be adversely affected by exposure to COPCs in aquatic and riparian habitats within the study area, including microbiota, aquatic and terrestrial plants, aquatic and terrestrial invertebrates, fish, amphibians, reptiles, aquatic-dependent birds, and aquatic-dependent mammals. While risks to all of these receptor groups may ultimately need to be evaluated [and, in some cases, were evaluated previously; See Dames and Moore (1993) and Black and Veatch Special Projects Corp. (1998) for additional information], this DERA was focused on evaluating contemporary risks (i.e., 2002 to 2009) to the benthic invertebrate community posed by exposure to COPCs in surface water, sediment, and pore water within the TSMD.

Information on six lines-of-evidence was used to determine if the survival, growth, or reproduction of benthic invertebrates (i.e., the assessment endpoint) have been adversely affected or are likely to have been adversely affected by exposure to contaminated surface water or sediments in the TSMD relative to reference conditions. The six lines-of-evidence that were considered in the assessment included:

- Surface-water chemistry;
- Sediment chemistry;
- Sediment toxicity;
- Pore-water chemistry;
- Invertebrate-tissue chemistry; and,
- Freshwater mussel species richness.

The measurement endpoints in this assessment included: the concentrations of COPCs in surface water; the concentrations of COPCs in sediment; the concentrations of COPCs in pore

water; the survival and biomass of amphipods, *Hyalella azteca*, in 28-d sediment toxicity tests; the survival and biomass of midges, *Chironomus dilutus*, in 10-d sediment toxicity tests; the survival and biomass of freshwater mussels, *Lampsilis siliquoidea*, in 28-d sediment toxicity tests; the concentrations of COPCs in invertebrate tissues, and species richness of freshwater mussels.

Sediment-chemistry data were available for 1162 samples collected within the TSMD. By comparison, surface-water chemistry (n = 537), pore-water chemistry (n = 96), sediment toxicity (n = 76), invertebrate-tissue chemistry (n = 239), mussel taxa richness (n = 16) data were somewhat less robust. Accordingly, sediment chemistry was used as a primary line-of-evidence for evaluating risks to the benthic community. For this line of evidence, risks to benthic invertebrates were evaluated using site-specific toxicity thresholds (SSTTs) derived using matching sediment chemistry and sediment toxicity data from the study area. These SSTTs were demonstrated to provide a reliable basis for classifying sediment samples from the study area as toxic and not toxic.

The results of this assessment indicated that exposure to COPCs in sediment from the TSMD posed low risks to benthic invertebrate communities at 51% of the locations (596 of 1162) that were sampled within the study area (Figure 63; Table 38). By comparison, the concentrations of cadmium, lead, and/or zinc in surficial sediments were sufficient to pose moderate risks to benthic invertebrates at about 9% (110 of 1162) of the sampling stations within the TSMD. High risks to the benthic invertebrate community were indicated for 39% (456 of 1162) of the locations sampled (Table 38). Of the 23 areas of interest (AoIs) that were evaluated, the locations with the highest proportions of sediment samples with COPC concentrations sufficient to pose high risks to the benthic invertebrate community were [note: sediment samples with sum probable effects concentration quotients for cadmium, lead, zinc ($\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$) of > 10.04 were classified as posing high risks to benthic invertebrates]:

- Short Creek AoI (100%; 44 of 44 samples);
- Middle Tar Creek AoI (100%; 52 of 52 samples);
- Lytle Creek AoI (95%; 39 of 41 samples);
- Empire Lake AoI (93%; 38 of 41 samples);
- Spring Brook AoI (93%; 14 of 15 samples);

- Elm Creek AoI (85%; 22 of 26 samples);
- Turkey Creek AoI (83; 40 of 48 samples);
- Lower Tar Creek AoI (81%; 88 of 108 samples);
- Beaver Creek AoI (51%; 33 of 65 samples);
- Shoal Creek AoI (49%; 55 of 112 samples);
- Lower Spring River AoI (48%; 32 of 66 samples);
- Willow Creek AoI (47%; 14 of 30 samples);
- Center Creek AoI (46%; 37 of 81 samples);
- Middle Spring River AoI (23%; 27 of 115 samples); and
- Upper Tar Creek AoI (21%; 8 of 39 samples).

Risks to the benthic invertebrate community were classified as moderate in the Cow Creek AoI [predicted incidence of toxicity (PIoT) of 15%; n = 34], Brush Creek AoI (PIoT of 14%; n = 14), and Lost Creek AoI PIoT of 12%; n = 33). The remaining AoIs (i.e., Upper Spring River, North Fork Spring River, Shawnee Creek, Warren Branch, and Neosho River) were all classified as posing low risks to benthic invertebrates, based on the measured concentrations of cadmium, lead, and zinc in surficial sediment samples (i.e., \sum PEC- $Q_{Cd,Pb,Zn}$; Table 38). Risks to the benthic invertebrate community were considered to be low for all of the reference sediment samples (Table 38). It is important to note that sediment hot spots may exist within AoIs that are considered to pose low risks to benthic invertebrates based on the frequency of exceedance of the selected toxicity thresholds.

Evaluation of the other five lines-of-evidence also indicated that risks to benthic invertebrates are elevated at numerous locations within the study area. More specifically, the available data confirmed that exposure to divalent metals in surface water posed moderate or high risks to benthic invertebrates in 17 of the 23 AoIs examined (Table 37; Figure 62). Similarly, examination of the available pore-water chemistry data indicated that exposure to a primary risk driver (zinc) posed moderate or high risks in 12 of the 23 AoIs (Table 39; Figure 43). Furthermore, the incidence of toxicity to amphipods, midges, or mussels in laboratory toxicity tests (endpoints: survival or biomass) exceeded 50% in 8 of the 23 AoIs within the study area (Table 40; Figures 34, 44, 45, 55). By comparison, invertebrate-tissue samples in 9 of the 16

AoIs had concentrations of metals sufficient to pose moderate or high risks to benthic invertebrates (Table 41; Figure 65). Finally, Angelo *et al.* (2007) reported that streams draining heavily mined areas exhibited depauperate (or fully extirpated) native mussel assemblages and correspondingly elevated concentrations of cadmium, lead, and zinc in water, sediment, and bivalve tissue. Collectively, these five additional lines-of-evidence confirmed that exposure to metal-contaminated surface water, sediment, and pore water posed elevated risks to benthic invertebrates throughout a large portion of the TSMD (Table 54).

The results of the biological investigations conducted during site investigations indicated that surface-water ($\sum TU_{\text{DIVALENT METALS}}$), sediment (i.e., $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$), pore-water (i.e., PW-TU_{Zn}), or invertebrate-tissue ($\sum \text{Metals-TUs}$) chemistry data provided reliable bases for classifying risks to benthic invertebrates in the TSMD (MacDonald *et al.* 2009; Tables 44 to 47). More specifically, these results showed that the magnitude of effects tended to increase with increasing risk to the benthic invertebrate community. For example, the survival of amphipods was lower for the locations that were designated as posing moderate and high risks than was the case for the locations that were classified as posing low risk to benthic invertebrates or those that were designated as reference sediment samples (Table 45). Likewise, the survival and biomass of midges and freshwater mussels tended to be lowest in the samples that were classified as posing high risks to the benthic invertebrate community (Table 45). Importantly, species richness of freshwater mussels was lowest in the locations that had the highest concentrations of metals in sediments (as measured by mean $\text{PEC-Q}_{\text{Cd,Pb,Zn}}$; Table 45). Together, these results implied that the survival and biomass of benthic invertebrates have been impaired in response to exposure to contaminated sediments in the TSMD. As the reproduction of benthic invertebrates is highly correlated with growth or biomass, it is likely that benthic invertebrate reproduction has also been adversely affected in the study area. These results also indicated that the low risk thresholds utilized in the DERA would provide a relevant basis for establishing restoration goals for the TSMD.

The results of this assessment indicated that a number of substances are causing or substantially contributing to adverse effects on the benthic invertebrate community in the TSMD (i.e., relative to reference conditions). More specifically, cadmium, lead, and zinc were identified as the primary contaminants of concern (COCs) in the study area. Several other metals may also be contributing to adverse effects on benthic invertebrates, including chromium, copper, mercury, and nickel. In certain locations (e.g., Turkey Creek), it is

possible that PAHs may be contributing to sediment toxicity and other adverse effects on the benthic invertebrate community.

11.5 Conclusions

In general accordance with USEPA (1997a) guidance, two ERAs of the TSMD were conducted following an eight-step process (See Appendix 1 for more information). These ERAs consisted of a SLERA for aquatic habitats and a DERA for the benthic invertebrate community. The results of the SLERA indicated that the presence of contaminants in surface water, sediment, and/or pore water posed potential risks to ecological receptors. Accordingly, risks to the benthic invertebrate community were further evaluated in the DERA. The results of the detailed assessment indicated that exposure to metals in sediment posed moderate or high risks to benthic invertebrates at about 78% of the locations that have been sampled in the study area (Table 38). The available surface-water chemistry, pore-water chemistry, sediment toxicity, invertebrate-tissue chemistry and freshwater mussel species richness data confirm that elevated risks to benthic invertebrates occurred in many AoIs within the TSMD (Tables 47, 54). Cadmium, lead, and zinc were identified as the primary COCs in the TSMD, with chromium, copper, mercury, nickel, and/or silver likely contributing to adverse effects on benthic invertebrates. The information provided by the SLERA, DERA, and companion documents (i.e., Ingersoll *et al.* 2008; MacDonald *et al.* 2009) is intended to support decisions regarding the need for remedial actions, including source control and other early action, within the Spring River and Neosho River watersheds. This data compilation and analysis may also be useful to the Natural Resources Trustees as they conduct natural resource damage assessments and evaluate restoration goals.

Chapter 12 References

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Tables

Table 1. Listing of chemicals of interest in surface water, pore water, sediment, and biological tissues in the Tri-State Mining District.

Chemicals of Interest	Surface and Pore Water	Sediment	Tissue
<i>Metals</i>			
Aluminum	Y	Y	N
Arsenic	Y	Y	N
Barium	Y	N	N
Cadmium	Y	Y	Y
Chromium	Y	Y	N
Cobalt	Y	Y	N
Copper	Y	Y	Y
Iron	Y	Y	N
Lead	Y	Y	Y
Mercury	Y	Y	Y
Molybdenum	Y	Y	N
Nickel	Y	Y	N
Selenium	Y	Y	N
Silver	Y	Y	N
Zinc	Y	Y	Y
<i>Polycyclic Aromatic Hydrocarbons (PAHs)</i>			
2-Methylnaphthalene	N	Y	N
Acenaphthene	N	Y	N
Acenaphthylene	N	Y	N
Anthracene	N	Y	N
Benz(<i>a</i>)anthracene	N	Y	Y
Benzo(<i>a</i>)pyrene	N	Y	Y
Benzo(<i>b</i>)fluoranthene	N	Y	Y
Benzo(<i>g,h,i</i>)perylene	N	Y	Y
Benzo(<i>k</i>)fluoranthene	N	Y	Y
Biphenyl	N	Y	N
Carbazole	N	Y	N
Chrysene	N	Y	N
Dibenz(<i>a,h</i>)anthracene	N	Y	Y
Dibenzofuran	N	Y	N
Fluoranthene	N	Y	N
Fluorene	N	Y	N
Indeno(1,2,3- <i>c,d</i>)pyrene	N	Y	N
Naphthalene	N	Y	N
Phenanthrene	N	Y	N
Pyrene	N	Y	N
PAHs, total high molecular weight PAHs	N	Y	Y
PAHs, total low molecular weight PAHs	N	Y	N
PAHs, total	N	Y	N

Table 1. Listing of chemicals of interest in surface water, pore water, sediment, and biological tissues in the Tri-State Mining District.

Chemicals of Interest	Surface and Pore Water	Sediment	Tissue
<i>Polychlorinated Biphenyls (PCBs)</i>			
Aroclor 1016	N	Y	Y
Aroclor 1221	N	Y	Y
Aroclor 1232	N	Y	Y
Aroclor 1242	N	Y	Y
Aroclor 1248	N	Y	Y
Aroclor 1254	N	Y	Y
Aroclor 1260	N	Y	Y
Aroclor 1262	N	Y	Y
Aroclor 1268	N	Y	Y
PCBs, total	N	Y	Y
<i>Organochlorine Pesticides</i>			
Aldrin	N	Y	Y
Chlordane, cis-	N	Y	Y
Chlordane, trans-	N	Y	Y
Dieldrin	N	Y	Y
Endosulfan sulfate	N	Y	Y
Endosulfan-alpha	N	Y	Y
Endosulfan-beta	N	Y	Y
Endrin	N	Y	Y
Endrin aldehyde	N	Y	Y
Endrin ketone	N	Y	Y
Heptachlor	N	Y	Y
Heptachlor epoxide	N	Y	Y
Hexachlorobenzene	N	Y	Y
Hexachlorocyclohexane-alpha	N	Y	Y
Hexachlorocyclohexane-beta	N	Y	Y
Hexachlorocyclohexane-delta	N	Y	Y
Hexachlorocyclohexane-gamma	N	Y	Y
Hexachlorocyclopentadiene	N	Y	Y
Isophorone	N	Y	Y
Methoxychlor	N	Y	Y
<i>p,p'</i> -DDD	N	Y	Y
<i>p,p'</i> -DDE	N	Y	Y
<i>p,p'</i> -DDT	N	Y	Y
Toxaphene	N	Y	Y
<i>Semi-Volatile Compounds</i>			
1,2,4-Trichlorobenzene	N	Y	N
1,2-Dichlorobenzene	N	Y	N
1,3-Dichlorobenzene	N	Y	N
1,4-Dichlorobenzene	N	Y	N
2,4,5-Trichlorophenol	N	Y	N
2,4,6-Trichlorophenol	N	Y	N

Table 1. Listing of chemicals of interest in surface water, pore water, sediment, and biological tissues in the Tri-State Mining District.

Chemicals of Interest	Surface and Pore Water	Sediment	Tissue
<i>Semi-Volatile Compounds (cont.)</i>			
2,4-Dichlorophenol	N	Y	N
2,4-Dimethylphenol	N	Y	N
2,4-Dinitrophenol	N	Y	N
2,4-Dinitrotoluene	N	Y	N
2,6-Dinitrotoluene	N	Y	N
2-Chloronaphthalene	N	Y	N
2-Chlorophenol	N	Y	N
2-Methylphenol	N	Y	N
2-Nitroaniline	N	Y	N
2-Nitrophenol	N	Y	N
3-Methylphenol and 4 Methylphenol	N	Y	N
3,3'-Dichlorobenzidine	N	Y	N
3-Nitroaniline	N	Y	N
4-Bromophenyl phenyl ether	N	Y	N
4-Chloro-3-methylphenol	N	Y	N
4-Chloroaniline	N	Y	N
4-Chlorophenyl phenyl ether	N	Y	N
4-Nitroaniline	N	Y	N
4-Nitrophenol	N	Y	N
Acetophenone	N	Y	N
Atrazine	N	Y	N
Benzaldehyde	N	Y	N
Benzoic acid	N	Y	N
Benzyl alcohol	N	Y	N
bis(2-chloroethoxy)methane	N	Y	N
bis(2-chloroethyl)ether	N	Y	N
bis(2-chloroisopropyl) ether	N	Y	N
bis(2-ethylhexyl) phthalate	N	Y	Y
Butylbenzyl phthalate	N	Y	Y
Caprolactam	N	Y	N
Diethyl phthalate	N	Y	Y
Dimethyl phthalate	N	Y	Y
Di- <i>n</i> -butyl phthalate	N	Y	Y
Dinitro- <i>o</i> -cresol	N	Y	N
Di- <i>n</i> -octyl phthalate	N	Y	Y
Hexachlorobutadiene	N	Y	Y
Hexachloroethane	N	Y	N
<i>n</i> -nitrosodi- <i>n</i> -propylamine	N	Y	N
<i>n</i> -nitrosodiphenylamine	N	Y	N
Nitrobenzene	N	Y	N
Pentachlorophenol	N	Y	Y
Phenol	N	Y	N

Table 1. Listing of chemicals of interest in surface water, pore water, sediment, and biological tissues in the Tri-State Mining District.

Chemicals of Interest	Surface and Pore Water	Sediment	Tissue
<i>Nutrients/Inorganics/Conventional</i>			
Ammonia	Y	N	N
Chlorine	Y	N	N
Nitrate, dissolved, NO ₃ ⁻ N	Y	N	N
Nitrate, total, NO ₃ ⁻ N	Y	N	N

Y = yes; N = no.

Table 2. Listing of classes of chemicals of interest in surface water, pore water, sediment, and biological tissues in the Tri-State Mining District.

Classes of Chemicals of Interest	Surface and Pore Water	Sediment	Tissue
Metals	Y	Y	Y
Polycyclic Aromatic Hydrocarbons	N	Y	Y
Polychlorinated Biphenyls	N	Y	Y
Organochlorine Pesticides	N	Y	Y
Semi-Volatile Compounds	N	Y	Y
Nutrients/Inorganics/Conventionals	Y	N	N

Y = yes; N = no.

Table 3. Summary of candidate and selected toxicity screening values for evaluating surface-water and pore-water chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Water Quality Criteria^{1,2}	Draft Freshwater Benchmarks³	Selected Toxicity Screening Value for Water
<i>Metals (µg/L)⁴</i>			
Aluminum	87	88.4	87
Arsenic	150	154	150
Barium	NB	1000 ⁵	1000
Cadmium	0.25	0.39	0.25
Chromium, III	74	79.2	74
Chromium	NB	2 ^{6,7}	2
Chromium, VI	11	10.8	10.8
Cobalt	NB	5 ⁸	5
Copper	9	4.17	4.17
Iron	1000	887	887
Lead	2.5	1.16	1.16
Mercury	0.77	0.182	0.182
Molybdenum	NB	395	395
Nickel	52	60.5	52
Selenium	5.0	4.96	4.96
Silver	0.32 ⁹	0.098	0.098
Thallium	NB	9.85	9.85
Tin	NB	84.8	84.8
Uranium	NB	2.6	2.6
Vanadium	NB	17.7	17.7
Zinc	120	60.8	60.8
<i>Organometallics (µg/L)</i>			
Methylmercury	NB	0.00277	0.00277
Tributyltin	0.072	0.0465	0.0465
Triphenyltin	NB	0.0223	0.0223
<i>Polycyclic Aromatic Hydrocarbons (PAHs; µg/L)</i>			
2-Methylnaphthalene	NB	31.2	31.2
2-Nitroaniline	NB	NB	NB
3,3'-Dichlorobenzidine	NB	NB	NB
3-Nitroaniline	NB	NB	NB
4-Nitroaniline	NB	NB	NB
Acenaphthene	NB	21.9	21.9
Acenaphthylene	NB	168	168
Anthracene	NB	0.391	0.391
Benz(<i>a</i>)anthracene	NB	0.0754	0.0754
Benzo(<i>a</i>)pyrene	NB	0.014	0.014
Benzo(<i>b</i>)fluoranthene	NB	0.495	0.495
Benzo(<i>g,h,i</i>)perylene	NB	7.64	7.64

Table 3. Summary of candidate and selected toxicity screening values for evaluating surface-water and pore-water chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Water Quality Criteria^{1,2}	Draft Freshwater Benchmarks³	Selected Toxicity Screening Value for Water
<i>PAHs (µg/L; cont.)</i>			
Benzo(<i>k</i>)fluoranthene	NB	0.027	0.027
Biphenyl	NB	14	14
Carbazole	NB	NB	NB
Chrysene	NB	0.172	0.172
Dibenz(<i>a,h</i>)anthracene	NB	0.367	0.367
Fluoranthene	NB	8.35	8.35
Fluorene	NB	4.23	4.23
Indeno(1,2,3- <i>c,d</i>)pyrene	NB	0.341	0.341
Naphthalene	NB	23.9	23.9
Phenanthrene	NB	11.5	11.5
Pyrene	NB	1.3	1.3
Total PAHs	NB	NB	NB
<i>Polychlorinated Biphenyls (PCBs; µg/L)</i>			
Aroclor 1016	NB	0.014	0.014
Aroclor 1221	NB	0.132	0.132
Aroclor 1232	NB	0.229	0.229
Aroclor 1242	NB	0.038	0.038
Aroclor 1248	NB	0.0522	0.0522
Aroclor 1254	NB	0.0266	0.0266
Aroclor 1260	NB	3.56	3.56
Aroclor 1262	NB	NB	NB
Aroclor 1268	NB	NB	NB
Total PCBs	0.014	0.00473	0.00473
<i>Organochlorine Pesticides (µg/L)</i>			
Aldrin	0.3 ⁹	0.663	0.3
Chlordane	0.0043	0.00427	0.00427
Dieldrin	0.056	0.0123	0.0123
Endosulfan sulfate	NB	0.0555 ¹¹	0.0555
Endosulfan-alpha	0.056	0.0555	0.0555
Endosulfan-beta	0.056	0.0555	0.0555
Endrin	0.036	0.0176	0.0176
Endrin aldehyde	NB	13.5	13.5
Endrin ketone	NB	NB	NB
Heptachlor	0.0038	0.00403	0.0038
Heptachlor epoxide	0.0038	0.0038	0.0038
Hexachlorobenzene	NB	0.00692	0.00692
Hexachlorocyclohexane-alpha	NB	32.2	32.2
Hexachlorocyclohexane-beta	NB	41.3	41.3
Hexachlorocyclohexane-delta	NB	237	237
Hexachlorocyclohexane-gamma	0.095 ⁹	0.154	0.095

Table 3. Summary of candidate and selected toxicity screening values for evaluating surface-water and pore-water chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Water Quality Criteria^{1,2}	Draft Freshwater Benchmarks³	Selected Toxicity Screening Value for Water
<i>Organochlorine Pesticides (µg/L; cont.)</i>			
Hexachlorocyclopentadiene	NB	NB	NB
Isophorone	NB	NB	NB
Kepon	NB	0.132	0.132
Methoxychlor	0.03	0.0276	0.0276
Mirex	0.001	0.001	0.001
<i>p,p'</i> -DDD	NB	0.00548	0.00548
<i>p,p'</i> -DDE	NB	0.141	0.141
<i>p,p'</i> -DDT	0.001	0.000823	0.000823
Toxaphene	0.0002	0.000373	0.0002
<i>Semi-Volatile Compounds (µg/L)</i>			
1,2,3,4-Tetrachlorobenzene	NB	1.8	1.8
1,2,3-Trichlorobenzene	NB	8	8
1,2,4-Trichlorobenzene	NB	61.7	61.7
1,2-Benzenedicarboxylic acid, dihexyl ester	NB	NB	NB
1,2-Dichlorobenzene	NB	18.4	18.4
1,3-Dichlorobenzene	NB	59	59
1,4-Dichlorobenzene	NB	16.9	16.9
2,3,4,6-Tetrachlorophenol	NB	1.2	1.2
2,3,6-Trichlorophenol	NB	NB	NB
2,4,5-Trichlorophenol	NB	64	64
2,4,6-Trichlorophenol	NB	NB	NB
2,4-Dichlorophenol	NB	34	34
2,4-Dimethylphenol	NB	NB	NB
2,4-Dinitrophenol	NB	NB	NB
2,4-Dinitrotoluene	NB	NB	NB
2,6-Dichlorophenol	NB	NB	NB
2,6-Dinitrotoluene	NB	NB	NB
2-Chloronaphthalene	NB	NB	NB
2-Chlorophenol	NB	43	43
2-Methylphenol	NB	NB	NB
2-Nitrophenol	NB	NB	NB
3&4 Methylphenol	NB	NB	NB
4-Bromophenyl phenyl ether	NB	NB	NB
4-Chloro-3-methylphenol	NB	NB	NB
4-Chloroaniline	NB	NB	NB
4-Chlorophenol	NB	NB	NB
4-Chlorophenyl phenyl ether	NB	NB	NB
4-Nitrophenol	NB	NB	NB
Acetophenone	NB	NB	NB
Aldicarb	NB	1	1
Atrazine	NB	1.8	1.8

Table 3. Summary of candidate and selected toxicity screening values for evaluating surface-water and pore-water chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Water Quality Criteria^{1,2}	Draft Freshwater Benchmarks³	Selected Toxicity Screening Value for Water
<i>Semi-Volatile Compounds (µg/L; cont.)</i>			
Azinphos methyl	NB	0.00926	0.00926
Benzaldehyde	NB	NB	NB
Benzoic acid	NB	NB	NB
Benzyl alcohol	NB	NB	NB
bis(2-chloroethoxy)methane	NB	NB	NB
bis(2-chloroethyl)ether	NB	NB	NB
bis(2-chloroisopropyl) ether	NB	NB	NB
bis(2-ethylhexyl) phthalate	NB	1.66	1.66
Bromacil	NB	5	5
Bromoxynil	NB	5	5
Butylbenzyl phthalate	NB	24.2	24.2
Caprolactam	NB	NB	NB
Captan	NB	1.3	1.3
Carbaryl	NB	0.2	0.2
Carbofuran	NB	1	1
Chlorobenzene	NB	57	57
Chlorothalonil	NB	0.18	0.18
Chlorpyrifos	0.041	0.041	0.041
Cyanazine	NB	2	2
Demeton-A/B	NB	0.1	0.1
Demeton-O	NB	NB	NB
Demeton-S	NB	NB	NB
Dicamba	NB	10	10
Diethyl phthalate	NB	293	293
Dimethoate	NB	6.2	6.2
Dimethyl phthalate	NB	330	330
Di- <i>n</i> -butyl phthalate	NB	17.4	17.4
Di- <i>n</i> -octyl phthalate	NB	94.8	94.8
Dinoseb	NB	0.48	0.48
Ethyl parathion	NB	0.013	0.013
Ethylbenzene	NB	38.7	38.7
Glyphosate	NB	65	65
Hexachlorobutadiene	NB	0.584	0.584
Hexachloroethane	NB	NB	NB
Linuron	NB	7	7
Malathion	0.1	0.0792	0.0792
<i>m</i> -Cresol	NB	62	62
Metolachlor	NB	7.8	7.8
Metribuzin	NB	1	1
<i>n</i> -nitrosodi- <i>n</i> -propylamine	NB	NB	NB
<i>n</i> -nitrosodiphenylamine	NB	NB	NB
<i>o</i> -Cresol	NB	35.9	35.9
<i>p</i> -Cresol	NB	195	195

Table 3. Summary of candidate and selected toxicity screening values for evaluating surface-water and pore-water chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Water Quality Criteria^{1,2}	Draft Freshwater Benchmarks³	Selected Toxicity Screening Value for Water
<i>Semi-Volatile Compounds (µg/L; cont.)</i>			
Pentachlorobenzene	NB	0.564	0.564
Pentachlorophenol	15	2.9	2.9
Phenol	NB	182	182
Picloram	NB	29	29
Simazine	NB	10	10
Styrene	NB	137	137
Tebuthiuron	NB	1.6	1.6
Trifluralin	NB	0.2	0.2
<i>Volatile Organic Compounds (µg/L)</i>			
1,1,1-Trichloroethane	NB	60.5	60.5
1,1,2,2-Tetrachloroethane	NB	378	378
1,2-Dichloroethane	NB	1340	1340
Acetone	NB	3470	3470
Aniline	NB	4.1	4.1
Benzene	NB	64.8	64.8
Carbon tetrachloride	NB	34.1	34.1
Chloroform	NB	80.6	80.6
Ethanol	NB	NB	NB
Ethyl acetate	NB	NB	NB
Methanol	NB	NB	NB
Methyl ethyl ketone	NB	10200	10200
Methylene chloride	NB	1640	1640
<i>m</i> -Xylene	NB	1.8	1.8
<i>o</i> -Xylene	NB	NB	NB
<i>p</i> -Dioxane	NB	22000	22000
<i>p</i> -Xylene	NB	NB	NB
Tetrachloroethene	NB	101	101
Toluene	NB	62.9	62.9
Trichloroethene	NB	98.4	98.4
Vinyl chloride	NB	2290	2290
<i>Dioxins and Furans (µg/L)</i>			
2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin	NB	0.000000392	0.000000392
<i>Nutrients/Inorganics/Conventionals (µg/L)</i>			
Ammonia	NB	3.87	3.87
Chloride	230000	230000	230000
Chlorine	11	10.1	10.1
Cyanide	5.2	5.55 ¹⁰	5.2
Hydrogen sulfide	2	2	2

Table 3. Summary of candidate and selected toxicity screening values for evaluating surface-water and pore-water chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Water Quality Criteria^{1,2}	Draft Freshwater Benchmarks³	Selected Toxicity Screening Value for Water
<i>Nutrients/Inorganics/Conventional (µg/L; cont.)</i>			
Nitrate	NB	13000	13000
Nitrite	NB	60	60
Perchlorate	NB	NB	NB
Sulfate	NB	NB	NB

NB = no benchmark; WQC = water quality criterion; TSV = Toxicity Screening Value.

¹WQC is a Criterion Continuous Concentration unless otherwise noted.

²The current national WQC (USEPA 2006a) for metals were used to evaluate surface and pore-water chemistry data. The Criterion Continuous Concentrations were used, assuming water hardness of 100 mg/L, except for molybdenum, silver, thallium, tin, uranium, and vanadium.

³TSVs as compiled by MacDonald *et al.* (2008), unless otherwise indicated.

⁴Metal TSVs were specified in MacDonald *et al.* (2008) and in USEPA (2006a) for the dissolved fraction of metals in fresh

⁵TSV from BCMOE (1998; 2001).

⁶TSV from Nagpal *et al.* (1995).

⁷The TSV for chromium is applied to the total fraction in Nagpal *et al.* (1995) .

⁸TSV from NYSDEC (2008).

⁹The Criterion Maximum Concentration (USEPA 2006a) divided by 10 was used to estimate a CCC for assessing the surface and pore-water chemistry data for silver.

¹⁰Cyanide in labile form.

¹¹Colorado Department of Public Health and Environment 2007

Table 4. Summary of candidate and selected toxicity screening values for evaluating sediment chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Threshold Effect Concentration¹	Draft Freshwater Sediment Benchmarks²	Selected Toxicity Screening Value for Sediment
<i>Metals (mg/kg)</i>			
Aluminum	NB	15900 ³	15900
Antimony	NB	0.4 ⁴	0.4
Arsenic	9.79	7.15	7.15
Barium	NB	20 ⁵	20
Beryllium	NB	0.46 ⁴	0.46
Cadmium	0.99	0.991	0.99
Chromium	43.4	20.2	20.2
Cobalt	NB	50 ⁶	50
Copper	31.6	25.2	25.2
Iron	NB	190000 ⁷	190000
Lead	35.8	35.3	35.3
Magnesium	NB	NB	NB
Manganese	NB	NB	NB
Mercury	0.18	0.158	0.158
Molybdenum	NB	NB	NB
Nickel	22.7	18.7	18.7
Potassium	NB	NB	NB
Selenium	NB	0.2 ⁸	0.2
Silver	NB	0.73 ⁹	0.73
Sodium	NB	NB	NB
Thallium	NB	NB	NB
Tin	NB	NB	NB
Uranium	NB	NB	NB
Vanadium	NB	NB	NB
Zinc	121	124	121
<i>Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg)</i>			
2-Methylnaphthalene	NB	114 ⁸	114
Acenaphthene	NB	98.3	98.3
Acenaphthylene	NB	78.3	78.3
Anthracene	57.2	151	57.2
Benz(<i>a</i>)anthracene	108	132	108
Benzo(<i>a</i>)pyrene	150	205	150
Benzo(<i>b</i>)fluoranthene	NB	4740	4740
Benzo(<i>g,h,i</i>)perylene	NB	252	252
Benzo(<i>k</i>)fluoranthene	NB	139	139
Biphenyl	NB	1100	1100
Carbazole	NB	923 ⁴	923

Table 4. Summary of candidate and selected toxicity screening values for evaluating sediment chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Threshold Effect Concentration¹	Draft Freshwater Sediment Benchmarks²	Selected Toxicity Screening Value for Sediment
<i>PAHs (µg/kg; cont.)</i>			
Chrysene	166	195	166
Dibenz(<i>a,h</i>)anthracene	33	59.6	33
Dibenzofuran	NB	150 ¹⁰	150
Fluoranthene	423	505	423
Fluorene	77.4	84.1	77.4
Indeno(1,2,3- <i>c,d</i>)pyrene	NB	193	193
Naphthalene	176	176	176
Nitrobenzene	NB	1650 ¹¹	1650
Phenanthrene	204	234	204
Pyrene	195	360	195
Total High Molecular Weight PAHs	NB	655 ⁹	655
Total Low Molecular Weight PAHs	NB	312 ⁹	312
Total PAHs	1610	NB	1610
<i>Polychlorinated Biphenyls (PCBs; µg/kg)</i>			
Aroclor 1016	59.8	4.42	4.42
Aroclor 1221	59.8	98.8	59.8
Aroclor 1232	59.8	600	59.8
Aroclor 1242	59.8	170	59.8
Aroclor 1248	59.8	30	30
Aroclor 1254	59.8	60	59.8
Aroclor 1260	59.8	5	5
Aroclor 1262	59.8	NB	59.8
Aroclor 1268	59.8	NB	59.8
Total PCBs	59.8	40.4	40.4
<i>Organochlorine Pesticides (µg/kg)</i>			
Aldrin	NB	2	2
Atrazine	NB	0.3 ¹²	0.3
Chlordane, cis-	3.24	NB	3.24
Chlordane, trans-	NB	2.62	2.62
Dieldrin	1.9	4.93	1.9
Endosulfan sulfate	NB	NB	NB
Endosulfan-alpha	NB	2.97	2.97
Endosulfan-beta	NB	9.43	9.43
Endrin	2.22	4.6	2.22
Endrin aldehyde	2.22	480	2.22
Endrin ketone	2.22	NB	2.22
Heptachlor	NB	5.37	5.37
Heptachlor epoxide	2.47	1.73	1.73
Hexachlorobenzene	NB	55.2	55.2

Table 4. Summary of candidate and selected toxicity screening values for evaluating sediment chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Threshold Effect Concentration¹	Draft Freshwater Sediment Benchmarks²	Selected Toxicity Screening Value for Sediment
<i>Organochlorine Pesticides (µg/kg; cont.)</i>			
Hexachlorocyclohexane-alpha	NB	6	6
Hexachlorocyclohexane-beta	NB	5	5
Hexachlorocyclohexane-delta	NB	71500	71500
Hexachlorocyclohexane-gamma	2.37	2.33	2.33
Hexachlorocyclopentadiene	NB	7 ¹³	7
Isophorone	NB	2400 ¹¹	2400
Kepone	NB	3.31	3.31
Methoxychlor	NB	14.1	14.1
Mirex	NB	7	7
<i>p,p'</i> -DDD	NB	5.09	5.09
<i>p,p'</i> -DDE	NB	2.61	2.61
<i>p,p'</i> -DDT	NB	2.66	2.66
Sum DDD	4.88	NB	4.88
Sum DDE	3.16	NB	3.16
Sum DDT	4.16	NB	4.16
Total DDTs	5.28	NB	5.28
Toxaphene	NB	2.79	2.79
<i>Semi-Volatile Compounds (µg/kg)</i>			
1,2,4-Trichlorobenzene	NB	8160	8160
1,2-Dichlorobenzene	NB	173	173
1,3-Dichlorobenzene	NB	1610	1610
1,4-Dichlorobenzene	NB	247	247
2,3,4,6-Tetrachlorophenol	NB	129	129
2,4,5-Trichlorophenol	NB	3 ⁵	3
2,4,6-Trichlorophenol	NB	6 ⁵	6
2,4-Dichlorophenol	NB	81.7	81.7
2,4-Dimethylphenol	NB	29 ¹⁴	29
2,4-Dinitrophenol	NB	NB	NB
2,4-Dinitrotoluene	NB	NB	NB
2,6-Dinitrotoluene	NB	NB	NB
2-Chloronaphthalene	NB	NB	NB
2-Chlorophenol	NB	31.9	31.9
2-Methylphenol	NB	NB	NB
2-Nitroaniline	NB	NB	NB
2-Nitrophenol	NB	NB	NB
3-3'-Dichlorobenzidine	NB	0.28 ¹²	0.28
3-Nitroaniline	NB	NB	NB
3&4 Methylphenol	NB	NB	NB
4-Bromophenyl phenyl ether	NB	NB	NB

Table 4. Summary of candidate and selected toxicity screening values for evaluating sediment chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Threshold Effect Concentration¹	Draft Freshwater Sediment Benchmarks²	Selected Toxicity Screening Value for Sediment
<i>Semi-Volatile Compounds (µg/kg; cont.)</i>			
4-Chloro-3-methylphenol	NB	NB	NB
4-Chloroaniline	NB	NB	NB
4-Chlorophenyl phenyl ether	NB	NB	NB
4-Nitroaniline	NB	NB	NB
4-Nitrophenol	NB	NB	NB
Acetophenone	NB	NB	NB
Azinphos methyl	NB	0.01	0.01
Benzaldehyde	NB	NB	NB
Benzoic acid	NB	650 ¹⁴	650
Benzyl alcohol	NB	57 ¹⁴	57
bis(2-chloroethoxy)methane	NB	NB	NB
bis(2-chloroethyl)ether	NB	NB	NB
bis(2-chloroisopropyl) ether	NB	NB	NB
bis(2-ethylhexyl) phthalate	NB	182 ⁹	182
Butylbenzyl phthalate	NB	49 ¹⁴	49
Caprolactam	NB	NB	NB
Carbofuran	NB	2	2
Chlorobenzene	NB	363	363
Chlorpyrifos	NB	53	53
Diethyl phthalate	NB	610 ¹⁴	610
Dimethyl phthalate	NB	530 ¹⁴	530
Di- <i>n</i> -butyl phthalate	NB	42 ¹⁵	42
Dinitro- <i>o</i> -cresol	NB	0.184 ¹²	0.184
Di- <i>n</i> -octyl phthalate	NB	580 ¹⁴	580
Ethyl parathion	NB	0.757	0.757
Hexachlorobutadiene	NB	20.5	20.5
Hexachloroethane	NB	1.4 ¹²	1.4
<i>m</i> -Cresol	NB	52.4	52.4
<i>o</i> -Cresol	NB	31.6	31.6
<i>p</i> -Cresol	NB	333	333
Malathion	NB	0.495	0.495
<i>n</i> -nitrosodi- <i>n</i> -propylamine	NB	NB	NB
<i>n</i> -nitrosodiphenylamine	NB	110 ¹⁴	110
Pentachlorophenol	NB	733	733
Phenol	NB	66.7	66.7

Table 4. Summary of candidate and selected toxicity screening values for evaluating sediment chemistry from the Tri-State Mining District.

Chemical of Interest/ Chemical of Interest Mixture	Threshold Effect Concentration¹	Draft Freshwater Sediment Benchmarks²	Selected Toxicity Screening Value for Sediment
<i>Volatile Organic Compounds (µg/kg)</i>			
1,1,1-Trichloroethane	NB	126	126
1,1,1,2,2-Tetrachloroethane	NB	921	921
1,2-Dichloroethane	NB	253	253
Acetone	NB	14.4	14.4
Benzene	NB	117	117
Carbon tetrachloride	NB	560	560
Chloroform	NB	388	388
Dinoseb	NB	14.5	14.5
Ethylbenzene	NB	471	471
Methyl ethyl ketone	NB	146	146
Methylene chloride	NB	279	279
<i>m</i> -Xylene	NB	25	25
<i>p</i> -Dioxane	NB	119	119
Styrene	NB	254	254
Tetrachloroethene	NB	397	397
Toluene	NB	581	581
Trichloroethene	NB	738	738
Vinyl chloride	NB	590	590
<i>Dioxins/Furans (µg/kg)</i>			
2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin	NB	0.00138	0.00138

NB = no benchmark; TSV = toxicity screening values

¹Threshold effect concentrations (MacDonald *et al.* 2000a).

²TSVs as compiled by MacDonald *et al.* (2008), unless otherwise indicated.

³Texas Natural Resource Conservation Commission 1996.

⁴TSV from Parametrix *et al.* (2008).

⁵TSV from USEPA (1977). I.e., the bottom value of the moderately polluted classification bracket.

⁶TSV from Persaud *et al.* (1993).

⁷TSV from Ingersoll *et al.* (1996).

⁸TSV from Becker *et al.* (1990).

⁹TSV from MacDonald *et al.* (1996).

¹⁰TSV from Nagpal *et al.* (1995).

¹¹TSV from Bolton *et al.* (1985).

¹²TSV from Stortelder *et al.* (1989).

¹³TSV from NYSDEC (1999).

¹⁴TSV from Washington State Department of Ecology (1990).

¹⁵TSV from Cabbage *et al.* (1997).

Table 5. Summary of surface-water chemistry data for the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution							Mean	Standard Deviation	Geometric Mean	Min	Max
				5th	10th	25th	50th	75th	90th	95th					
Metals (µg/L)															
Aluminum, total	629	397	37%	100	100	150	421	1130	3880	7050	1700	4230	485	55.2	39600
Arsenic, total	629	26	96%	1.00	5.00	5.00	5.00	5.00	5.00	5.00	4.97	1.99	4.40	<0.4	24
Barium, total	538	279	48%	12.0	22.2	44.3	100	100	100	128	78.8	45.2	61.7	<5	400
Cadmium, total	688	212	69%	0.781	2.50	2.50	2.50	2.50	12.0	19.8	5.89	11.8	3.18	0.027	158
Chromium, total	629	44	93%	2.50	2.50	2.50	5.00	5.00	5.00	7.00	4.54	3.68	3.92	3.4	41
Cobalt, total	483	68	86%	2.50	2.50	2.50	25.0	25.0	25.0	25.0	16.6	10.8	11.3	0.41	59
Copper, total	648	142	78%	1.59	2.50	2.50	9.05	12.5	12.5	28.2	9.22	9.48	5.90	0.222	55.9
Iron, total	669	616	8%	50.0	123	346	930	3290	11100	15000	3790	11900	967	<20	272000
Lead, total	676	223	67%	2.63	5.00	5.00	5.00	5.22	29.0	49.2	14.4	37.5	6.84	0.255	446
Mercury, total	321	8	98%	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.0367	1.11	0.025	0.52
Molybdenum, total	146	0	100%	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	0	2.50	<5	<5
Nickel, total	607	202	67%	5.00	5.00	10.0	20.0	22.0	106	137	41.6	75.0	20.1	2.1	645
Selenium, total	459	1	100%	0.200	5.00	5.00	17.5	17.5	17.5	17.5	12.2	6.67	8.57	<0.2	<35
Silver, total	459	6	99%	2.50	2.50	2.50	5.00	5.00	5.00	5.00	4.15	1.24	3.89	0.34	<10
Zinc, total	694	564	19%	8.47	30.0	32.1	363	3050	5720	7500	1980	3140	342	5	23500
Dissolved Metals (µg/L)															
Aluminum, dissolved	551	73	87%	100	100	100	150	150	221	281	153	73.4	144	<200	1040
Arsenic, dissolved	551	16	97%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.30	1.99	5.16	10	28
Barium, dissolved	483	228	53%	9.10	20.0	36.0	100	100	100	100	69.6	34.7	54.5	<5	127
Cadmium, dissolved	596	113	81%	2.50	2.50	2.50	2.50	2.50	9.01	15.0	4.92	8.92	3.10	<0.1	107
Chromium, dissolved	551	4	99%	2.50	2.50	2.50	2.50	5.00	5.00	5.00	3.62	1.37	3.39	5	17
Cobalt, dissolved	376	32	91%	2.50	2.50	2.50	25.0	25.0	25.0	25.0	17.6	10.6	12.1	5	49
Copper, dissolved	588	49	92%	1.14	2.50	2.50	2.50	12.5	12.5	12.5	6.51	4.99	4.51	0.109	<25
Iron, dissolved	587	241	59%	10.0	10.0	20.0	50.0	109	3240	7370	1290	4260	79.5	9	39700
Lead, dissolved	597	22	96%	0.220	5.00	5.00	5.00	5.00	5.00	5.00	4.82	2.97	3.96	<0.1	70.9
Molybdenum, dissolved	144	0	100%	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	0	2.50	<5	<5
Mercury, dissolved	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel, dissolved	534	153	71%	5.00	5.00	5.00	20.0	20.0	103	145	40.6	74.7	19.1	8	615
Selenium, dissolved	381	3	99%	5.00	5.00	5.00	17.5	17.5	17.5	17.5	12.8	6.03	11.0	10	<35

Table 5. Summary of surface-water chemistry data for the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution							Mean	Standard Deviation	Geometric Mean	Min	Max
				5th	10th	25th	50th	75th	90th	95th					
Metals (µg/L; cont.)															
Silver, dissolved	381	0	100%	2.50	2.50	2.50	5.00	5.00	5.00	5.00	4.06	1.21	3.85	<5	<10
Zinc, dissolved	685	479	30%	2.50	2.50	30.0	180	2440	5150	6520	1630	2750	196	5	21900
Nutrients/Inorganics/Conventionals (mg/L)															
Chlorine, dissolved	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nitrate, total, NO3-N	86	68	21%	0.0250	0.0250	0.0650	0.505	1.13	1.63	1.94	0.668	0.679	0.279	0.05	2.94
Nitrate, dissolved, NO3-N	51	43	16%	0.0250	0.0250	0.145	0.320	0.895	1.20	1.61	0.565	0.604	0.284	0.05	2.94

n = sample size; ND = no data; min = minimum; max = maximum.

Table 6. Summary of surface-water chemistry data for reference stations within the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution							Mean	Standard Deviation	Geometric Mean	Min	Max
				5th	10th	25th	50th	75th	90th	95th					
Metals (µg/L)															
Aluminum, total	19	19	0%	713	730	775	920	1030	1150	1415	1040	622	955	608	3530
Arsenic, total	19	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Barium, total	19	0	100%	100	100	100	100	100	100	100	100	0	100	<200	<200
Cadmium, total	19	0	100%	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	0	2.50	<5	<5
Chromium, total	19	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Cobalt, total	19	0	100%	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	0	25.0	<50	<50
Copper, total	19	0	100%	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	0	12.5	<25	<25
Iron, total	19	19	0%	527	551	721	891	1190	1410	1520	989	451	908	447	2370
Lead, total	19	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Mercury, total	19	0	100%	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0	0.100	<0.2	<0.2
Molybdenum, total	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel, total	19	1	95%	20.0	20.0	20.0	20.0	20.0	20.0	22.1	21.1	4.77	20.8	<40	40.8
Selenium, total	19	0	100%	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	0	17.5	<35	<35
Silver, total	19	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Zinc, total	19	1	95%	30.0	30.0	30.0	30.0	30.0	30.0	333	189	695	38.3	<60	3060
Dissolved Metals (µg/L)															
Aluminum, dissolved	18	6	67%	100	100	100	100	218	254	266	148	71	134	<200	286
Arsenic, dissolved	18	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Barium, dissolved	18	0	100%	100	100	100	100	100	100	100	100	0	100	<200	<200
Cadmium, dissolved	18	0	100%	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	0	2.50	<5	<5
Chromium, dissolved	18	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Cobalt, dissolved	18	0	100%	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	0	25.0	<50	<50
Copper, dissolved	18	0	100%	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	0	12.5	<25	<25
Iron, dissolved	18	4	78%	50.0	50.0	50.0	50.0	50.0	108	110	62.8	24.6	59.3	<100	110
Lead, dissolved	18	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Molybdenum, dissolved	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Mercury, dissolved	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel, dissolved	18	0	100%	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	0	20.0	<40	<40
Selenium, dissolved	18	0	100%	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	0	17.5	<35	<35
Silver, dissolved	18	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Zinc, dissolved	18	1	95%	30.0	30.0	30.0	30.0	30.0	30.0	474	194	698	38.7	<60	2990

Table 6. Summary of surface-water chemistry data for reference stations within the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max
				5th	10th	25th	50th	75th	90th					
Nutrients/Inorganics/Conventionals (mg/L)														
Chlorine, dissolved	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nitrate, dissolved, NO3-N	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nitrate, total, NO3-N	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

n = sample size; ND = no data; min = minimum; max = maximum.

Table 7. Summary of sediment chemistry data for the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
<i>Metals (mg/kg DW)</i>															
Aluminum	784	784	0%	694	1270	3090	6750	18000	48900	54000	15400	18300	7110	113	83000
Arsenic	843	697	17%	1.38	2.16	4.4	6.20	9.90	16.0	25.0	9.88	21.1	6.24	0.69	351
Barium	753	663	12%	13.0	20	46.4	94.80	216	490	520	173	179	97.8	7.00	811
Cadmium	1154	1034	10%	0.50	0.637	1.50	6.42	25.1	75.1	132	37.7	202	6.51	0.1	4610
Chromium	784	763	3%	3.11	6.77	11.2	21.0	51.1	69.0	87.2	33.6	31.6	21.5	0.26	204
Cobalt	695	494	29%	3.10	3.30	5.00	10.0	16.0	23.6	32.1	13.1	18.1	9.53	1	390
Copper	987	937	5%	2.50	5.00	8.00	13.0	22.7	56.2	118	31.4	70.90	14.7	2.4	760
Iron	843	843	0%	5730	7500	12100	18500	27000	43100	87000	27300	36900	18700	790	497000
Lead	1156	1137	2%	11.8	15.8	29.1	91.1	266	934	2030	480	1900	102	<1	40400
Mercury	608	258	58%	0.0250	0.0300	0.0600	0.0735	0.157	0.504	1.03	0.262	0.703	0.102	<0.01	7.92
Molybdenum	311	173	44%	0.500	0.500	0.500	1.00	2.00	9.00	18.0	4.22	11.1	1.45	0.71	110
Nickel	784	640	18%	3.46	4.17	8.20	16.9	30.0	47.4	65.6	24.6	43.60	15.8	1.1	199
Selenium	694	258	63%	0.6	0.7	1.06	2.2	2.67	3.71	6	2.47	2.72	1.88	0.3	<60
Silver	695	171	75%	0.0700	0.130	0.250	0.630	0.800	1.06	1.75	0.747	1.23	0.495	<0.03	<40
Zinc	1156	1156	0%	85.3	115	249	1220	4560	12200	25000	4980	11600	1130	16	159000
<i>Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)</i>															
2-Methylnaphthalene	70	8	89%	10.4	10.5	11.4	12.5	15.7	23.1	25.3	15.2	9.06	14.1	<20	78.7
Acenaphthene	70	2	97%	10.4	10.5	11.1	12.3	14.4	17.1	19.2	14.9	14.4	13.3	<20	129
Acenaphthylene	70	2	97%	10.4	10.5	11.1	12.2	14.1	17.1	19.2	13.2	3.44	12.9	<20	<46
Anthracene	70	9	87%	10.4	10.5	11.4	12.6	16.0	26.9	39.5	20.4	33.2	15.2	<20	268
Benz(a)anthracene	70	24	66%	10.4	10.5	11.5	14.2	41.8	94.8	233	55.1	136	23.6	<20	1050
Benzo(a)pyrene	70	28	60%	10.4	10.5	11.6	14.5	51.4	119	246	61.3	141	26.5	<20	1090
Benzo(b)fluoranthene	70	30	57%	10.4	10.5	11.6	15.1	68.9	135	260	66.1	135	28.8	17.6	992
Benzo(g,h,i)perylene	70	27	61%	10.4	10.5	11.6	15.1	38.7	75.6	139	40.2	73.9	22.6	<20	547
Benzo(k)fluoranthene	70	25	64%	10.4	10.5	11.5	14.5	48.1	91.1	193	51.7	121	23.6	19.1	934
Biphenyl	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
Carbazole	70	7	90%	10.4	10.5	11.3	12.4	15.6	23.4	51.3	18.2	21.7	14.7	<20	171

Table 7. Summary of sediment chemistry data for the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
<i>PAHs (µg/kg DW; cont.)</i>															
Chrysene	70	33	53%	10.5	10.7	12.0	18.0	60.2	129	276	68.4	148	30	<20.1	1110
Dibenz(<i>a,h</i>)anthracene	70	9	87%	10.4	10.5	11.3	12.4	16.0	26.4	55.3	19.9	28.7	15.2	19.6	230
Dibenzofuran	70	5	93%	10.4	10.5	11.3	12.3	14.5	18.7	27.3	15.3	11	13.8	<20	90
Fluoranthene	70	31	56%	10.4	10.6	11.7	15.7	74.5	205	497	113	322	33.9	<20	2550
Fluorene	70	2	97%	10.4	10.5	11.1	12.3	14.4	17.1	19.2	15.7	19.2	13.4	<20	168
Indeno(1,2,3- <i>c,d</i>)pyrene	70	23	67%	10.4	10.5	11.5	13.9	34.8	67.7	147	39.4	77	21.3	18.5	569
Naphthalene	70	2	97%	10.4	10.5	11.1	12.3	14.4	17.1	19.2	13.5	4.52	13.1	<20	<46
Nitrobenzene	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
Phenanthrene	70	32	54%	10.5	10.7	12.2	17.5	55.4	167	279	78.2	203	29.8	<20.1	1590
Pyrene	70	32	54%	10.4	10.6	11.9	16.6	78.9	211	479	108	267	34.9	<20	2010
PAHs, total high molecular weight PAHs	70	33	53%	62.7	64.2	71.8	98.5	306	806	1840	426	1040	172	84.1	8050
PAHs, total low molecular weight PAHs	70	32	54%	73.2	75.2	85.3	102	139	262	428	171	274	125	91.6	2240
PAHs, total	70	37	47%	136	140	160	225	441	1090	2340	597	1310.00	313	168	10300
<i>Polychlorinated Biphenyls (PCBs; µg/kg DW)</i>															
Aroclor 1016	70	0	100%	20.2	20.5	21.5	24.0	26.4	31.1	33.6	24.8	4.17	24.5	<39	<77
Aroclor 1221	70	0	100%	20.2	20.5	21.5	24.0	26.4	31.1	33.6	24.8	4.17	24.5	<39	<77
Aroclor 1232	70	0	100%	20.2	20.5	21.5	24.0	26.4	31.1	33.6	24.8	4.17	24.5	<39	<77
Aroclor 1242	70	0	100%	20.2	20.5	21.5	24.0	26.4	31.1	33.6	24.8	4.17	24.5	<39	<77
Aroclor 1248	70	0	100%	20.2	20.5	21.5	24.0	26.4	31.1	33.6	24.8	4.17	24.5	<39	<77
Aroclor 1254	70	0	100%	20.2	20.5	21.5	24.0	26.4	31.1	33.6	24.8	4.17	24.5	<39	<77
Aroclor 1260	70	0	100%	20.2	20.5	21.5	24.0	26.4	31.1	33.6	24.8	4.17	24.5	<39	<77
Aroclor 1262	70	0	100%	20.2	20.5	21.5	24.0	26.4	31.1	33.6	24.8	4.17	24.5	<39	<77
Aroclor 1268	70	0	100%	20.2	20.5	21.5	24.0	26.4	31.1	33.6	24.8	4.17	24.5	<39	<77
PCBs, total	70	0	100%	182	185	194	216	237	279	302	223	37.5	220	<351	<693

Table 7. Summary of sediment chemistry data for the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
<i>Organochlorine Pesticides (µg/kg DW)</i>															
Aldrin	70	0	100%	1.05	1.05	1.10	1.25	1.35	1.61	1.73	1.28	0.217	1.26	<2	<3.9
Chlordane, cis-	70	0	100%	1.05	1.05	1.10	1.25	1.35	1.61	1.73	1.28	0.217	1.26	<2	<3.9
Chlordane, trans-	70	0	100%	1.05	1.05	1.10	1.25	1.35	1.61	1.73	1.28	0.217	1.26	<2	<3.9
Dieldrin	70	0	100%	2.02	2.05	2.15	2.40	2.64	3.11	3.36	2.48	0.415	2.44	<3.9	<7.6
Endosulfan sulfate	70	0	100%	2.02	2.05	2.15	2.40	2.64	3.11	3.36	2.48	0.415	2.44	<3.9	<7.6
Endosulfan-alpha	70	0	100%	1.05	1.05	1.10	1.25	1.35	1.61	1.73	1.28	0.217	1.26	<2	<3.9
Endosulfan-beta	70	0	100%	2.02	2.05	2.15	2.40	2.64	3.11	3.36	2.48	0.415	2.44	<3.9	<7.6
Endrin	70	0	100%	2.02	2.05	2.15	2.40	2.64	3.11	3.36	2.48	0.415	2.44	<3.9	<7.6
Endrin aldehyde	70	0	100%	2.00	2.05	2.15	2.40	2.64	3.11	3.36	2.46	0.442	2.42	<2.4	<7.6
Endrin ketone	70	0	100%	2.00	2.05	2.15	2.40	2.64	3.11	3.36	2.46	0.442	2.42	<2.4	<7.6
Heptachlor	70	0	100%	1.05	1.05	1.10	1.25	1.35	1.61	1.73	1.28	0.217	1.26	<2	<3.9
Heptachlor epoxide	70	0	100%	1.05	1.05	1.10	1.25	1.35	1.61	1.73	1.28	0.217	1.26	<2	<3.9
Hexachlorobenzene	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
Hexachlorocyclohexane-alpha	70	0	100%	1.05	1.05	1.10	1.25	1.35	1.61	1.73	1.28	0.217	1.26	<2	<3.9
Hexachlorocyclohexane-beta	70	0	100%	1.05	1.05	1.10	1.25	1.35	1.61	1.73	1.28	0.217	1.26	<2	<3.9
Hexachlorocyclohexane-delta	70	0	100%	1.05	1.05	1.10	1.25	1.35	1.61	1.73	1.28	0.217	1.26	<2	<3.9
Hexachlorocyclohexane-gamma	70	0	100%	1.05	1.05	1.10	1.25	1.35	1.61	1.73	1.28	0.217	1.26	<2	<3.9
Hexachlorocyclopentadiene	66	0	100%	10.7	11.1	12.8	18.0	46.6	54.5	66.6	31.5	20.7	25.0	<20.7	<184
Isophorone	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
Methoxychlor	70	0	100%	10.5	10.5	11.0	12.5	13.5	16.1	17.3	12.8	2.17	12.6	<20	<39
<i>p,p'</i> -DDD	70	0	100%	2.02	2.05	2.15	2.40	2.64	3.11	3.36	2.48	0.415	2.44	<3.9	<7.6
<i>p,p'</i> -DDE	70	0	100%	2.02	2.05	2.15	2.40	2.64	3.11	3.36	2.48	0.415	2.44	<3.9	<7.6
<i>p,p'</i> -DDT	70	0	100%	2.02	2.05	2.15	2.40	2.64	3.11	3.36	2.48	0.415	2.44	<3.9	<7.6
Toxaphene	70	0	100%	105	105	110	125	135	161	173	128	21.7	126	<200	<390
<i>Semi-Volatile Compounds (µg/kg DW)</i>															
1,2,4-Trichlorobenzene	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
1,2-Dichlorobenzene	70	0	100%	10.4	10.5	11.1	12.3	14.4	17.1	19.2	14	6.71	13.2	<20.1	<100
1,3-Dichlorobenzene	70	0	100%	10.4	10.5	11.1	12.3	14.4	17.1	19.2	14	6.71	13.2	<20.1	<100
1,4-Dichlorobenzene	70	0	100%	10.4	10.5	11.1	12.3	14.4	17.1	19.2	14	6.71	13.2	<20.1	<100

Table 7. Summary of sediment chemistry data for the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
<i>Semi-Volatile Compounds (µg/kg DW; cont.)</i>															
2,4,5-Trichlorophenol	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
2,4,6-Trichlorophenol	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
2,4-Dichlorophenol	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
2,4-Dimethylphenol	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
2,4-Dinitrophenol	70	0	100%	104	105	111	122	139	166	175	129	25.60	127	<200	<460
2,4-Dinitrotoluene	70	0	100%	20.7	20.9	22.2	24.4	27.9	33.3	35.0	25.8	5.12	25.3	<40.1	<92
2,6-Dinitrotoluene	70	0	100%	20.7	20.9	22.2	24.4	27.9	33.3	35.0	25.8	5.12	25.3	<40.1	<92
2-Chloronaphthalene	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
2-Chlorophenol	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
2-Methylphenol	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
2-Nitroaniline	70	0	100%	20.7	20.9	22.2	24.4	27.9	33.3	35	25.8	5.12	25.3	<40.1	<92
2-Nitrophenol	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
3&/or4 Methylphenol	70	1	99%	10.4	10.5	11.1	12.2	14.1	16.9	18.1	13.5	5.68	12.9	<20	55.3
3,3'-Dichlorobenzidine	70	1	99%	10.4	10.5	11.1	12.3	14.5	17.4	21.5	15.2	12.6	13.6	<20	<210
3-Nitroaniline	70	0	100%	20.7	20.9	22.2	24.4	27.9	33.3	35.0	25.8	5.12	25.3	<40.1	<92
4-Bromophenyl phenyl ether	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
4-Chloro-3-methylphenol	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
4-Chloroaniline	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
4-Chlorophenyl phenyl ether	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
4-Nitroaniline	70	0	100%	20.7	20.9	22.2	24.4	27.9	33.3	35.0	25.8	5.12	25.3	<40.1	<92
4-Nitrophenol	70	0	100%	104	105	111	122	139	166	175	129	25.60	127	<200	<460
Acetophenone	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
Atrazine	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
Benzaldehyde	70	0	100%	20.7	20.9	22.2	24.4	27.9	33.3	35.0	25.8	5.12	25.3	<40.1	<92
Benzoic acid	70	4	94%	104	105	111	122	143	175	271	145	83.1	134	<200	601
Benzyl alcohol	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
bis(2-chloroethoxy)methane	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
bis(2-chloroethyl)ether	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
bis(2-chloroisopropyl) ether	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
bis(2-ethylhexyl) phthalate	70	5	93%	104	106	113	123	151	187	254	145	66.1	136	<200	533

Table 7. Summary of sediment chemistry data for the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
<i>Semi-Volatile Compounds (µg/kg DW; cont.)</i>															
Butylbenzyl phthalate	70	10	86%	104	106	113	125	160	456	782	219	272.00	160	<200	1550
Caprolactam	70	8	89%	10.4	10.5	11.2	12.5	15.7	21.7	31.5	15.3	8.31	14.1	17.7	58.2
Diethyl phthalate	70	0	100%	104	105	111	122	139	166	175	129	25.60	127	<200	<460
Dimethyl phthalate	70	0	100%	104	105	111	122	139	166	175	129	25.60	127	<200	<460
Di- <i>n</i> -butyl phthalate	70	0	100%	104	105	111	122	139	166	175	129	25.60	127	<200	<460
Dinitro- <i>o</i> -cresol	70	0	100%	104	105	111	122	139	166	175	129	25.60	127	<200	<460
Di- <i>n</i> -octyl phthalate	70	0	100%	104	105	111	122	139	166	175	129	25.60	127	<200	<460
Hexachlorobutadiene	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
Hexachloroethane	70	0	100%	10.4	10.5	11.1	12.3	14.4	17.1	19.2	13.6	4.74	13.1	<20	<77.6
<i>n</i> -nitrosodi- <i>n</i> -propylamine	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
<i>n</i> -nitrosodiphenylamine	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46
Pentachlorophenol	70	0	100%	10.7	11.1	12.8	19.3	23.3	26.4	32.5	19.2	7.43	17.9	<20.7	<92
Phenol	70	0	100%	10.4	10.5	11.1	12.2	13.9	16.6	17.5	12.9	2.56	12.7	<20	<46

n = sample size; ND = no data; min = minimum; max = maximum; DW = dry weight.

Table 8. Summary of sediment chemistry data for reference sediment samples within the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
<i>Metals (mg/kg DW)</i>															
Aluminum	8	8	0%	6930	6940	7430	7810	10800	11600	11700	8860	2050	8660	6930	11700
Arsenic	8	3	63%	0.807	0.879	1.50	2.81	3.16	6.03	8.81	3.40	3.47	2.42	<1.47	11.6
Barium	8	8	0%	78.5	83.7	88.7	108	127	142	149	110	27.9	107	73.3	157
Cadmium	8	5	38%	0.345	0.353	0.436	0.905	1.21	1.88	2.34	1.05	0.819	0.822	<0.673	2.81
Chromium	8	8	0%	10.3	10.5	11.8	15.5	26.3	31.3	35.1	19.6	10.3	17.5	10.2	38.8
Cobalt	8	5	38%	3.62	3.65	4.90	8.44	11.2	14.4	16.3	8.89	5.04	7.68	7.03	18.2
Copper	8	8	0%	5.46	5.48	5.56	7.63	9.42	10.7	11.3	7.88	2.41	7.57	5.44	12
Iron	8	8	0%	8060	8280	9510	11900	16700	26800	33500	15800	10800	13600	7850	40300
Lead	8	8	0%	11.6	11.7	12.1	16.9	21.8	27.7	27.9	18.1	6.71	17.1	11.6	28
Mercury	8	0	100%	0.0643	0.0660	0.0709	0.0770	0.0861	0.0961	0.100	0.0796	0.0138	0.0786	<0.125	<0.209
Nickel	8	7	13%	5.23	6.22	7.58	9.60	14.9	18.5	19.4	11.3	5.58	10.1	7.06	20.2
Selenium	8	0	100%	2.24	2.26	2.33	2.55	3.01	3.38	3.55	2.73	0.526	2.69	<4.46	<7.43
Silver	8	0	100%	0.640	0.646	0.703	0.778	0.861	0.966	1.01	0.798	0.144	0.787	<1.27	<2.12
Zinc	8	8	0%	35.4	35.7	63.1	118	176	243	258	130	86.7	103	35.2	272
<i>Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)</i>															
2-Methylnaphthalene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Acenaphthene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Acenaphthylene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Anthracene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Benz(a)anthracene	8	2	75%	12.4	12.6	14.1	17.2	23.3	38.4	43.5	22.0	12.8	19.6	<24.5	48.6
Benzo(a)pyrene	8	3	63%	12.4	12.6	14.1	18.6	45.4	48.0	50.6	27.6	17.3	23.3	<24.5	53.2
Benzo(b)fluoranthene	8	3	63%	12.4	12.6	14.1	18.6	67.7	68.9	69.5	35.3	27.7	26.6	<24.5	70.1
Benzo(g,h,i)perylene	8	2	75%	12.4	12.6	14.1	17.2	23.1	36.3	39.8	21.3	11.1	19.3	<24.5	43.3
Benzo(k)fluoranthene	8	2	75%	12.4	12.6	14.1	17.2	26.2	46.8	48.0	23.6	15.0	20.4	<24.5	49.2
Biphenyl	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Carbazole	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Chrysene	8	3	63%	12.4	12.6	14.1	18.6	53.6	64.7	77.3	34.2	28.5	25.9	<24.5	89.9
Dibenz(a,h)anthracene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Dibenzofuran	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Fluoranthene	8	3	63%	12.4	12.6	14.1	18.6	71.9	93.3	108	43.6	42.0	29.2	<24.5	123

Table 8. Summary of sediment chemistry data for reference sediment samples within the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
<i>PAHs (µg/kg DW; cont.)</i>															
Fluorene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Indeno(1,2,3-c,d)pyrene	8	2	75%	12.4	12.6	14.1	17.2	23.0	35.2	38.1	20.9	10.4	19.1	<24.5	40.9
Naphthalene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Nitrobenzene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Phenanthrene	8	2	75%	13.4	14.0	15.3	17.2	21.0	42.1	62.1	25.5	23.1	20.7	25	82
Pyrene	8	3	63%	12.4	12.6	14.1	18.6	59.9	86.3	111	42.0	43.5	28.2	<24.5	136
Total high molecular weight PAHs	8	3	63%	74.7	75.8	84.5	111	270	349	403	185	141	147	<147	457
Total low molecular weight PAHs	8	2	75%	92.7	95.8	101	113	126	147	157	118	24.9	116	98.5	<275.8
Total PAHs	8	4	50%	168	170	184	241	386	475	550	303	159	272	172	624
<i>Polychlorinated Biphenyls (PCBs; µg/kg DW)</i>															
Aroclor 1016	8	0	100%	22.1	23.7	25.4	27.8	33.1	35.5	36.0	28.8	5.45	28.4	<41	<73
Aroclor 1221	8	0	100%	22.1	23.7	25.4	27.8	33.1	35.5	36.0	28.8	5.45	28.4	<41	<73
Aroclor 1232	8	0	100%	22.1	23.7	25.4	27.8	33.1	35.5	36.0	28.8	5.45	28.4	<41	<73
Aroclor 1242	8	0	100%	22.1	23.7	25.4	27.8	33.1	35.5	36.0	28.8	5.45	28.4	<41	<73
Aroclor 1248	8	0	100%	22.1	23.7	25.4	27.8	33.1	35.5	36.0	28.8	5.45	28.4	<41	<73
Aroclor 1254	8	0	100%	22.1	23.7	25.4	27.8	33.1	35.5	36.0	28.8	5.45	28.4	<41	<73
Aroclor 1260	8	0	100%	22.1	23.7	25.4	27.8	33.1	35.5	36.0	28.8	5.45	28.4	<41	<73
Aroclor 1262	8	0	100%	22.1	23.7	25.4	27.8	33.1	35.5	36.0	28.8	5.45	28.4	<41	<73
Aroclor 1268	8	0	100%	22.1	23.7	25.4	27.8	33.1	35.5	36.0	28.8	5.45	28.4	<41	<73
PCBs	8	0	100%	199	213	228	250	298	319	324	259	49.1	255	<369	<657
<i>Organochlorine Pesticides (µg/kg DW)</i>															
Aldrin	8	0	100%	1.14	1.23	1.30	1.43	1.73	1.83	1.87	1.49	0.289	1.46	<2.1	<3.8
Chlordane, cis-	8	0	100%	1.14	1.23	1.30	1.43	1.73	1.83	1.87	1.49	0.289	1.46	<2.1	<3.8
Chlordane, trans-	8	0	100%	1.14	1.23	1.30	1.43	1.73	1.83	1.87	1.49	0.289	1.46	<2.1	<3.8
Dieldrin	8	0	100%	2.24	2.38	2.54	2.78	3.35	3.55	3.60	2.89	0.539	2.85	<4.2	<7.3
Endosulfan sulfate	8	0	100%	2.24	2.38	2.54	2.78	3.35	3.55	3.60	2.89	0.539	2.85	<4.2	<7.3
Endosulfan-alpha	8	0	100%	1.14	1.23	1.30	1.43	1.73	1.83	1.87	1.49	0.289	1.46	<2.1	<3.8
Endosulfan-beta	8	0	100%	2.24	2.38	2.54	2.78	3.35	3.55	3.60	2.89	0.539	2.85	<4.2	<7.3
Endrin	8	0	100%	2.24	2.38	2.54	2.78	3.35	3.55	3.60	2.89	0.539	2.85	<4.2	<7.3

Table 8. Summary of sediment chemistry data for reference sediment samples within the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
<i>Organochlorine Pesticides (µg/kg DW; cont.)</i>															
Endrin aldehyde	8	0	100%	2.24	2.38	2.54	2.78	3.35	3.55	3.60	2.89	0.539	2.85	<4.2	<7.3
Endrin ketone	8	0	100%	2.24	2.38	2.54	2.78	3.35	3.55	3.60	2.89	0.539	2.85	<4.2	<7.3
Heptachlor	8	0	100%	1.14	1.23	1.30	1.43	1.73	1.83	1.87	1.49	0.289	1.46	<2.1	<3.8
Heptachlor epoxide	8	0	100%	1.14	1.23	1.30	1.43	1.73	1.83	1.87	1.49	0.289	1.46	<2.1	<3.8
Hexachlorobenzene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Hexachlorocyclohexane-alpha	8	0	100%	1.14	1.23	1.30	1.43	1.73	1.83	1.87	1.49	0.289	1.46	<2.1	<3.8
Hexachlorocyclohexane-beta	8	0	100%	1.14	1.23	1.30	1.43	1.73	1.83	1.87	1.49	0.289	1.46	<2.1	<3.8
Hexachlorocyclohexane-delta	8	0	100%	1.14	1.23	1.30	1.43	1.73	1.83	1.87	1.49	0.289	1.46	<2.1	<3.8
Hexachlorocyclohexane-gamma	8	0	100%	1.14	1.23	1.30	1.43	1.73	1.83	1.87	1.49	0.289	1.46	<2.1	<3.8
Hexachlorocyclopentadiene	8	0	100%	12.4	12.6	14.8	17.2	56.9	64.3	71.7	33.5	26.6	25.6	<24.5	<158
Isophorone	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Methoxychlor	8	0	100%	11.4	12.3	13.0	14.3	17.3	18.3	18.7	14.9	2.89	14.6	<21	<38
<i>p,p'</i> -DDD	8	0	100%	2.24	2.38	2.54	2.78	3.35	3.55	3.60	2.89	0.539	2.85	<4.2	<7.3
<i>p,p'</i> -DDE	8	0	100%	2.24	2.38	2.54	2.78	3.35	3.55	3.60	2.89	0.539	2.85	<4.2	<7.3
<i>p,p'</i> -DDT	8	0	100%	2.24	2.38	2.54	2.78	3.35	3.55	3.60	2.89	0.539	2.85	<4.2	<7.3
Toxaphene	8	0	100%	114	123	130	143	173	183	187	149	28.9	146	<210	<380
<i>Semi-Volatile Compounds (µg/kg DW)</i>															
1,2,4-Trichlorobenzene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
1,2-Dichlorobenzene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
1,3-Dichlorobenzene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
1,4-Dichlorobenzene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
2,4,5-Trichlorophenol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
2,4,6-Trichlorophenol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
2,4-Dichlorophenol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
2,4-Dimethylphenol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
2,4-Dinitrophenol	8	0	100%	124	126	138	150	170	181	189	154	25.0	152	<245	<394
2,4-Dinitrotoluene	8	0	100%	24.9	25.3	27.6	30.0	34.1	36.2	37.8	30.8	5.00	30.4	<49.1	<78.8
2,6-Dinitrotoluene	8	0	100%	24.9	25.3	27.6	30.0	34.1	36.2	37.8	30.8	5.00	30.4	<49.1	<78.8
2-Chloronaphthalene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
2-Chlorophenol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4

Table 8. Summary of sediment chemistry data for reference sediment samples within the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
<i>Semi-Volatile Compounds (µg/kg DW; cont.)</i>															
2-Methylphenol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
2-Nitroaniline	8	0	100%	24.9	25.3	27.6	30.0	34.1	36.2	37.8	30.8	5.00	30.4	<49.1	<78.8
2-Nitrophenol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
3&/or4 Methylphenol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
3,3'-Dichlorobenzidine	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
3-Nitroaniline	8	0	100%	24.9	25.3	27.6	30.0	34.1	36.2	37.8	30.8	5.00	30.4	<49.1	<78.8
4-Bromophenyl phenyl ether	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
4-Chloro-3-methylphenol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
4-Chloroaniline	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
4-Chlorophenyl phenyl ether	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
4-Nitroaniline	8	0	100%	24.9	25.3	27.6	30.0	34.1	36.2	37.8	30.8	5.00	30.4	<49.1	<78.8
4-Nitrophenol	8	0	100%	124	126	138	150	170	181	189	154	25.0	152	<245	<394
Acetophenone	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Atrazine	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Benzaldehyde	8	0	100%	24.9	25.3	27.6	30.0	34.1	36.2	37.8	30.8	5.00	30.4	<49.1	<78.8
Benzoic acid	8	1	88%	124	126	141	162	180	318	460	211	159	182	<245	601
Benzyl alcohol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
bis(2-chloroethoxy)methane	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
bis(2-chloroethyl)ether	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
bis(2-chloroisopropyl) ether	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
bis(2-ethylhexyl) phthalate	8	0	100%	124	126	138	150	170	181	189	154	25.0	152	<245	<394
Butylbenzyl phthalate	8	0	100%	124	126	138	150	170	181	189	154	25.0	152	<245	<394
Caprolactam	8	1	88%	12.4	12.6	14.1	16.2	18.0	31.3	44.7	20.9	15.3	18.2	<24.5	58.2
Diethyl phthalate	8	0	100%	124	126	138	150	170	181	189	154	25.0	152	<245	<394
Dimethyl phthalate	8	0	100%	124	126	138	150	170	181	189	154	25.0	152	<245	<394
Di- <i>n</i> -butyl phthalate	8	0	100%	124	126	138	150	170	181	189	154	25.0	152	<245	<394
Dinitro- <i>o</i> -cresol	8	0	100%	124	126	138	150	170	181	189	154	25.0	152	<245	<394
Di- <i>n</i> -octyl phthalate	8	0	100%	124	126	138	150	170	181	189	154	25.0	152	<245	<394
Hexachlorobutadiene	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Hexachloroethane	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4

Table 8. Summary of sediment chemistry data for reference sediment samples within the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
<i>Semi-Volatile Compounds (µg/kg DW; cont.)</i>															
<i>n</i> -nitrosodi- <i>n</i> -propylamine	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
<i>n</i> -nitrosodiphenylamine	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4
Pentachlorophenol	8	0	100%	12.4	12.6	14.8	17.2	28.4	32.1	35.7	21.4	9.69	19.7	<24.5	<78.8
Phenol	8	0	100%	12.4	12.6	13.8	15.0	17.0	18.1	18.9	15.4	2.50	15.2	<24.5	<39.4

n = sample size; ND = no data; min = minimum; max = maximum; DW = dry weight.

Table 9. Summary of pore-water chemistry data for the Tri-State Mining District (2002 - 2009).

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution						Mean	Standard Deviation	Geometric Mean	Min	Max	
				5th	10th	25th	50th	75th	90th						95th
Metals (µg/L)															
Aluminum, total	26	6	77%	100	100	100	100	100	1260	1760	469	1000	179	<200	4820
Arsenic, total	26	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Barium, total	26	1	96%	100	100	100	100	100	100	100	105	23.1	103	<200	<200
Cadmium, total	26	3	88%	2.50	2.50	2.50	2.50	2.50	7.6	13.7	4.85	8.13	3.17	<5	42
Chromium, total	26	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Cobalt, total	26	0	100%	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	0	25.0	<50	<50
Copper, total	26	2	92%	12.5	12.5	12.5	12.5	12.5	12.5	25.3	13.9	4.94	13.4	<25	31.8
Iron, total	26	11	58%	50.0	50.0	50.0	50.0	524	1850	3760	696	1490	164	<100	6400
Lead, total	26	3	88%	5.00	5.00	5.00	5.00	5.00	7.95	73.5	12.8	26.9	6.5	<10	113
Mercury, total	26	0	100%	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0	0.100	<0.2	<0.2
Nickel, total	26	1	96%	20.0	20.0	20.0	20.0	20.0	20.0	22.8	21.0	4.17	20.7	<40	<47.4
Selenium, total	26	0	100%	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	0	17.5	<35	<35
Silver, total	26	0	100%	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	0	5.00	<10	<10
Zinc, total	26	13	50%	30.0	30.0	30.0	46.2	547	2260	2940	1060	3090	135	<60	15600
Aluminum, dissolved	70	66	6%	0.118	0.570	1.00	4.50	17.5	50.0	75.5	15.1	24.2	4.03	<0.1	100
Arsenic, dissolved	70	70	0%	0.900	0.990	2.00	4.00	8.75	10.0	10.0	5.74	5.83	3.79	0.3	40
Barium, dissolved	70	70	0%	39.0	59.0	90.0	100	200	300	355	153	96.0	124	20	400
Cadmium, dissolved	70	17	76%	0.0300	0.0300	0.0300	0.0800	0.0800	0.383	3.23	0.732	2.96	0.0923	<0.06	20.4
Chromium, dissolved	70	0	100%	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.00000000291	0.0500	<0.1	<0.1
Cobalt, dissolved	70	70	0%	2.00	2.00	4.25	8.00	10.0	21.0	30.0	11.0	11.4	7.24	0.3	70
Copper, dissolved	70	15	79%	0.265	0.265	0.265	0.700	0.700	0.939	1.86	0.658	0.557	0.523	0.3675	3.21
Iron, dissolved	70	65	7%	5.00	29.0	825	2500	8000	17000	19600	5850	7560	1520	<10	38000
Lead, dissolved	70	43	39%	0.0750	0.0750	0.0950	0.213	1.20	3.74	10.8	2.36	8.64	0.358	0.1025	67.9
Molybdenum, dissolved	70	69	1%	0.300	0.390	0.700	1.00	3.00	4.00	5.00	1.83	1.65	1.24	<0.1	8
Mercury, dissolved	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel, dissolved	70	70	0%	1.27	1.54	2.06	3.19	4.61	8.34	13.3	4.70	5.36	3.37	0.8	33.4
Selenium, dissolved	70	29	59%	0.500	0.500	0.500	0.500	1.00	2.00	2.00	0.936	0.613	0.781	1	2
Silver, dissolved	70	0	100%	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.00000000291	0.0500	<0.1	<0.1
Zinc, dissolved	70	43	39%	1.20	1.20	2.85	12.8	216	813	1610	370	1110	20.6	<2.4	7020

n = sample size; ND = no data; min = minimum; max = maximum.

Table 10. Summary of pore-water chemistry data from reference stations within the Tri-State Mining District (2002 - 2009)¹.

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution							Mean	Standard Deviation	Geometric Mean	Min	Max
				5th	10th	25th	50th	75th	90th	95th					
Metals (µg/L)															
Aluminum, dissolved	8	7	13%	0.243	0.435	3.15	15.0	50.0	59.0	69.5	26.8	29.7	6.84	<0.1	80
Arsenic, dissolved	8	8	0%	1.35	1.70	2.75	8.00	9.25	19.0	29.5	10.1	12.6	5.84	1	40
Barium, dissolved	8	8	0%	135	170	200	200	225	330	365	225	88.6	210	100	400
Cadmium, dissolved	8	0	100%	0.0300	0.0300	0.0300	0.0300	0.0800	0.0800	0.0800	0.0488	0.0259	0.0433	<0.06	<0.16
Chromium, dissolved	8	0	100%	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500		0.0500	<0.1	<0.1
Cobalt, dissolved	8	8	0%	5.40	6.80	8.00	9.50	10.0	10.0	10.0	8.63	2.07	8.32	4	10
Copper, dissolved	8	1	88%	0.265	0.265	0.265	0.700	0.700	0.901	1.14	0.621	0.372	0.529	<0.53	<1.4
Iron, dissolved	8	8	0%	415	730	2500	9000	17300	24000	31000	11900	12700	4670	100	38000
Lead, dissolved	8	2	75%	0.0750	0.0750	0.0750	0.0950	0.0981	0.132	0.160	0.101	0.0371	0.0961	0.1075	<0.19
Molybdenum, dissolved	8	7	13%	0.138	0.225	0.525	0.900	2.00	2.30	2.65	1.22	1.01	0.737	<0.1	3
Mercury, dissolved	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel, dissolved	8	8	0%	2.02	2.10	2.83	3.19	3.48	4.10	4.27	3.16	0.827	3.06	1.945	4.44
Selenium, dissolved	8	5	38%	0.500	0.500	0.500	1.00	2.00	2.00	2.00	1.19	0.704	1.00	<1	2
Silver, dissolved	8	0	100%	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500		0.0500	<0.1	<0.1
Zinc, dissolved	8	0	100%	1.20	1.20	1.20	1.20	2.85	2.85	2.85	1.82	0.854	1.66	<2.4	<5.7

n = sample size; ND = no data; min = minimum; max = maximum.

¹ The selected reference stations for pore water are the same as those that were selected for sediments (Figure 14).

Table 11. Results of screening of the surface-water chemistry data collected in the Tri-State Mining District (2002 - 2009).

Chemical of Interest (CoI)	# of Samples	# of N-D Samples Excluded ¹	# of Samples Excluding HN-D	EPC ²	TSV	Maximum HQ ³	FOE (%) ⁴
Metals (µg/L)							
Aluminum, total	629	232 (37%)	397	39600	87	455	99%
Arsenic, total	629	0 (0%)	629	24	150	0.16	0%
Barium, total	538	0 (0%)	538	400	1000	0.4	0%
Cadmium, total	688	474 (69%)	214	158	0.25	632	93%
Chromium, total	629	585 (93%)	44	41	2	20.5	100%
Cobalt, total	483	0 (0%)	483	59	5	11.8	72%
Copper, total	648	506 (78%)	142	55.9	4.17	13.4	69%
Iron, total	669	0 (0%)	669	272000	887	307	52%
Lead, total	676	450 (67%)	226	446	1.16	384	92%
Mercury, total	321	313 (98%)	8	0.52	0.182	2.86	63%
Molybdenum, total	146	0 (0%)	145	<5	395	0.00633	0%
Nickel, total	607	0 (0%)	607	645	52	12.4	19%
Selenium, total	459	421 (92%)	38	10	4.96	2.02	3%
Silver, total	459	453 (99%)	6	0.65	0.098	6.63	100%
Zinc, total	694	0 (0%)	694	23500	60.8	387	72%
Aluminum, dissolved	551	478 (87%)	73	1040	87	12	100%
Arsenic, dissolved	551	0 (0%)	551	28	150	0.187	0%
Barium, dissolved	483	0 (0%)	483	127	1000	0.127	0%
Cadmium, dissolved	596	477 (80%)	119	107	0.25	428	92%
Chromium, dissolved	551	547 (99%)	4	17	2	8.5	100%
Cobalt, dissolved	376	0 (0%)	376	49	5	9.8	69%
Copper, dissolved	588	384 (65%)	204	<25	4.17	3	6%
Iron, dissolved	587	0 (0%)	587	39700	887	44.8	16%
Lead, dissolved	597	494 (83%)	103	70.9	1.16	61.1	67%
Molybdenum, dissolved	144	0 (0%)	144	<5	395	0.00633	0%
Mercury, dissolved	ND	NA	NA	ND	ND	NC	NC
Nickel, dissolved	534	169 (32%)	365	615	52	11.8	27%
Selenium, dissolved	381	378 (99%)	3	11	4.96	2.22	100%
Silver, dissolved	381	353 (93%)	28	<10	0.098	51	100%
Zinc, dissolved	685	33 (5%)	652	21900	60.8	360	63%
Nutrients/Inorganics/Conventionals (mg/L)							
Ammonia	ND	NA	NA	ND	3.87	NC	NC
Chlorine	ND	NA	NA	ND	10.1	NC	NC
Nitrate, total, NO3-N	86	0 (0%)	86	2.94	13000	0.000226	0%
Nitrate, dissolved, NO3-N	51	0 (0%)	51	2.94	13000	0.000226	0%

EPC = exposure point concentration; FOE = frequency of exceedance; HN-D = high non-detect; HQ = hazard quotient; NA = not applicable; N-D = non detect; ND = no data; NC = not calculated; TSV = toxicity screening value.

¹ When a TSV exists for a given CoI, data below the analytical detection limit, but greater than the TSV were excluded from the frequency of exceedance analysis.

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Table 11. Results of screening of the surface-water chemistry data collected in the Tri-State Mining District (2002 - 2009).

Chemical of Interest (CoI)	# of Samples	# of N-D Samples Excluded¹	# of Samples Excluding HN-D	EPC²	TSV	Maximum HQ³	FOE (%)⁴
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² The maximum concentration of each CoI was selected as the EPC for the Screening Level Environmental Risk Assessment.

³ Where the EPC was below the analytical detection limit, but less than the TSV, one half of the detection limit was used to calculate the HQ.

⁴ All samples were compared to the TSV as reported in this table, assuming a hardness of 100mg/L for all samples.

Table 12. Results of screening of the sediment chemistry data collected in the Tri-State Mining District (2002 - 2009).

Chemical of Interest (CoI)	# of Samples	# of N-D Samples Excluded ¹	# of Samples Excluding HN-D	EPC ²	TSV	Maximum HQ ³	FOE (%)
Metals (mg/kg DW)							
Aluminum	784	0 (0%)	784	83000	15900	5.22	28%
Arsenic	843	84 (10%)	759	351	7.15	49.1	47%
Barium	753	90 (12%)	663	811	20	40.6	99%
Cadmium	1154	106 (9%)	1048	4610	0.99	4660	85%
Chromium	784	0 (0%)	784	204	20.2	10.1	52%
Cobalt	695	0 (0%)	695	390	50	7.8	1%
Copper	987	0 (0%)	987	760	25.2	30.2	22%
Iron	843	0 (0%)	843	497000	190000	2.62	1%
Lead	1156	1 (0%)	1155	40400	35.3	1140	69%
Mercury	608	82 (13%)	526	7.92	0.158	50.1	27%
Molybdenum	311	0 (0%)	311	110	ND	NC	NC
Nickel	784	1 (0%)	783	1050	18.7	56.1	45%
Selenium	694	0 (0%)	694	<60	0.2	150	100%
Silver	695	0 (0%)	695	<40	0.73	27.4	32%
Zinc	1156	0 (0%)	1156	159000	121	1310	89%
Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)							
2-Methylnaphthalene	70	0 (0%)	70	78.7	114	0.69	0%
Acenaphthene	70	0 (0%)	70	129.15	98.3	1.31	1%
Acenaphthylene	70	0 (0%)	70	<46	78.3	0.384	0%
Anthracene	70	0 (0%)	70	267.5	57.2	4.68	4%
Benz(<i>a</i>)anthracene	70	0 (0%)	70	1054	108	9.76	10%
Benzo(<i>a</i>)pyrene	70	0 (0%)	70	1088	150	7.25	9%
Benzo(<i>b</i>)fluoranthene	70	0 (0%)	70	991.5	4740	0.209	0%
Benzo(<i>g,h,i</i>)perylene	70	0 (0%)	70	546.5	252	2.17	1%
Benzo(<i>k</i>)fluoranthene	70	0 (0%)	70	933.5	139	6.72	9%
Biphenyl	70	0 (0%)	70	<46	1100	0.0209	0%
Carbazole	70	0 (0%)	70	171	923	0.185	0%
Chrysene	70	0 (0%)	70	1114	166	6.71	9%
Dibenz(<i>a,h</i>)anthracene	70	8 (11%)	62	230	33	6.97	10%
Dibenzofuran	70	0 (0%)	70	89.95	150	0.6	0%
Fluoranthene	70	0 (0%)	70	2550	423	6.03	7%
Fluorene	70	0 (0%)	70	168.35	77.4	2.18	1%
Indeno(1,2,3- <i>c,d</i>)pyrene	70	0 (0%)	70	569	193	2.95	3%
Naphthalene	70	0 (0%)	70	<46	176	0.215	0%
Nitrobenzene	70	0 (0%)	70	<46	1650	0.0139	0%
Phenanthrene	70	0 (0%)	70	1590	204	7.77	9%
Pyrene	70	0 (0%)	70	2010	195	10.3	13%
Total HMWPAHs	70	0 (0%)	70	8050	655	12.3	13%
Total LMWPAHs	70	0 (0%)	70	2240	312	7.19	9%
Total PAHs	70	0 (0%)	70	10300	1610	NC	7%

Table 12. Results of screening of the sediment chemistry data collected in the Tri-State Mining District (2002 - 2009).

Chemical of Interest (CoI)	# of Samples	# of N-D Samples Excluded ¹	# of Samples Excluding HN-D	EPC ²	TSV	Maximum HQ ³	FOE (%)
<i>Polychlorinated Biphenyls (PCBs; µg/kg DW)</i>							
Aroclor 1016	70	70(100%)	0	ND	4.42	NC	NC
Aroclor 1221	70	8 (11%)	62	<58	59.8	0.644	0%
Aroclor 1232	70	8 (11%)	62	<58	59.8	0.644	0%
Aroclor 1242	70	8 (11%)	62	<58	59.8	0.644	0%
Aroclor 1248	70	70(100%)	0	ND	30	NC	NC
Aroclor 1254	70	8 (11%)	62	<58	59.8	0.644	0%
Aroclor 1260	70	70(100%)	0	ND	5	NC	NC
Aroclor 1262	70	8 (11%)	62	<58	59.8	0.644	0%
Aroclor 1268	70	8 (11%)	62	<58	59.8	0.644	0%
PCBs, total	70	70(100%)	0	ND	40.4	NC	NC
<i>Organochlorine Pesticides (µg/kg DW)</i>							
Aldrin	70	68 (97%)	2	<2	2	0.975	0%
Chlordane, cis-	70	7 (10%)	63	<3.2	3.24	0.602	0%
Chlordane, trans-	70	19 (27%)	51	<2.6	2.62	0.744	0
Dieldrin	70	70(100%)	0	ND	1.9	NC	NC
Endosulfan sulfate	70	0 (0%)	70	<7.6	ND	NC	NC
Endosulfan-alpha	70	9 (13%)	61	<2.9	2.97	0.657	0
Endosulfan-beta	70	0 (0%)	70	<7.6	9.43	0.403	0%
Endrin	70	70(100%)	0	ND	2.22	NC	NC
Endrin aldehyde	70	70(100%)	0	ND	2.22	NC	NC
Endrin ketone	70	70(100%)	0	ND	2.22	NC	NC
Heptachlor	70	0 (0%)	70	<3.9	5.37	0.363	0%
Heptachlor epoxide	70	70(100%)	0	ND	1.73	NC	NC
Hexachlorobenzene	70	0 (0%)	70	<46	55.2	0.417	0%
Hexachlorocyclohexane-alpha	70	0 (0%)	70	<3.9	6	0.325	0%
Hexachlorocyclohexane-beta	70	0 (0%)	70	<3.9	5	0.39	0%
Hexachlorocyclohexane-delta	70	0 (0%)	70	<3.9	71500	0.0000273	0%
Hexachlorocyclohexane-gamma	70	42 (60%)	28	<2.3	2.33	0.837	0%
Hexachlorocyclopentadiene	66	0 (0%)	66	<184	7	13.1	100%
Isophorone	70	0 (0%)	70	<46	2400	0.00958	0%
Methoxychlor	70	70(100%)	0	ND	14.1	NC	NC
<i>p,p'</i> -DDD	70	22 (31%)	48	<5	5.09	0.747	0%
<i>p,p'</i> -DDE	70	70(100%)	0	ND	2.61	NC	NC
<i>p,p'</i> -DDT	70	70(100%)	0	ND	2.66	NC	NC
Toxaphene	70	70(100%)	0	ND	2.79	NC	NC
<i>Semi-Volatile Compounds (µg/kg DW)</i>							
1,2,4-Trichlorobenzene	70	0 (0%)	70	<46	8160	0.00282	0%
1,2-Dichlorobenzene	70	0 (0%)	70	<100	173	0.289	0%
1,3-Dichlorobenzene	70	0 (0%)	70	<100	1610	0.0311	0%
1,4-Dichlorobenzene	70	0 (0%)	70	<100	247	0.202	0%

Table 12. Results of screening of the sediment chemistry data collected in the Tri-State Mining District (2002 - 2009).

Chemical of Interest (CoI)	# of Samples	# of N-D Samples Excluded ¹	# of Samples Excluding HN-D	EPC ²	TSV	Maximum HQ ³	FOE (%)
<i>Semi-Volatile Compounds (µg/kg DW; cont.)</i>							
2,4,5-Trichlorophenol	70	0 (0%)	70	<46	3	7.67	100%
2,4,6-Trichlorophenol	70	0 (0%)	70	<46	6	3.83	100%
2,4-Dichlorophenol	70	0 (0%)	70	<46	81.7	0.282	0%
2,4-Dimethylphenol	70	0 (0%)	70	<46	29	0.793	0%
2,4-Dinitrophenol	70	0 (0%)	70	<460	ND	NC	NC
2,4-Dinitrotoluene	70	0 (0%)	70	<92	ND	NC	NC
2,6-Dinitrotoluene	70	0 (0%)	70	<92	ND	NC	NC
2-Chloronaphthalene	70	0 (0%)	70	<46	ND	NC	NC
2-Chlorophenol	70	9 (13%)	61	<31.4	31.9	0.721	0%
2-Methylphenol	70	0 (0%)	70	<46	ND	NC	NC
2-Nitroaniline	70	0 (0%)	70	<92	ND	NC	NC
2-Nitrophenol	70	0 (0%)	70	<46	ND	NC	NC
3-Methylphenol and/or 4 Methylphenol	70	0 (0%)	70	55.3	ND	NC	NC
3,3'-Dichlorobenzidine	70	0 (0%)	70	<210	0.28	375	100%
3-Nitroaniline	70	0 (0%)	70	<92	ND	NC	NC
4-Bromophenyl phenyl ether	70	0 (0%)	70	<46	ND	NC	NC
4-Chloro-3-methylphenol	70	0 (0%)	70	<46	ND	NC	NC
4-Chloroaniline	70	0 (0%)	70	<46	ND	NC	NC
4-Chlorophenyl phenyl ether	70	0 (0%)	70	<46	ND	NC	NC
4-Nitroaniline	70	0 (0%)	70	<92	ND	NC	NC
4-Nitrophenol	70	0 (0%)	70	<460	ND	NC	NC
Acetophenone	70	0 (0%)	70	<46	ND	NC	NC
Atrazine	70	0 (0%)	70	<46	0.3	76.7	100%
Benzaldehyde	70	0 (0%)	70	<92	ND	NC	NC
Benzoic acid	70	0 (0%)	70	601	650	0.925	0%
Benzyl alcohol	70	0 (0%)	70	<46	57	0.404	0%
bis(2-chloroethoxy)methane	70	0 (0%)	70	<46	ND	NC	NC
bis(2-chloroethyl)ether	70	0 (0%)	70	<46	ND	NC	NC
bis(2-chloroisopropyl) ether	70	0 (0%)	70	<46	ND	NC	NC
bis(2-ethylhexyl) phthalate	70	0 (0%)	70	533	182	2.93	11%
Butylbenzyl phthalate	70	0 (0%)	70	1550	49	31.6	100%
Caprolactam	70	0 (0%)	70	58.2	ND	NC	NC
Diethyl phthalate	70	0 (0%)	70	<460	610	0.377	0%
Dimethyl phthalate	70	0 (0%)	70	<460	530	0.434	0%
Di- <i>n</i> -butyl phthalate	70	0 (0%)	70	<460	42	5.48	100%
Dinitro- <i>o</i> -cresol	70	0 (0%)	70	<460	0.184	1250	100%
Di- <i>n</i> -octyl phthalate	70	0 (0%)	70	<460	580	0.397	0%
Hexachlorobutadiene	70	68 (97%)	2	<20.1	20.5	1.12	0%
Hexachloroethane	70	0 (0%)	70	<77.6	1.4	27.7	100%
<i>n</i> -nitrosodi- <i>n</i> -propylamine	70	0 (0%)	70	<46	ND	NC	NC
<i>n</i> -nitrosodiphenylamine	70	0 (0%)	70	<46	110	0.209	0%

Table 12. Results of screening of the sediment chemistry data collected in the Tri-State Mining District (2002 - 2009).

Chemical of Interest (CoI)	# of Samples	# of N-D Samples Excluded¹	# of Samples Excluding HN-D	EPC²	TSV	Maximum HQ³	FOE (%)
<i>Semi-Volatile Compounds (µg/kg DW; cont.)</i>							
Pentachlorophenol	70	0 (0%)	70	<92	733	0.0628	0%
Phenol	70	0 (0%)	70	<46	66.7	0.345	0%

EPC = exposure point concentration; FOE = frequency of exceedance; HN-D = high non-detect; HQ = hazard quotient; LMW = low molecular weight; HMW = high molecular weight; NA = not applicable; NC = not calculated; ND = no data; N-D = non-detect; TSV = toxicity screening value.

¹ When a TSV exists for a given CoI, data below the analytical detection limit, but greater than the TSV were excluded from the frequency of exceedance analysis.

² The maximum concentration of each CoI was selected as the EPC for the Screening Level Environmental Risk Assessment.

³ Where the EPC was below the analytical detection limit, but less than the TSV, one half of the detection limit was used to calculate the HQ.

Table 13. Results of screening of the pore-water chemistry data collected in the Tri-State Mining District (2002 - 2009).

Chemical of Interest (CoI)	# of Samples	# of N-D Samples Excluded ¹	# of Samples Excluding HN-D	EPC ²	TSV	Maximum HQ ³	FOE (%)
Metals (µg/L)							
Aluminum, total	26	20 (76%)	6	4820	87	55.4	100%
Arsenic, total	26	0 (0%)	26	<10	150	0.0333	0%
Barium, total	26	0 (0%)	26	<200	1000	0.1	0%
Cadmium, total	26	23 (88%)	3	42	0.25	168	100%
Chromium, total	26	26 (0%)	0	ND	2	NC	NC
Cobalt, total	26	0 (0%)	26	<50	5	5	100%
Copper, total	26	24 (92%)	2	31.8	4.17	7.63	100%
Iron, total	26	0 (0%)	26	6400	887	7.22	15%
Lead, total	26	23 (88%)	3	113	1.16	97.4	100%
Mercury, total	26	26 (100%)	0	ND	0.182	NC	NC
Molybdenum, total	ND	NA	NA	ND	395	NC	NC
Nickel, total	26	0 (0%)	26	<47.4	52	0.79	0%
Selenium, total	26	26 (100%)	0	ND	4.96	NC	NC
Silver, total	26	26 (100%)	0	ND	0.098	NC	NC
Zinc, total	26	0 (0%)	26	15600	60.8	257	50%
Aluminum, dissolved	70	0 (0%)	70	100	87	1.15	3%
Arsenic, dissolved	70	0 (0%)	70	40	150	0.267	0%
Barium, dissolved	70	0 (0%)	70	400	1000	0.4	0%
Cadmium, dissolved	70	0 (0%)	70	20.4	0.25	81.6	16%
Chromium, dissolved	70	0 (0%)	70	<0.1	2	0.025	0%
Cobalt, dissolved	70	0 (0%)	70	70	5	14	64%
Copper, dissolved	70	0 (0%)	70	3.21	4.17	0.77	0%
Iron, dissolved	70	0 (0%)	70	38000	887	42.8	74%
Lead, dissolved	70	0 (0%)	70	67.9	1.16	58.5	26%
Molybdenum, dissolved	70	0 (0%)	70	8	395	0.0203	0%
Mercury, dissolved	ND	NA	NA	ND	ND	NC	NC
Nickel, dissolved	70	0 (0%)	70	33.4	52	0.642	0%
Selenium, dissolved	70	0 (0%)	70	2	4.96	0.403	0%
Silver, dissolved	70	70 (100%)	0	ND	0.098	NC	NC
Zinc, dissolved	70	0 (0%)	70	7020	60.8	115	33%

EPC = exposure point concentration; FOE = frequency of exceedance; HN-D = high non-detect; HQ = hazard quotient; NA = not applicable; NC = not calculated; ND = no data; N-D = non-detect; TSV = toxicity screening value.

¹ When a TSV exists for a given CoI, data below the analytical detection limit, but greater than the TSV were excluded from the frequency of exceedance analysis.

² The maximum concentration of each CoI was selected as the EPC for the Screening Level Environmental Risk Assessment.

³ Where the EPC was below the analytical detection limit, but less than the TSV, one half of the detection limit was used to calculate the HQ.

Table 14. Comparison of the 95th percentile concentrations of chemicals of potential concern in surface-water samples from reference areas to the 95th percentile concentrations of chemicals of potential concern in surface-water samples from the Tri-State Mining District (TSMD).

Chemical of Potential Concern	Reference				Tri-State Mining District				Ratio TSMD:Ref ¹	Preliminary COC ²
	n	95th Percentile Concentration	Frequency of Detection	Maximum Detected Concentration	n	95th Percentile Concentration	Frequency of Detection	Maximum Detected Concentration		
<i>Metals (µg/L)</i>										
Aluminum, total	19	1415	100%	3530	629	7050	63%	39600	5.34	Y
Cadmium, total	19	2.50	0%	ND	688	19.8	31%	158	7.92	Y
Chromium, total	19	5.00	0%	ND	629	7.00	7%	41	1.40	N
Cobalt, total	19	25.0	0%	ND	483	25.0	14%	59	1.00	N
Copper, total	19	12.5	0%	ND	648	28.2	22%	55.9	2.26	Y
Iron, total	19	1520	100%	2370	669	15000	92%	272000	9.87	Y
Lead, total	19	5.00	0%	ND	676	49.2	33%	446	9.84	Y
Mercury, total	19	0.1	0%	ND	321	0.100	2%	0.52	1.00	N
Nickel, total	19	22.1	5%	40.8	607	137	33%	645	6.37	Y
Selenium, total	19	17.5	0%	ND	459	17.5	0%	10	1.00	N
Silver, total	19	5.00	0%	ND	459	5.00	1%	0.65	1.00	N
Zinc, total	19	333	5%	3060	694	7500	81%	23500	158	Y
Aluminum, dissolved	18	266	33%	286	551	281	13%	1040	1.06	N
Cadmium, dissolved	18	2.50	0%	ND	596	15	19%	107	6.00	Y
Chromium, dissolved	18	5.00	0%	ND	551	5	1%	17	1.00	N
Cobalt, dissolved	18	25.0	0%	ND	376	25	9%	49	1.00	N
Copper, dissolved	18	12.5	0%	ND	588	12.5	8%	9	1.00	N
Iron, dissolved	18	110	22%	110	587	7370	41%	39700	67.0	Y
Lead, dissolved	18	5.00	0%	ND	597	5	4%	70.9	1.00	N
Mercury, dissolved	ND	ND	ND	ND	ND	ND	ND	ND	NC	Y (Uncertain)
Nickel, dissolved	18	20.0	0%	ND	534	145	29%	615	7.25	Y
Selenium, dissolved	18	17.5	0%	ND	381	17.5	1%	11	1.00	N
Silver, dissolved	18	5.00	0%	ND	381	5	0%	ND	1.00	N
Zinc, dissolved	18	474	5%	2990	685	6520	70%	21900	109	Y

Table 14. Comparison of the 95th percentile concentrations of chemicals of potential concern in surface-water samples from reference areas to the 95th percentile concentrations of chemicals of potential concern in surface-water samples from the Tri-State Mining District (TSMD).

Chemical of Potential Concern	Reference				Tri-State Mining District				Ratio TSMD:Ref ¹	Preliminary COC ²
	n	95th Percentile Concentration	Frequency of Detection	Maximum Detected Concentration	n	95th Percentile Concentration	Frequency of Detection	Maximum Detected Concentration		
<i>Nutrients/Inorganics/Conventionals</i>										
Chlorine, dissolved	ND	ND	ND	ND	ND	ND	ND	ND	NC	Y (Uncertain)

COC = contaminant of concern; COPC = chemical of potential concern; n = number of samples; N = no ND = no data; NC = not calculated; Ref = reference; Y = yes.

¹ Ratio of the 95th percentile for TSMD samples to the 95th percentile for reference samples.

² A COPC was retained as a preliminary COC if the ratio (TSMD:Ref) was ≥ 2.0 or if the COPC was designated as uncertain (NC).

Table 15. Comparison of the 95th percentile concentrations of chemicals of potential concern in sediment samples from reference areas to the 95th percentile concentrations of chemicals of potential concern in sediment samples from the Tri-State Mining District (TSMD).

Chemical of Potential Concern	Reference			Tri-State Mining District				Ratio TSMD:Ref ¹	Preliminary COC ²	
	n	95th Percentile Concentration	Frequency of Detection	Maximum Detected Concentration	n	95th Percentile Concentration	Frequency of Detection			Maximum Detected Concentration
Metals (mg/kg DW)										
Aluminum	8	11700	100%	11700	784	54000	100%	83000	4.62	Y
Arsenic	8	8.81	37%	11.6	843	25	83%	351	2.84	Y
Barium	8	149	100%	157	753	520	88%	811	3.49	Y
Cadmium	8	2.34	62%	2.81	1154	132	90%	4610	56.4	Y
Chromium	8	35.1	100%	38.8	784	87.2	97%	204	2.48	Y
Cobalt	8	16.3	62%	18.2	695	32.1	71%	390	1.97	N
Copper	8	11.3	100%	12	987	118	95%	760	10.4	Y
Iron	8	33500	100%	40300	843	87000	100%	497000	2.60	Y
Lead	8	27.9	100%	28	1156	2020	98%	40400	72.4	Y
Mercury	8	0.100	0%	ND	608	1.03	42%	7.92	10.3	Y
Molybdenum	ND	ND	ND	ND	311	18	56%	110	NC	Y (Uncertain)
Nickel	8	19.4	87%	20.2	784	65.6	82%	199	3.38	Y
Selenium	8	3.55	0%	ND	694	6	37%	21.8	1.69	N
Silver	8	1.01	0%	ND	695	1.75	25%	5.76	1.73	N
Zinc	8	258	100%	272	1156	25000	100%	159000	96.9	Y
Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)										
Acenaphthene	8	18.9	0%	ND	70	19.2	3%	129	1.02	N
Anthracene	8	18.9	0%	ND	70	39.5	13%	268	2.09	Y
Benz(a)anthracene	8	43.5	25%	48.6	70	233	34%	1050	5.36	Y
Benzo(a)pyrene	8	50.6	37%	53.2	70	245	40%	1090	4.84	Y
Benzo(g,h,i)perylene	8	39.8	25%	43.3	70	138	39%	547	3.47	Y
Benzo(k)fluoranthene	8	48.0	25%	49.2	70	189	36%	934	3.94	Y
Chrysene	8	77.3	37%	89.9	70	274	47%	1110	3.54	Y
Dibenz(a,h)anthracene	8	18.9	0%	ND	70	54.4	13%	230	2.88	Y
Fluoranthene	8	108	37%	123	70	497	44%	2550	4.60	Y

Table 15. Comparison of the 95th percentile concentrations of chemicals of potential concern in sediment samples from reference areas to the 95th percentile concentrations of chemicals of potential concern in sediment samples from the Tri-State Mining District (TSMD).

Chemical of Potential Concern	Reference			Tri-State Mining District				Ratio TSMD:Ref ¹	Preliminary COC ²	
	n	95th Percentile Concentration	Frequency of Detection	Maximum Detected Concentration	n	95th Percentile Concentration	Frequency of Detection			Maximum Detected Concentration
<i>PAHs (µg/kg DW; cont.)</i>										
Fluorene	8	18.9	0%	ND	70	19.2	3%	168	1.02	N
Indeno(1,2,3- <i>c,d</i>)pyrene	8	38.1	25%	40.9	70	144	33%	569	3.78	Y
Phenanthrene	8	62.1	25%	82	70	279	46%	1590	4.49	Y
Pyrene	8	111	37%	136	70	479	46%	2010	4.32	Y
Total high molecular weight PAHs	8	403	37%	457	70	1840	47%	8050	4.57	Y
Total low molecular weight PAHs	8	157	25%	167	70	428	46%	2240	2.73	Y
Total PAHs	8	550	50%	624	70	2340	53%	10300	4.25	Y
<i>Polychlorinated Biphenyls (PCBs; µg/kg DW)</i>										
Aroclor 1016	8	36.0	0%	ND	70	33.5	0%	ND	0.931	N
Aroclor 1248	8	36.0	0%	ND	70	33.5	0%	ND	0.931	N
Aroclor 1260	8	36.0	0%	ND	70	33.5	0%	ND	0.931	N
PCBs, total	8	324	0%	ND	70	302	0%	ND	0.932	N
<i>Organochlorine Pesticides (µg/kg DW)</i>										
Dieldrin	8	3.60	0%	ND	70	3.35	0%	ND	0.931	N
Endosulfan sulfate	8	3.60	0%	ND	70	3.35	0%	ND	0.931	N
Endrin	8	3.60	0%	ND	70	3.35	0%	ND	0.931	N
Endrin aldehyde	8	3.60	0%	ND	70	3.35	100%	ND	0.931	N
Endrin ketone	8	3.60	0%	ND	70	3.35	100%	ND	0.931	N
Heptachlor epoxide	8	1.87	0%	ND	70	1.73	0%	ND	0.925	N
Hexachlorocyclopentadiene	8	71.1	0%	ND	66	66.5	0%	ND	0.935	N
Methoxychlor	8	18.7	0%	ND	70	17.3	0%	ND	0.925	N
<i>p,p'</i> -DDE	8	3.60	0%	ND	70	3.35	0%	ND	0.931	N
<i>p,p'</i> -DDT	8	3.60	0%	ND	70	3.35	0%	ND	0.931	N
Toxaphene	8	187	0%	ND	70	173	0%	ND	0.925	N

Table 15. Comparison of the 95th percentile concentrations of chemicals of potential concern in sediment samples from reference areas to the 95th percentile concentrations of chemicals of potential concern in sediment samples from the Tri-State Mining District (TSMD).

Chemical of Potential Concern	Reference			Tri-State Mining District			Ratio TSMD:Ref ¹	Preliminary COC ²		
	n	95th Percentile Concentration	Frequency of Detection	Maximum Detected Concentration	n	95th Percentile Concentration			Frequency of Detection	Maximum Detected Concentration
<i>Semi-Volatile Compounds (µg/kg DW)</i>										
2,4,5-Trichlorophenol	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
2,4,6-Trichlorophenol	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
2,4-Dinitrophenol	8	189	0%	ND	70	175	0%	ND	0.926	N
2,4-Dinitrotoluene	8	37.8	0%	ND	70	35	0%	ND	0.926	N
2,6-Dinitrotoluene	8	37.8	0%	ND	70	35	0%	ND	0.926	N
2-Chloronaphthalene	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
2-Methylphenol	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
2-Nitroaniline	8	37.8	0%	ND	70	35	0%	ND	0.926	N
2-Nitrophenol	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
3&/or4 Methylphenol	8	18.9	0%	ND	70	18.1	1%	55.3	0.958	N
3,3'-Dichlorobenzidine	8	18.9	0%	ND	70	21.5	1%	40.2	1.14	N
3-Nitroaniline	8	37.8	0%	ND	70	35	0%	ND	0.926	N
4-Bromophenyl phenyl ether	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
4-Chloro-3-methylphenol	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
4-Chloroaniline	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
4-Chlorophenyl phenyl ether	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
4-Nitroaniline	8	37.8	0%	ND	70	35	0%	ND	0.926	N
4-Nitrophenol	8	189	0%	ND	70	175	0%	ND	0.926	N
Acetophenone	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
Atrazine	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
Benzaldehyde	8	37.8	0%	ND	70	35	0%	ND	0.926	N
Benzoic Acid	8	460	12%	601	70	269	6%	513	0.585	N
bis(2-chloroethoxy)methane	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
bis(2-chloroethyl)ether	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
bis(2-chloroisopropyl) ether	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
bis(2-ethylhexyl) phthalate	8	189	0%	ND	70	253	7%	533	1.34	N
Butylbenzyl phthalate	8	189	0%	ND	70	746	14%	1550	3.95	Y

Table 15. Comparison of the 95th percentile concentrations of chemicals of potential concern in sediment samples from reference areas to the 95th percentile concentrations of chemicals of potential concern in sediment samples from the Tri-State Mining District (TSMD).

Chemical of Potential Concern	Reference			Tri-State Mining District			Ratio TSMD:Ref ¹	Preliminary COC ²		
	n	95th Percentile Concentration	Frequency of Detection	Maximum Detected Concentration	n	95th Percentile Concentration			Frequency of Detection	Maximum Detected Concentration
<i>Semi-Volatile Compounds (µg/kg DW; cont.)</i>										
Caprolactam	8	39.8	12%	58.2	70	31.2	11%	45.9	0.784	N
Di- <i>n</i> -butyl phthalate	8	189	0%	ND	70	175	0%	ND	0.926	N
Dinitro- <i>o</i> -cresol	8	189	0%	ND	70	175	0%	ND	0.926	N
Hexachlorobutadiene	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N
Hexachloroethane	8	18.9	0%	ND	70	19.2	0%	ND	1.02	N
<i>n</i> -nitrosodi- <i>n</i> -propylamine	8	18.9	0%	ND	70	17.5	0%	ND	0.926	N

COC = contaminant of concern; COPC = chemical of potential concern; n = number of samples; N = no ND = no data; NC = not calculated; Ref = reference; Y = yes.

¹ Ratio of the 95th percentile for TSMD samples to the 95th percentile for reference samples.

² A COPC was retained as a preliminary COC if the ratio (TSMD:Ref) was ≥ 2.0 or if the COPC was designated as uncertain (NC).

Table 16. Comparison of the 95th percentile concentrations of chemicals of potential concern in pore-water samples from reference areas to the 95th percentile concentrations of chemicals of potential concern in pore-water samples from the Tri-State Mining District (TSMD).

Chemical of Potential Concern	Reference				Tri-State Mining District				Ratio TSMD:Ref ¹	Preliminary COC ²
	n	95th percentile Concentration	Frequency of Detection	Maximum Detected Concentration	n	95th percentile Concentration	Frequency of Detection	Maximum Detected Concentration		
<i>Metals (µg/L)</i>										
Aluminum, total	ND	ND	ND	ND	26	1760	33%	4820	NC	Y (Uncertain)
Cadmium, total	ND	ND	ND	ND	26	13.7	12%	42	NC	Y (Uncertain)
Chromium, total	ND	ND	ND	ND	26	5.00	0%	ND	NC	Y (Uncertain)
Cobalt, total	ND	ND	ND	ND	26	25.0	0%	ND	NC	Y (Uncertain)
Copper, total	ND	ND	ND	ND	26	25.3	8%	31.8	NC	Y (Uncertain)
Iron, total	ND	ND	ND	ND	26	3760	42%	6400	NC	Y (Uncertain)
Lead, total	ND	ND	ND	ND	26	73.5	12%	113	NC	Y (Uncertain)
Mercury, total	ND	ND	ND	ND	26	0.100	0%	ND	NC	Y (Uncertain)
Molybdenum, total	ND	ND	ND	ND	ND	ND	ND	ND	NC	Y (Uncertain)
Selenium, total	ND	ND	ND	ND	26	17.5	0%	ND	NC	Y (Uncertain)
Silver, total	ND	ND	ND	ND	26	5.00	0%	ND	NC	Y (Uncertain)
Zinc, total	ND	ND	ND	ND	26	2940	50%	15600	NC	Y (Uncertain)
Aluminum, dissolved	8	69.5	87%	80	70	75.5	94%	100	1.09	N
Cadmium, dissolved	8	0.080	0%	ND	70	3.23	24%	20.4	40.4	Y
Cobalt, dissolved	8	10.0	100%	10	70	30.0	100%	70	3.00	Y
Iron, dissolved	8	31000	100%	38000	70	19600	93%	26000	0.632	N
Lead, dissolved	8	0.16	25%	0.188	70	10.8	61%	67.9	67.5	Y
Mercury, dissolved	ND	ND	ND	ND	ND	ND	ND	ND	NC	Y (Uncertain)
Selenium, dissolved	8	2.00	62%	2	70	2	41%	2	1.00	N
Silver, dissolved	8	0.050	0%	ND	70	0.0500	0%	ND	1.00	N
Zinc, dissolved	8	2.85	0%	ND	70	1610	61%	7020	565	Y

COC = contaminant of concern; COPC = chemical of potential concern; n = number of samples; N = no ND = no data; NC = not calculated; Ref = reference; Y = yes.

¹ Ratio of the 95th percentile for TSMD samples to the 95th percentile for reference samples.

² A COPC was retained as a preliminary COC if the ratio (TSMD:Ref) was ≥ 2.0 or if the COPC was designated as uncertain (NC).

Table 17. Refined list of chemicals of potential concern in surface water, pore water, sediment, and biological tissues for evaluation in the detailed ecological risk assessment of the Tri-State Mining District.

Chemical of Potential Concern/Mixture	Surface Water¹	Sediment¹	Pore Water¹	Tissue²
<i>Metals</i>				
Aluminum, total	Y	Y	U	N
Arsenic, total	N	Y	N	Y
Barium, total	N	Y	N	N
Cadmium, total	Y	Y	U	Y
Chromium, total	N	Y	U	N
Cobalt, total	N	N	U	N
Copper, total	Y	Y	U	Y
Iron, total	Y	Y	U	N
Lead, total	Y	Y	U	Y
Mercury, total	N	Y	U	Y
Molybdenum, total	N	U	U	N
Nickel, total	Y	Y	N	N
Selenium, total	N	N	U	Y
Silver, total	N	N	U	N
Zinc, total	Y	Y	U	Y
Aluminum, dissolved	N	N	N	N
Cadmium, dissolved	Y	N	Y	N
Chromium, dissolved	N	N	N	N
Cobalt, dissolved	N	N	Y	N
Copper, dissolved	N	N	N	N
Iron, dissolved	Y	N	N	N
Lead, dissolved	N	N	Y	N
Molybdenum, dissolved	N	N	N	N
Mercury, dissolved	U	N	U	N
Nickel, dissolved	Y	N	N	N
Selenium, dissolved	N	N	N	N
Silver, dissolved	N	N	N	N
Zinc, dissolved	Y	N	Y	N
<i>Polycyclic Aromatic Hydrocarbons (PAHs)</i>				
2-Methylnaphthalene	N	N	N	N
Acenaphthene	N	N	N	N
Acenaphthylene	N	N	N	Y
Anthracene	N	Y	N	Y
Benz(<i>a</i>)anthracene	N	Y	N	Y
Benzo(<i>a</i>)pyrene	N	Y	N	Y
Benzo(<i>b</i>)fluoranthene	N	N	N	Y
Benzo(<i>g,h,i</i>)perylene	N	Y	N	Y
Benzo(<i>k</i>)fluoranthene	N	Y	N	Y
Biphenyl	N	N	N	N

Table 17. Refined list of chemicals of potential concern in surface water, pore water, sediment, and biological tissues for evaluation in the detailed ecological risk assessment of the Tri-State Mining District.

Chemical of Potential Concern/Mixture	Surface Water¹	Sediment¹	Pore Water¹	Tissue²
<i>PAHs (cont.)</i>				
Carbazole	N	N	N	N
Chrysene	N	Y	N	Y
Dibenz(<i>a,h</i>)anthracene	N	Y	N	Y
Dibenzofuran	N	N	N	N
Fluoranthene	N	Y	N	Y
Fluorene	N	N	N	Y
Indeno(1,2,3- <i>c,d</i>)pyrene	N	Y	N	Y
Naphthalene	N	N	N	N
Phenanthrene	N	Y	N	Y
Pyrene	N	Y	N	Y
Total high molecular weight PAHs	N	Y	N	Y
Total low molecular weight PAHs	N	Y	N	Y
Total PAHs	N	Y	N	Y
<i>Polychlorinated Biphenyls (PCBs)</i>				
Aroclor 1016	N	N	N	Y
Aroclor 1221	N	N	N	Y
Aroclor 1232	N	N	N	Y
Aroclor 1242	N	N	N	Y
Aroclor 1248	N	N	N	Y
Aroclor 1254	N	N	N	Y
Aroclor 1260	N	N	N	Y
Aroclor 1262	N	N	N	Y
Aroclor 1268	N	N	N	Y
PCBs, total	N	N	N	Y
<i>Organochlorine Pesticides</i>				
Aldrin	N	N	N	Y
Chlordane, cis-	N	N	N	Y
Chlordane, trans-	N	N	N	Y
Dieldrin	N	N	N	Y
Endosulfan sulfate	N	N	N	Y
Endosulfan-alpha	N	N	N	Y
Endosulfan-beta	N	N	N	Y
Endrin	N	N	N	Y
Endrin aldehyde	N	N	N	Y
Endrin ketone	N	N	N	Y
Heptachlor	N	N	N	Y
Heptachlor epoxide	N	N	N	Y
Hexachlorobenzene	N	N	N	Y

Table 17. Refined list of chemicals of potential concern in surface water, pore water, sediment, and biological tissues for evaluation in the detailed ecological risk assessment of the Tri-State Mining District.

Chemical of Potential Concern/Mixture	Surface Water¹	Sediment¹	Pore Water¹	Tissue²
<i>Organochlorine Pesticides (cont.)</i>				
Hexachlorocyclohexane-alpha	N	N	N	Y
Hexachlorocyclohexane-beta	N	N	N	Y
Hexachlorocyclohexane-delta	N	N	N	Y
Hexachlorocyclohexane-gamma	N	N	N	Y
Hexachlorocyclopentadiene	N	N	N	Y
Isophorone	N	N	N	Y
Methoxychlor	N	N	N	Y
<i>p,p'</i> -DDD	N	N	N	Y
<i>p,p'</i> -DDE	N	N	N	Y
<i>p,p'</i> -DDT	N	N	N	Y
Toxaphene	N	N	N	Y
<i>Semi-Volatile Compounds</i>				
1,2,4-Trichlorobenzene	N	N	N	Y
1,2-Dichlorobenzene	N	N	N	Y
1,3-Dichlorobenzene	N	N	N	Y
1,4-Dichlorobenzene	N	N	N	Y
2,4,5-Trichlorophenol	N	N	N	Y
2,4,6-Trichlorophenol	N	N	N	Y
2,4-Dichlorophenol	N	N	N	Y
2,4-Dimethylphenol	N	N	N	Y
2,4-Dinitrophenol	N	N	N	Y
2,4-Dinitrotoluene	N	N	N	Y
2,6-Dinitrotoluene	N	N	N	Y
2-Chloronaphthalene	N	N	N	Y
2-Chlorophenol	N	N	N	Y
2-Methylphenol	N	N	N	Y
2-Nitroaniline	N	N	N	Y
2-Nitrophenol	N	N	N	Y
3&/or4 Methylphenol	N	N	N	Y
3,3'-Dichlorobenzidine	N	N	N	Y
3-Nitroaniline	N	N	N	Y
4-Bromophenyl phenyl ether	N	N	N	Y
4-Chloro-3-methylphenol	N	N	N	N
4-Chloroaniline	N	N	N	N
4-Chlorophenyl phenyl ether	N	N	N	Y
4-Nitroaniline	N	N	N	N
4-Nitrophenol	N	N	N	N
Acetophenone	N	N	N	N
Atrazine	N	N	N	N

Table 17. Refined list of chemicals of potential concern in surface water, pore water, sediment, and biological tissues for evaluation in the detailed ecological risk assessment of the Tri-State Mining District.

Chemical of Potential Concern/Mixture	Surface Water¹	Sediment¹	Pore Water¹	Tissue²
<i>Semi-Volatile Compounds (cont.)</i>				
Benzaldehyde	N	N	N	N
Benzoic acid	N	N	N	N
Benzyl alcohol	N	N	N	N
bis(2-chloroethoxy)methane	N	N	N	N
bis(2-chloroethyl)ether	N	N	N	N
bis(2-chloroisopropyl) ether	N	N	N	N
bis(2-ethylhexyl) phthalate	N	N	N	Y
Butylbenzyl phthalate	N	Y	N	Y
Caprolactam	N	N	N	N
Diethyl phthalate	N	N	N	Y
Dimethyl phthalate	N	N	N	N
Di- <i>n</i> -butyl phthalate	N	N	N	Y
Dinitro- <i>o</i> -cresol	N	N	N	N
Di- <i>n</i> -octyl phthalate	N	N	N	Y
Hexachlorobutadiene	N	N	N	Y
Hexachloroethane	N	N	N	Y
<i>n</i> -nitrosodi- <i>n</i> -propylamine	N	N	N	N
<i>n</i> -nitrosodiphenylamine	N	N	N	N
Nitrobenzene	N	N	N	Y
Pentachlorophenol	N	N	N	Y
Phenol	N	N	N	N
<i>Nutrients/Inorganics/Conventionals</i>				
Ammonia	Y	N	N	N
Chlorine, dissolved	U	N	N	N
Nitrate, dissolved, NO3-N	N	N	N	N
Nitrate, total, NO3-N	N	N	N	N

TSMD = Tri-State Mining District; COPC = chemical of potential concern; Y = yes; N = no; U = uncertain.
 HQ = hazard quotient; TSV = toxicity screening value; COC = contaminant of concern.

¹ A COPC was retained as a preliminary COC if the HQ was >1.0 and if the 95th percentile concentration for the TSMD exceeded the 95th percentile concentration for reference samples by a factor of two or more for a given COPC. COPCs were also retained as uncertain COCs if no TSV or no data were available.

² All bioaccumulative COPCs were retained because no basis for COPC refinement was available (ie., it was not possible to make comparisons to levels in tissues from reference areas).

Table 18. Summary of candidate data sets compiled to support the screening level ecological risk assessment of the Tri-State Mining District.

Source	Number of Samples						Invertebrate Tissue	Fish Tissue	Soil
	Surface Water	SeepWater	Pore Water	Sediment	Seep Sediment				
Angelo <i>et al.</i> (2007)	NA	NA	NA	144	NA	218	NA	NA	
Eastern Shawnee Tribe of Oklahoma (2005)	25	NA	NA	NA	NA	NA	NA	NA	
HSPH (2007)	38	NA	NA	59	NA	NA	NA	104	
Juracek (2006)	NA	NA	NA	68	NA	NA	NA	NA	
Kirschner (2008)	NA	NA	NA	117	NA	NA	NA	NA	
ODEQ (2005)	666	NA	NA	114	NA	NA	NA	NA	
ODEQ (2008)	6	NA	NA	6	NA	NA	164	NA	
Pope (2005)	NA	NA	NA	101	NA	NA	NA	NA	
Quapaw Tribe of Oklahoma (2005)	89	NA	NA	NA	NA	NA	NA	NA	
USEPA (2006b)	240	NA	26	310	NA	NA	NA	NA	
USEPA (2007)	NA	NA	70	70	NA	21	NA	NA	
USEPA (2009)	163	22	NA	75	16	NA	NA	NA	
USFWS (2006)	NA	NA	NA	172	NA	NA	NA	NA	
USFWS (2007)	NA	NA	NA	6	NA	NA	NA	NA	
USGS (2004)	NA	NA	NA	53	NA	NA	NA	NA	
USGS (2006)	NA	NA	NA	6	NA	NA	NA	NA	
Total Number of Samples	1227	22	96	1301	16	239	164	104	

NA = not applicable

Table 19. Summary of the preliminary concentration-response relationships. Bold, italicized font indicates preliminary plots that were selected for further analysis (MacDonald *et al.* 2009).

Media Type / Toxicity Test Endpoint	Sediment Sample Size Fraction	COPC/COPC Mixture	Regression Equation Type	r ²	p
Sediment					
Amphipod 28-d Survival	< 2 mm	<i>Cadmium</i>	<i>Sig3</i>	0.46	<0.0001
		Chromium	Sig3	0.03	0.4059
		Copper	Sig3	0.27	<0.0001
		<i>Lead</i>	<i>Sig3</i>	0.48	<0.0001
		Nickel	Sig3	0.002	0.9276
		<i>Zinc</i>	<i>Sig3</i>	0.51	<0.0001
		Total PAH	Sig3	0.16	0.0033
		<i>ΣSEM-AVS¹</i>	<i>Sig3</i>	0.49	<0.0001
		(ΣSEM-AVS)/f _{OC} ¹	Sig3	0.28	<0.0001
		ΣESB-TU _{FCV}	Sig3	0.07	0.0888
		<i>Mean PEC-Q</i>	<i>Sig3</i>	0.51	<0.0001
		<i>Mean PEC-Q_{METAL}</i>	<i>Sig3</i>	0.53	<0.0001
		Mean PEC-Q _{METAL(1%OC)}	Log3	0.34	<0.0001
		<i>ΣPEC-Q_{Cd,Pb,Zn}</i>	<i>Sig3</i>	0.52	<0.0001
		<i>ΣSTT-Q_{Cd,Cu,Pb,Zn}</i>	<i>Sig3</i>	0.52	<0.0001
Sediment					
Amphipod 28-d Biomass	< 2 mm	Cadmium	Sig3	0.27	<0.0001
		Chromium	Sig3	0.007	0.7832
		Copper	Sig3	0.20	0.0003
		Lead	Sig3	0.33	<0.0001
		Nickel	Sig3	0.003	0.8825
		Zinc	Sig3	0.28	<0.0001
		Total PAH	Sig3	0.09	0.0415
		ΣSEM-AVS ¹	Sig3	0.24	<0.0001
		(ΣSEM-AVS)/f _{OC} ¹	Sig3	0.13	0.0074
		ΣESB-TU _{FCV}	Sig3	0.05	0.1545
		Mean PEC-Q	Sig3	0.34	<0.0001
		Mean PEC-Q _{METAL}	Sig3	0.35	<0.0001
		Mean PEC-Q _{METAL(1%OC)}	Sig3	0.15	0.0046
		ΣPEC-Q _{Cd,Pb,Zn}	Sig3	0.31	<0.0001
		ΣSTT-Q _{Cd,Cu,Pb,Zn}	Sig3	0.32	<0.0001
Sediment					
Mussel 28-d Survival	<250 μm (unless otherwise noted)	Cadmium	Sig3	0.28	0.0005
		Chromium	Sig3	0.28	0.0016
		<i>Copper</i>	<i>Sig3</i>	0.66	<0.0001
		Lead	Sig3	0.32	0.0002
		Nickel	Log3	0.08	0.1453

Table 19. Summary of the preliminary concentration-response relationships. Bold, italicized font indicates preliminary plots that were selected for further analysis (MacDonald *et al.* 2009).

Media Type / Toxicity Test Endpoint	Sediment Sample Size Fraction	COPC/COPC Mixture	Regression Equation Type	r ²	p
Sediment		<i>Zinc</i>	<i>Sig3</i>	<i>0.54</i>	<i><0.0001</i>
Mussel		Total PAH ²	Sig3	0.003	0.9457
28-d Survival		<i>ΣSEM-AVS^{1,3}</i>	<i>Sig3</i>	<i>0.68</i>	<i><0.0001</i>
(cont.)		(ΣSEM-AVS)/f _{OC} ^{1,3}	Sig3	0.19	0.0089
		ΣESB-TU _{FCV} ²	Sig3	0.02	0.7361
		Mean PEC-Q ²	Sig3	0.09	0.1646
		<i>Mean PEC-Q_{METAL}</i>	<i>Sig3</i>	<i>0.53</i>	<i><0.0001</i>
		<i>Mean PEC-Q_{METAL(1%OC)}</i>	<i>Sig3</i>	<i>0.92</i>	<i><0.0001</i>
		<i>ΣPEC-Q_{Cd,Pb,Zn}</i>	<i>Log3</i>	<i>0.47</i>	<i><0.0001</i>
		<i>ΣSTT-Q_{Cd,Cu,Pb,Zn}</i>	<i>Sig3</i>	<i>0.67</i>	<i><0.0001</i>
Sediment					
Mussel	<250 μm	Cadmium	Sig3	0.30	0.0003
28-d Biomass	(unless otherwise noted)	Chromium	Sig3	0.25	0.0035
		<i>Copper</i>	<i>Sig3</i>	<i>0.49</i>	<i><0.0001</i>
		<i>Lead</i>	<i>Sig3</i>	<i>0.48</i>	<i><0.0001</i>
		Nickel	Sig3	0.21	0.0051
		Zinc	Sig3	0.37	<0.0001
		Total PAH ²	Sig3	0.003	0.9494
		<i>ΣSEM-AVS^{1,3}</i>	<i>Sig3</i>	<i>0.50</i>	<i><0.0001</i>
		(ΣSEM-AVS)/f _{OC} ^{1,3}	Sig3	0.19	0.0083
		ΣESB-TU _{FCV} ²	Log3	0.05	0.3380
		Mean PEC-Q ²	Sig3	0.30	0.0009
		<i>Mean PEC-Q_{METAL}</i>	<i>Sig3</i>	<i>0.45</i>	<i><0.0001</i>
		<i>Mean PEC-Q_{METAL(1%OC)}</i>	<i>Sig3</i>	<i>0.63</i>	<i><0.0001</i>
		ΣPEC-Q _{Cd,Pb,Zn}	Sig3	0.39	<0.0001
		<i>ΣSTT-Q_{Cd,Cu,Pb,Zn}</i>	<i>Sig3</i>	<i>0.43</i>	<i><0.0001</i>
Sediment					
Midge	< 2 mm	Cadmium	Sig3	0.10	0.0312
10-d Survival		Chromium	Sig3	0.08	0.0564
		Copper	Sig3	0.05	0.1889
		Lead	Sig3	0.09	0.0383
		Nickel	Sig3	0.009	0.7361
		Zinc	Sig3	0.14	0.0056
		Total PAH	Sig3	0.02	0.5541
		ΣSEM-AVS ⁴	Log3	0.23	0.0001
		(ΣSEM-AVS)/f _{OC} ⁴	Sig4	0.22	0.0007

Table 19. Summary of the preliminary concentration-response relationships. Bold, italicized font indicates preliminary plots that were selected for further analysis (MacDonald *et al.* 2009).

Media Type / Toxicity Test Endpoint	Sediment Sample Size Fraction	COPC/COPC Mixture	Regression Equation Type	r ²	p
Sediment		Σ ESB-TU _{FCV}	Linear	0.001	0.7961
Midge		Mean PEC-Q	Sig3	0.13	0.0079
10-d Survival		Mean PEC-Q _{METAL}	Sig3	0.14	0.0070
(cont.)		Mean PEC-Q _{METAL(1%OC)}	Sig3	0.03	0.3504
		Σ PEC-Q _{Cd,Pb,Zn}	Log3	0.16	0.0035
		Σ STT-Q _{Cd,Cu,Pb,Zn}	Sig3	0.14	0.0066
Sediment					
Midge	< 2 mm	Cadmium	Sig3	0.08	0.0513
10-d Biomass		Chromium	Sig3	0.03	0.3903
		Copper	Sig3	0.15	0.0050
		Lead	Sig3	0.19	0.0010
		Nickel	Sig3	0.03	0.3074
		Zinc	Sig3	0.11	0.0229
		Total PAH	Sig3	0.06	0.1227
		Σ SEM-AVS ⁴	Log3	0.22	0.0003
		(Σ SEM-AVS)/ <i>f</i> _{OC} ⁴	Log3	0.16	0.0028
		Σ ESB-TU _{FCV}	Sig3	0.04	0.2164
		Mean PEC-Q	Sig3	0.14	0.0068
		Mean PEC-Q _{METAL}	Sig3	0.14	0.0066
		Mean PEC-Q _{METAL(1%OC)}	Sig3	0.04	0.2789
		Σ PEC-Q _{Cd,Pb,Zn}	Log3	0.16	0.0030
		Σ STT-Q _{Cd,Cu,Pb,Zn}	Sig3	0.16	0.0031
Pore Water⁵					
Amphipod	NA	Σ PW-TU _{METALS}	Sig3	0.082	0.0565
28-d Survival		<i>ΣPW-TU_{DIVALENT METALS}</i>	<i>Sig3</i>	<i>0.84</i>	<i><0.0001</i>
		PW-TU _{ALUMINUM}	Sig3	0.003	0.9162
		PW-TU _{ARSENIC}	Sig3	0.10	0.0279
		PW-TU _{CADMIUM (7-d)}	Sig3	0.40	<0.0001
		PW-TU _{CADMIUM (28-d)}	Sig3	0.39	<0.0001
		<i>PW-TU_{CADMIUM (Mean)}</i>	<i>Sig3</i>	<i>0.40</i>	<i><0.0001</i>
		PW-TU _{CHROMIUM}	Sig3	0.04	0.2481
		PW-TU _{COPPER (7-d)}	Sig3	0.001	0.9606
		PW-TU _{COPPER (28-d)}	Linear	0.0006	0.8391
		PW-TU _{COPPER (Mean)}	Linear	0.0	0.9636
		PW-TU _{IRON}	Sig3	0.11	0.0186
		PW-TU _{LEAD (7-d)}	Sig3	0.56	<0.0001
		PW-TU _{LEAD (28-d)}	Sig3	0.52	<0.0001

Table 19. Summary of the preliminary concentration-response relationships. Bold, italicized font indicates preliminary plots that were selected for further analysis (MacDonald *et al.* 2009).

Media Type / Toxicity Test Endpoint	Sediment Sample Size Fraction	COPC/COPC Mixture	Regression Equation Type	r ²	p
Pore Water⁵		<i>PW-TU_{LEAD} (Mean)</i>	<i>Sig3</i>	<i>0.59</i>	<i><0.0001</i>
Amphipod		PW-TU _{NICKEL} (7-d)	Sig3	0.14	0.0076
28-d Survival		PW-TU _{NICKEL} (28-d)	Sig3	0.003	0.9171
(cont.)		PW-TU _{NICKEL} (Mean)	Sig3	0.05	0.1594
		PW-TU _{SELENIUM}	Sig3	0.01	0.6168
		PW-TU _{SILVER}	Sig3	0.04	0.2383
		PW-TU _{ZINC} (7-d)	Sig3	0.81	<0.0001
		PW-TU _{ZINC} (28-d)	Sig3	0.82	<0.0001
		<i>PW-TU_{ZINC} (Mean)</i>	<i>Sig3</i>	<i>0.83</i>	<i><0.0001</i>
		<i>PW-TU_{LEAD(DOC)}</i>	<i>Sig3</i>	<i>0.59</i>	<i><0.0001</i>
		<i>PW-TU_{ZINC(DOC)}</i>	<i>Sig3</i>	<i>0.72</i>	<i><0.0001</i>
Pore Water⁵					
Amphipod	NA	ΣPW-TU _{METALS}	Sig3	0.05	0.1781
28-d Biomass		<i>ΣPW-TU_{DIVALENT METALS}</i>	<i>Sig3</i>	<i>0.52</i>	<i><0.0001</i>
		PW-TU _{ALUMINUM}	Sig3	0.004	0.8775
		PW-TU _{ARSENIC}	Sig3	0.03	0.4094
		PW-TU _{CADMIUM} (7-d)	Sig3	0.24	0.0001
		PW-TU _{CADMIUM} (28-d)	Sig3	0.23	0.0002
		PW-TU _{CADMIUM} (Mean)	Sig3	0.24	0.0001
		PW-TU _{CHROMIUM}	Linear	0.0002	0.9112
		PW-TU _{COPPER} (7-d)	Linear	0.004	0.6228
		PW-TU _{COPPER} (28-d)	Sig3	0.06	0.1494
		PW-TU _{COPPER} (Mean)	Sig3	0.04	0.2517
		PW-TU _{IRON}	Sig3	0.14	0.0054
		PW-TU _{LEAD} (7-d)	Sig3	0.42	<0.0001
		PW-TU _{LEAD} (28-d)	Sig3	0.41	<0.0001
		<i>PW-TU_{LEAD} (Mean)</i>	<i>Sig3</i>	<i>0.45</i>	<i><0.0001</i>
		PW-TU _{NICKEL} (7-d)	Sig3	0.14	0.0059
		PW-TU _{NICKEL} (28-d)	Linear	0.005	0.5709
		PW-TU _{NICKEL} (Mean)	Sig3	0.07	0.0988
		PW-TU _{SELENIUM}	Linear	0.0	0.9605
		PW-TU _{SILVER}	Linear	0.003	0.6534
		PW-TU _{ZINC} (7-d)	Sig3	0.50	<0.0001
		PW-TU _{ZINC} (28-d)	Sig3	0.49	<0.0001
		<i>PW-TU_{ZINC} (Mean)</i>	<i>Sig3</i>	<i>0.50</i>	<i><0.0001</i>
		<i>PW-TU_{LEAD(DOC)}</i>	<i>Sig3</i>	<i>0.45</i>	<i><0.0001</i>
		<i>PW-TU_{ZINC(DOC)}</i>	<i>Sig3</i>	<i>0.44</i>	<i><0.0001</i>

Table 19. Summary of the preliminary concentration-response relationships. Bold, italicized font indicates preliminary plots that were selected for further analysis (MacDonald *et al.* 2009).

Media Type / Toxicity Test Endpoint	Sediment Sample Size Fraction	COPC/COPC Mixture	Regression Equation Type	r ²	p
Pore Water⁵					
Mussel 28-d Survival	NA	<i>ΣPW-TU METALS</i>	<i>Sig3</i>	<i>0.77</i>	<i><0.0001</i>
		<i>ΣPW-TU DIVALENT METALS</i>	<i>Sig3</i>	<i>0.82</i>	<i><0.0001</i>
		PW-TU _{ALUMINUM}	Sig3	0.02	0.659
		PW-TU _{ARSENIC}	Sig3	0.04	0.4673
		<i>PW-TU CADMIUM (7-d)</i>	<i>Sig3</i>	<i>0.79</i>	<i><0.0001</i>
		PW-TU _{CADMIUM} (28-d)	Sig3	0.31	0.0007
		PW-TU _{CADMIUM} (Mean)	Linear	0.35	<0.0001
		PW-TU _{CHROMIUM}	Sig3	0.009	0.8415
		<i>PW-TU COPPER (7-d)</i>	<i>Sig3</i>	<i>0.84</i>	<i><0.0001</i>
		PW-TU _{COPPER} (28-d)	Linear	0.008	0.5626
		PW-TU _{COPPER} (Mean)	Linear	0.12	0.0255
		PW-TU _{IRON}	Sig3	0.05	0.3376
		PW-TU _{LEAD} (7-d)	Sig3	0.47	<0.0001
		PW-TU _{LEAD} (28-d)	Sig3	0.78	<0.0001
		<i>PW-TU LEAD (Mean)</i>	<i>Sig3</i>	<i>0.51</i>	<i><0.0001</i>
		PW-TU _{NICKEL} (7-d)	Sig3	0.79	<0.0001
		PW-TU _{NICKEL} (28-d)	Sig3	0.68	<0.0001
		<i>PW-TU NICKEL (Mean)</i>	<i>Sig3</i>	<i>0.79</i>	<i><0.0001</i>
		PW-TU _{SELENIUM}	Sig3	0.02	0.664
		PW-TU _{SILVER}	Sig3	0.02	0.7356
		PW-TU _{ZINC} (7-d)	Sig3	0.93	<0.0001
		PW-TU _{ZINC} (28-d)	Sig3	0.93	<0.0001
		<i>PW-TU ZINC (Mean)</i>	<i>Sig3</i>	<i>0.93</i>	<i><0.0001</i>
		PW-TU _{LEAD(DOC)}	Sig3	0.38	<0.0001
		<i>PW-TU ZINC(DOC)</i>	<i>Sig3</i>	<i>0.91</i>	<i><0.0001</i>
Pore Water⁵					
Mussel 28-d Biomass	NA	<i>ΣPW-TU METALS</i>	<i>Sig3</i>	<i>0.47</i>	<i><0.0001</i>
		<i>ΣPW-TU DIVALENT METALS</i>	<i>Sig3</i>	<i>0.60</i>	<i><0.0001</i>
		PW-TU _{ALUMINUM}	Sig3	0.01	0.7857
		PW-TU _{ARSENIC}	Sig3	0.007	0.8775
		PW-TU _{CADMIUM} (7-d)	Sig3	0.52	<0.0001
		PW-TU _{CADMIUM} (28-d)	Sig3	0.38	<0.0001
		<i>PW-TU CADMIUM (Mean)</i>	<i>Sig3</i>	<i>0.46</i>	<i><0.0001</i>
		PW-TU _{CHROMIUM}	Sig3	0.08	0.1939
		<i>PW-TU COPPER (7-d)</i>	<i>Sig3</i>	<i>0.47</i>	<i><0.0001</i>
		PW-TU _{COPPER} (28-d)	Sig3	0.01	0.7857

Table 19. Summary of the preliminary concentration-response relationships. Bold, italicized font indicates preliminary plots that were selected for further analysis (MacDonald *et al.* 2009).

Media Type / Toxicity Test Endpoint	Sediment Sample Size Fraction	COPC/COPC Mixture	Regression Equation Type	r ²	p
Pore Water⁵		PW-TU _{COPPER} (Mean)	Sig3	0.07	0.2353
Mussel		PW-TU _{IRON}	Sig3	0.004	0.9303
28-d Biomass		PW-TU _{LEAD} (7-d)	Sig3	0.31	0.0008
(cont.)		PW-TU _{LEAD} (2-d)	Sig3	0.48	<0.0001
		<i>PW-TU_{LEAD} (Mean)</i>	<i>Sig3</i>	<i>0.41</i>	<i><0.0001</i>
		PW-TU _{NICKEL} (7-d)	Sig3	0.47	<0.0001
		PW-TU _{NICKEL} (28-d)	Sig3	0.32	0.0005
		<i>PW-TU_{NICKEL} (Mean)</i>	<i>Sig3</i>	<i>0.47</i>	<i><0.0001</i>
		PW-TU _{SELENIUM}	Sig3	0.0006	0.9893
		PW-TU _{SILVER}	Linear	0.09	0.0488
		PW-TU _{ZINC} (7-d)	Sig3	0.61	<0.0001
		PW-TU _{ZINC} (28-d)	Sig3	0.59	<0.0001
		<i>PW-TU_{ZINC} (Mean)</i>	<i>Sig3</i>	<i>0.60</i>	<i><0.0001</i>
		<i>PW-TU_{LEAD(DOC)}</i>	<i>Sig3</i>	<i>0.42</i>	<i><0.0001</i>
		<i>PW-TU_{ZINC(DOC)}</i>	<i>Sig3</i>	<i>0.61</i>	<i><0.0001</i>
Pore Water⁵					
Midge	NA	ΣPW-TU _{METALS} (7-d))	Sig3	0.01	0.6967
10-d Survival		ΣPW-TU _{DIVALENT METALS} (7-d)	Log3	0.33	<0.0001
		PW-TU _{ALUMINUM}	Sig3	0.08	0.0591
		PW-TU _{ARSENIC}	Sig3	0.17	0.002
		PW-TU _{CADMIUM} (7-d)	Linear	0.03	0.132
		PW-TU _{CHROMIUM}	Sig3	0.08	0.0608
		PW-TU _{COPPER} (7-d)	Sig3	0.06	0.1086
		PW-TU _{IRON}	Sig3	0.19	0.0009
		PW-TU _{LEAD} (7-d)	Sig3	0.02	0.5069
		PW-TU _{NICKEL} (7-d)	Sig3	0.02	0.5735
		PW-TU _{SELENIUM}	Sig3	0.01	0.6267
		PW-TU _{SILVER}	Sig3	0.07	0.0812
		PW-TU _{ZINC} (7-d)	Sig3	0.28	<0.0001
		PW-TU _{LEAD (DOC)} - 7-d	Log3	0.05	0.1524
		PW-TU _{ZINC (DOC)} - 7-d	Log3	0.37	<0.0001
Pore Water⁵					
Midge	NA	ΣPW-TU _{METALS} (7-d)	Sig3	0.07	0.0962
10-d Biomass		ΣPW-TU _{DIVALENT METALS} (7-d)	Log3	0.30	<0.0001
		PW-TU _{ALUMINUM}	Sig3	0.004	0.887
		PW-TU _{ARSENIC}	Sig3	0.08	0.0575

Table 19. Summary of the preliminary concentration-response relationships. Bold, italicized font indicates preliminary plots that were selected for further analysis (MacDonald *et al.* 2009).

Media Type / Toxicity Test Endpoint	Sediment Sample Size Fraction	COPC/COPC Mixture	Regression Equation Type	r ²	p
Pore Water⁵		PW-TU _{CADMIUM} (7-d)	Sig3	0.21	0.0003
Midge		PW-TU _{CHROMIUM}	Log3	0.0002	0.9935
10-d Biomass		PW-TU _{COPPER} (7-d)	Sig3	0.03	0.3345
(cont.)		PW-TU _{IRON}	Sig3	0.15	0.0052
		PW-TU _{LEAD} (7-d)	Sig3	0.14	0.0056
		PW-TU _{NICKEL} (7-d)	Sig3	0.13	0.01
		PW-TU _{SELENIUM}	Sig3	0.006	0.8243
		PW-TU _{SILVER}	Sig3	0.004	0.8616
		PW-TU _{ZINC} (7-d)	Sig3	0.26	<0.0001
		PW-TU _{LEAD(DOC)} - 7-d	Log3	0.18	0.0011
		PW-TU _{ZINC(DOC)} - 7-d	Log3	0.25	<0.0001

COPC = chemical of potential concern; r² = coefficients of determination; d = day; DOC = dissolved organic carbon; ESB-TU = equilibrium partitioning; sediment benchmark toxic units; FCV = final chronic value; f_{OC} = fraction organic carbon; OC = organic carbon; PAHs = polycyclic aromatic hydrocarbons; PEC-Q = probable effect concentration-quotient; PW-TU = pore-water toxic units; SEM-AVS = simultaneously extracted metals minus acid volatile sulfides; STT-Q = sediment toxicity threshold-quotient.

¹Sediment samples were collected for SEM and AVS measurement on Day 7 and on Day 28 of the sediment toxicity tests with amphipods. Preliminary concentration-response relationships for amphipods and mussels were developed using the mean of the 7-d and 28-d results.

²Concentration-response relationships for total PAHs, ΣESB-TU_{FCV}, and mean PEC-Q and the mussel toxicity test endpoints were developed with concentration measurement data from the <2 mm size fraction.

³Concentration-response relationships for ΣSEM-AVS and the mussel toxicity test endpoints were developed with concentration measurement data from the <2 mm size fraction for the Set 1 and 2 samples (n=42) and the <250 μm size fraction for the Set 3 samples (n = 6).

⁴Sediment samples were collected for SEM and AVS measurement on Day 7 and on Day 28 of the sediment toxicity tests with amphipods. Preliminary concentration-response relationships for midges were developed using the 7-day results.

⁵Pore-water peeper samples were collected on Day 7 and on Day 28 of the sediment toxicity tests. The mean of the pore-water chemistry results for the Day 7 and Day 28 samples was calculated for cadmium, copper, lead, nickel, and zinc. For these COPCs, the preliminary concentration-response relationships were developed using the 7-d, 28-d, and mean results. For the remaining COPCs (i.e., aluminum, arsenic, chromium, iron, selenium, and silver), pore-water chemistry from centrifuged samples was only measured on Day 7 of the toxicity tests, so the preliminary concentration-response relationships were developed using the 7-d results. For the pore-water mixture models (i.e., ΣPW-TU_{METALS} and ΣPW-TU_{DIVALENT METALS}) and PW-TU_{LEAD(DOC)} and PW-TU_{ZINC(DOC)}, the concentration-response models were developed using the mean of the 7-d and 28-d results (except for the models developed for the midge endpoints, where the 7-d results were used).

Table 20. Predictive ability of the site-specific sediment toxicity thresholds (SSTTs) derived from results of 28-d toxicity tests using *Hyalella azteca* survival endpoint and three methods for reference envelope calculations¹

COPC/COPC Mixture / Toxicity Test Endpoint Used to Evaluate SSTT	n	T ₁₀	T ₂₀	Incidence of Toxicity							
				<T ₁₀	≥T ₁₀	Correct Class. Rate for T ₁₀ Value	T ₁₀ -T ₂₀	≤T ₂₀	>T ₂₀	Correct Class. Rate for T ₂₀ Value	
Scenario 1: T₁₀ Corresponds to minimum value of reference envelope											
ΣPEC-Q_{Cd,Pb,Zn}											
<i>C. dilutus</i> 10-d B	70	6.47	10.04	29% (12 of 41)	62% (18 of 29)	67%	60% (3 of 5)	33% (15 of 46)	63% (15 of 24)	66%	
<i>C. dilutus</i> 10-d S	70	6.47	10.04	17% (7 of 41)	45% (13 of 29)	67%	20% (1 of 5)	17% (8 of 46)	50% (12 of 24)	71%	
<i>H. azteca</i> 28-d B	76	6.47	10.04	2% (1 of 45)	45% (14 of 31)	76%	17% (1 of 6)	4% (2 of 51)	52% (13 of 25)	82%	
<i>H. azteca</i> 28-d S	76	6.47	10.04	4% (2 of 45)	65% (20 of 31)	83%	33% (2 of 6)	8% (4 of 51)	72% (18 of 25)	86%	
<i>L. siliquioidea</i> 28-d B	48	6.47	10.04	0% (0 of 27)	29% (6 of 21)	69%	0% (0 of 5)	0% (0 of 32)	38% (6 of 16)	79%	
<i>L. siliquioidea</i> 28-d S	48	6.47	10.04	7% (2 of 27)	67% (14 of 21)	81%	40% (2 of 5)	13% (4 of 32)	75% (12 of 16)	83%	
Overall ²	76	6.47	10.04	36% (16 of 45)	87% (27 of 31)	74%	83% (5 of 6)	41% (21 of 51)	88% (22 of 25)	68%	
Overall HaLs ³	76	6.47	10.04	9% (4 of 45)	77% (24 of 31)	86%	50% (3 of 6)	14% (7 of 51)	84% (21 of 25)	86%	
ΣPEC-Q_{Cd,Cu,Pb,Hg,Ni,Zn}											
<i>C. dilutus</i> 10-d B	70	6.92	10.55	29% (12 of 41)	62% (18 of 29)	67%	67% (4 of 6)	34% (16 of 47)	61% (14 of 23)	64%	
<i>C. dilutus</i> 10-d S	70	6.92	10.55	17% (7 of 41)	45% (13 of 29)	67%	17% (1 of 6)	17% (8 of 47)	52% (12 of 23)	73%	
<i>H. azteca</i> 28-d B	76	6.92	10.55	2% (1 of 45)	45% (14 of 31)	76%	14% (1 of 7)	4% (2 of 52)	54% (13 of 24)	83%	
<i>H. azteca</i> 28-d S	76	6.92	10.55	4% (2 of 45)	65% (20 of 31)	83%	43% (3 of 7)	10% (5 of 52)	71% (17 of 24)	84%	
<i>L. siliquioidea</i> 28-d B	48	6.92	10.55	0% (0 of 27)	29% (6 of 21)	69%	0% (0 of 5)	0% (0 of 32)	38% (6 of 16)	79%	
<i>L. siliquioidea</i> 28-d S	48	6.92	10.55	7% (2 of 27)	67% (14 of 21)	81%	40% (2 of 5)	13% (4 of 32)	75% (12 of 16)	83%	
Overall ²	76	6.92	10.55	36% (16 of 45)	87% (27 of 31)	74%	86% (6 of 7)	42% (22 of 52)	88% (21 of 24)	67%	
Overall HaLs ³	76	6.92	10.55	9% (4 of 45)	77% (24 of 31)	86%	57% (4 of 7)	15% (8 of 52)	83% (20 of 24)	84%	

Table 20. Predictive ability of the site-specific sediment toxicity thresholds (SSTTs) derived from results of 28-d toxicity tests using *Hyalella azteca* survival endpoint and three methods for reference envelope calculations¹

COPC/COPC Mixture / Toxicity Test Endpoint Used to Evaluate SSTT	n	T ₁₀	T ₂₀	Incidence of Toxicity							
				<T ₁₀	≥T ₁₀	Correct Class. Rate for T ₁₀ Value	T ₁₀ -T ₂₀	≤T ₂₀	>T ₂₀	Correct Class. Rate for T ₂₀ Value	
Scenario 2: T₁₀ Corresponds to 10% below minimum value of reference envelope											
ΣPEC-Q_{Cd,Pb,Zn}											
<i>C. dilutus</i> 10-d B	70	10.04	13.12	33% (15 of 46)	63% (15 of 24)	66%	50% (2 of 4)	34% (17 of 50)	65% (13 of 20)	66%	
<i>C. dilutus</i> 10-d S	70	10.04	13.12	17% (8 of 46)	50% (12 of 24)	71%	50% (2 of 4)	20% (10 of 50)	50% (10 of 20)	71%	
<i>H. azteca</i> 28-d B	76	10.04	13.12	4% (2 of 51)	52% (13 of 25)	82%	50% (2 of 4)	7% (4 of 55)	52% (11 of 21)	82%	
<i>H. azteca</i> 28-d S	76	10.04	13.12	8% (4 of 51)	72% (18 of 25)	86%	100% (4 of 4)	15% (8 of 55)	67% (14 of 21)	80%	
<i>L. siliquioidea</i> 28-d B	48	10.04	13.12	0% (0 of 32)	38% (6 of 16)	79%	No Data	0% (0 of 32)	38% (6 of 16)	79%	
<i>L. siliquioidea</i> 28-d S	48	10.04	13.12	13% (4 of 32)	75% (12 of 16)	83%	No Data	13% (4 of 32)	75% (12 of 16)	83%	
Overall ²	76	10.04	13.12	41% (21 of 51)	88% (22 of 25)	68%	100% (4 of 4)	45% (25 of 55)	86% (18 of 21)	63%	
Overall HaLs ³	76	10.04	13.12	14% (7 of 51)	84% (21 of 25)	86%	100% (4 of 4)	20% (11 of 55)	81% (17 of 21)	80%	
ΣPEC-Q_{Cd,Cu,Pb,Hg,Ni,Zn}											
<i>C. dilutus</i> 10-d B	70	10.55	13.68	34% (16 of 47)	61% (14 of 23)	64%	33% (1 of 3)	34% (17 of 50)	65% (13 of 20)	66%	
<i>C. dilutus</i> 10-d S	70	10.55	13.68	17% (8 of 47)	52% (12 of 23)	73%	67% (2 of 3)	20% (10 of 50)	50% (10 of 20)	71%	
<i>H. azteca</i> 28-d B	76	10.55	13.68	4% (2 of 52)	54% (13 of 24)	83%	67% (2 of 3)	7% (4 of 55)	52% (11 of 21)	82%	
<i>H. azteca</i> 28-d S	76	10.55	13.68	10% (5 of 52)	71% (17 of 24)	84%	100% (3 of 3)	15% (8 of 55)	67% (14 of 21)	80%	
<i>L. siliquioidea</i> 28-d B	48	10.55	13.68	0% (0 of 32)	38% (6 of 16)	79%	No Data	0% (0 of 32)	38% (6 of 16)	79%	
<i>L. siliquioidea</i> 28-d S	48	10.55	13.68	13% (4 of 32)	75% (12 of 16)	83%	No Data	13% (4 of 32)	75% (12 of 16)	83%	
Overall ²	76	10.55	13.68	42% (22 of 52)	88% (21 of 24)	67%	100% (3 of 3)	45% (25 of 55)	86% (18 of 21)	63%	
Overall HaLs ³	76	10.55	13.68	15% (8 of 52)	83% (20 of 24)	84%	100% (3 of 3)	20% (11 of 55)	81% (17 of 21)	80%	

Table 20. Predictive ability of the site-specific sediment toxicity thresholds (SSTTs) derived from results of 28-d toxicity tests using *Hyalella azteca* survival endpoint and three methods for reference envelope calculations¹

COPC/COPC Mixture / Toxicity Test Endpoint Used to Evaluate SSTT	n	T ₁₀	T ₂₀	Incidence of Toxicity								
				<T ₁₀	≥T ₁₀	Correct Class. Rate for T ₁₀ Value	T ₁₀ -T ₂₀	≤T ₂₀	>T ₂₀	Correct Class. Rate for T ₂₀ Value		
Scenario 3: T₁₀ Corresponds to 10% below mean of reference envelope												
ΣPEC-Q_{Cd,Pb,Zn}												
<i>C. dilutus</i> 10-d B	70	7.92	11.26	33% (15 of 45)	60% (15 of 25)	64%	67% (2 of 3)	35% (17 of 48)	59% (13 of 22)	63%		
<i>C. dilutus</i> 10-d S	70	7.92	11.26	18% (8 of 45)	48% (12 of 25)	70%	33% (1 of 3)	19% (9 of 48)	50% (11 of 22)	71%		
<i>H. azteca</i> 28-d B	76	7.92	11.26	4% (2 of 49)	48% (13 of 27)	79%	25% (1 of 4)	6% (3 of 53)	52% (12 of 23)	82%		
<i>H. azteca</i> 28-d S	76	7.92	11.26	8% (4 of 49)	67% (18 of 27)	83%	50% (2 of 4)	11% (6 of 53)	70% (16 of 23)	83%		
<i>L. siliquoidea</i> 28-d B	48	7.92	11.26	0% (0 of 30)	33% (6 of 18)	75%	0% (0 of 2)	0% (0 of 32)	38% (6 of 16)	79%		
<i>L. siliquoidea</i> 28-d S	48	7.92	11.26	10% (3 of 30)	72% (13 of 18)	83%	50% (1 of 2)	13% (4 of 32)	75% (12 of 16)	83%		
Overall ²	76	7.92	11.26	41% (20 of 49)	85% (23 of 27)	68%	75% (3 of 4)	43% (23 of 53)	87% (20 of 23)	66%		
Overall HaLs ³	76	7.92	11.26	12% (6 of 49)	81% (22 of 27)	86%	75% (3 of 4)	17% (9 of 53)	83% (19 of 23)	83%		
ΣPEC-Q_{Cd,Cu,Pb,Hg,Ni,Zn}												
<i>C. dilutus</i> 10-d B	70	8.4	11.79	34% (15 of 44)	58% (15 of 26)	63%	50% (2 of 4)	35% (17 of 48)	59% (13 of 22)	63%		
<i>C. dilutus</i> 10-d S	70	8.4	11.79	16% (7 of 44)	50% (13 of 26)	71%	50% (2 of 4)	19% (9 of 48)	50% (11 of 22)	71%		
<i>H. azteca</i> 28-d B	76	8.4	11.79	4% (2 of 48)	46% (13 of 28)	78%	20% (1 of 5)	6% (3 of 53)	52% (12 of 23)	82%		
<i>H. azteca</i> 28-d S	76	8.4	11.79	6% (3 of 48)	68% (19 of 28)	84%	60% (3 of 5)	11% (6 of 53)	70% (16 of 23)	83%		
<i>L. siliquoidea</i> 28-d B	48	8.4	11.79	0% (0 of 29)	32% (6 of 19)	73%	0% (0 of 3)	0% (0 of 32)	38% (6 of 16)	79%		
<i>L. siliquoidea</i> 28-d S	48	8.4	11.79	7% (2 of 29)	74% (14 of 19)	85%	67% (2 of 3)	13% (4 of 32)	75% (12 of 16)	83%		
Overall ²	76	8.4	11.79	40% (19 of 48)	86% (24 of 28)	70%	80% (4 of 5)	43% (23 of 53)	87% (20 of 23)	66%		
Overall HaLs ³	76	8.4	11.79	10% (5 of 48)	82% (23 of 28)	87%	80% (4 of 5)	17% (9 of 53)	83% (19 of 23)	83%		

B = biomass; Class. = classification; COPC = chemical of potential concern; d = day; HaLs = *H. azteca*, *L. siliquoidea*; n = number of samples; S = survival;

T₁₀, T₂₀ - risk threshold associated with a 10% and 20% reduction in a measured endpoint

ΣPEC-Q_{Cd,Pb,Zn} = sum probable effect concentration-quotient for cadmium, lead, zinc; ΣPEC-Q_{Cd,Cu,Pb,Hg,Ni,Zn} = ΣPEC-Q for cadmium, copper, lead, mercury, nickel, zinc.

¹ See Section 7 for a complete description of the three scenarios for deriving SSTTs that were developed.

² Considering one or more endpoints of survival or biomass for *Hyalella azteca*, *Chironomus dilutus*, *Lampsilis siliquoidea*.

³ Considering one or more endpoints of survival or biomass for *Hyalella azteca*, *Lampsilis siliquoidea*.

Table 21. No observed effect level (NOEL) and lowest observed effect level (LOEL) data compiled from the literature to support the creation of toxicity thresholds for invertebrate tissues for the Tri-State Mining District study. Study criteria included paired NOEL and LOEL data measuring survival and based on whole body analysis of the contaminant of potential concern.

Test Species	Media Type	Life Stage	Exposure Route	Test Duration (d)	Effect	NOEL	LOEL	Geomean
<i>Cadmium (mg/kg WW)</i>								
Oligochaete	Freshwater	Adult	Water	10	40% reduction	60	134	134
Snail	Freshwater	Adult	Water; Sediment	10	50% reduction	78	125	125
Snail	Freshwater	6-15 mm	Water	28	80% reduction	10	30	30.0
Zebra mussel	Freshwater	NA	Water	77	96% reduction	114	180	180
Cladoceran	Freshwater	24 hr	Diet	20	Reduced	6.4	8.8	8.80
Cladoceran	Freshwater	12 hr	Diet	8	Reduced	8.5	14.5	14.5
Amphipod	Freshwater	Adult	Water	14	Reduced	53.4	101.6	102
Amphipod	Freshwater	Young	Water	42	Reduced	4.6	6	6.00
Amphipod	Freshwater	Young	Water	42	Reduced	6.4	7.8	7.80
Amphipod	Freshwater	Young	Water	42	Reduced	8.4	15.2	15.2
Crayfish	Freshwater	Adult	Water	150	Reduced	14.9	22	22.0
Crayfish	Freshwater	Adult	Water	14	25% reduction	0.9	5.7	5.70
Crayfish	Freshwater	Adult	Water	14	74% reduction	0.9	11.2	11.2
Midge	Freshwater	Larvae	Water	28-56	Reduced	5.6	7.6	7.60
Midge	Freshwater	Larvae-Adult	Water	180	Reduced	17.8	33	33.0
Mysid	Saltwater	Adult	Water	33	50% reduction	1.3	2.4	2.40
Oligochaete	NA	NA	NA	NA	40% mortality	310	670	670
Cladoceran	NA	NA	NA	NA	Reduced survival	10.6	16.4	16.4
Amphipod	NA	NA	NA	NA	NA	6	11	11.0
						<i>20th Percentile:</i>		<i>6.02</i>
<i>Copper (mg/kg WW)</i>								
Worm	Saltwater	Adult	Water	21	Reduced	95.5	62.7	62.7
Worm	Salwater	Adult; male	Water	85	Reduced - Death	6.32	54	54.0
Worm	Salwater	Adult	Water	34	Reduced	6.42	10.68	10.7
Bivalve	Saltwater	Adult	Water	108	Reduced	18	5	5.00
Bivalve	Saltwater	Adult	Water	110	Reduced 32%	18	22	22.0
Amphipod	Freshwater	<= 1 wk	Sediment	28	Reduced 55%	29.2	32.8	32.8

Table 21. No observed effect level (NOEL) and lowest observed effect level (LOEL) data compiled from the literature to support the creation of toxicity thresholds for invertebrate tissues for the Tri-State Mining District study. Study criteria included paired NOEL and LOEL data measuring survival and based on whole body analysis of the contaminant of potential concern.

Test Species	Media Type	Life Stage	Exposure Route	Test Duration (d)	Effect	NOEL	LOEL	Geomean
Copper (mg/kg WW; continued)								
Amphipod	Freshwater	<= 1 wk	Sediment	28	Reduced -Death	29.2	81.2	81.2
Midge	NA	NA	NA	NA	Significant mortality	86.2	107	107
<i>20th Percentile:</i>								17.6
Lead (mg/kg WW)								
Zebra Mussel	Freshwater	Adult	Water	70	Reduced	36	200	84.9
<i>20th Percentile:</i>								84.9
Mercury (mg/kg WW)								
Marsh Clam	NA	NA	NA	NA	Lethal body burden	6	73.14	73.1
Cladoceran	NA	NA	NA	NA	25% reduction	7.57	18.4	18.4
<i>20th Percentile:</i>								13.6
Zinc (mg/kg WW)								
Amphipod	Saltwater	Juv, 1st instar	Water	28	Reduced 30%	26	30	27.9
Amphipod	Saltwater	Juv, 1st instar	Water	28	Reduced 90%	26	24	25.0
Amphipod	Freshwater	0 - 1 wk	Sediment	28	Reduced	53.6	60.8	57.1
Amphipod	Freshwater	0 - 1 wk	Sediment	28	Reduced - Death	53.6	117.8	79.5
Blue Mussel	Saltwater	50-70 mm	Water	14	Reduced - Death	78	171	115
Blue Mussel	Saltwater	50-70 mm	Water	15	Reduced - Death	71	130	96.1
Zebra Mussel	Freshwater	Adult	Water	70	Reduced	150	600	300
Crayfish	Freshwater	Adult	Water	13	Reduced 22%	12.7	35.2	21.1
Crayfish	Freshwater	Adult	Water	14	Reduced 42%	12.7	37.8	21.9
<i>20th Percentile:</i>								23.8

d = day; hr = hour; wk = week; LOEL = lowest observed effect level; NOEL = no observed effect level; NA = not available; WW = wet weight.

Table 22. Abundance of mussel taxa associated with sediment samples from the Tri-State Mining District that were classified into low risk, moderate risk, and high risk categories using the selected sediment toxicity thresholds of 0.6 and 3.0 for Σ PEC-Q_{Cd,Pb,Zn}.

Endpoint Measured	Average Number of Taxa		
	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
Number of Live Mussel Taxa	14.5 (2)	7.0 (9)	4.2 (5)
Number of Live Mussel Taxa Classified as Threatened, Endangered, or of Special Concern	5.5 (2)	2.8 (9)	0.8 (5)
Total Number of Mussel Taxa	20.0 (2)	9.9 (9)	6.0 (5)

Σ PEC-Q = sum probable effect concentration quotient; Cd = cadmium; Pb = lead; Zn = zinc; n = sample size.

¹ Σ PEC-Q_{Cd,Pb,Zn} < 0.6

² Σ PEC-Q_{Cd,Pb,Zn} = 0.6 to 3.0

³ Σ PEC-Q_{Cd,Pb,Zn} > 3.0

Table 23. Summary of surface-water chemistry data showing the 95th percentile data for the Upper/Middle Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ³	Area of Interest (AoI)											
	n	95th Percentile ^{1,2}		Upper Spring River			North Fork Spring River			Middle Spring River			Cow Creek		
				n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴
<i>Metals (µg/L)</i>															
Aluminum, total	19	1420	87	5	1110	N	9	2590	N	20	2000	N	5	1230	N
Cadmium, total	0	ND	0.25	0	ND	U	0	ND	U	1	5.12	U	1	7.22	U
Copper, total	0	ND	4.17	0	ND	U	0	ND	U	4	40.0	U	3	44.8	U
Iron, total	19	1520	887	5	862	N	9	1990	N	20	2650	N	5	1370	N
Lead, total	0	ND	1.16	0	ND	U	0	ND	U	4	17.7	U	0	ND	U
Nickel, total	19	22.1	52	5	20.0	N	9	20.0	N	20	21.0	N	5	20.0	N
Zinc, total	19	333	60.8	5	30.0	N	9	30.0	N	20	1170	Y	5	1250	Y
Cadmium, dissolved	0	ND	0.25	0	ND	U	0	ND	U	0	ND	U	1	7.72	U
Iron, dissolved	18	110	887	5	50.0	N	8	110	N	20	58.4	N	5	50.0	N
Mercury, dissolved	0	ND	0.182	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Nickel, dissolved	7	20.0	52	3	20.0	N	0	ND	U	12	20.0	N	3	20.0	N
Zinc, dissolved	17	622	60.8	5	30.0	N	7	30.0	N	20	774	N	5	1330	Y
<i>Nutrients/Inorganics/Conventionals</i>															
Ammonia	0	ND	ND	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Chlorine, dissolved	0	ND	10.1	0	ND	U	0	ND	U	0	ND	U	0	ND	U

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹The 95th percentile was calculated excluding data less than the analytical detection limit, but greater than the TRV. These excluded data are referred to as high non-detects (HN-Ds).

²The 95th percentile for surface water reference stations excludes HN-Ds; the 95th percentile for surface water reference stations presented in Table 6, includes HN-Ds.

³TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

⁴A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

⁵A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 23. Summary of surface-water chemistry data showing the 95th percentile data for the Upper/Middle Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)												Upper/Middle Spring River Sub-basin	
	Center Creek			Turkey Creek			Shawnee Creek			Short Creek			n	COC ⁵
	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴		
<i>Metals (µg/L)</i>														
Aluminum, total	36	1380	N	19	478	N	7	1800	N	6	550	N	107	N
Cadmium, total	2	60.3	U	0	ND	U	0	ND	U	6	32.6	U	10	U
Copper, total	1	27.0	U	0	ND	U	4	49.8	U	0	ND	U	12	U
Iron, total	36	1210	N	19	379	N	7	2620	N	6	325	N	107	N
Lead, total	11	33.1	U	1	11.4	U	0	ND	U	1	13.0	U	17	U
Nickel, total	36	20.0	N	19	20.0	N	7	20.0	N	6	20.0	N	107	N
Zinc, total	36	3150	Y	19	533	N	7	67.7	N	6	4470	Y	107	Y
Cadmium, dissolved	2	59.8	U	0	ND	U	0	ND	U	5	32.5	U	8	U
Iron, dissolved	36	114	N	19	59.2	N	7	280	N	6	50.0	N	106	N
Mercury, dissolved	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Nickel, dissolved	19	20.0	N	14	20.0	N	1	20.0	N	1	20.0	N	53	U
Zinc, dissolved	35	3150	Y	18	515	N	4	238	N	6	4530	Y	100	Y
<i>Nutrients/Inorganics/Conventionals</i>														
Ammonia	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Chlorine, dissolved	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹The 95th percentile was calculated excluding data less than the analytical detection limit, but greater than the TRV. These excluded data are referred to as high non-detects (HN-Ds).

²The 95th percentile for surface water reference stations excludes HN-Ds; the 95th percentile for surface water reference stations presented in Table 6, includes HN-Ds.

³TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

⁴A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

⁵A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 24. Summary of surface-water chemistry data showing the 95th percentile data for the Lower Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ³	Area of Interest (AoI)											
	n	95th Percentile ^{1,2}		Empire Lake			Lower Spring River			Shoal Creek			Brush Creek		
				n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴
<i>Metals (µg/L)</i>															
Aluminum, total	19	1420	87	2	764	N	33	7630	Y	34	888	N	1	914	N
Cadmium, total	0	ND	0.25	0	ND	U	11	3.38	U	0	ND	U	0	ND	U
Copper, total	0	ND	4.17	0	ND	U	8	53.1	U	0	ND	U	0	ND	U
Iron, total	19	1520	887	2	698	N	39	5010	Y	56	4230	Y	1	806	N
Lead, total	0	ND	1.16	0	ND	U	16	36.3	U	3	42.8	U	0	ND	U
Nickel, total	19	22.1	52	2	20.0	N	39	20.0	N	56	48.5	N	1	20.0	N
Zinc, total	19	333	60.8	2	253	N	52	302	N	56	1380	Y	1	240	N
Cadmium, dissolved	0	ND	0.25	0	ND	U	0	ND	U	1	6.56	U	0	ND	U
Iron, dissolved	18	110	887	2	50.0	N	38	60.0	N	56	118	N	1	50.0	N
Mercury, dissolved	0	ND	0.182	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Nickel, dissolved	7	20.0	52	1	20.0	N	26	11.0	N	15	69.3	Y	0	ND	U
Zinc, dissolved	17	622	60.8	2	161	N	39	126	N	55	1080	N	1	130	N
<i>Nutrients/Inorganics/Conventionals</i>															
Ammonia	0	ND	ND	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Chlorine, dissolved	0	ND	10.1	0	ND	U	0	ND	U	0	ND	U	0	ND	U

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹The 95th percentile was calculated excluding data less than the analytical detection limit, but greater than the TRV. These excluded data are referred to as high non-detects (HN-Ds).

²The 95th percentile for surface water reference stations excludes HN-Ds; the 95th percentile for surface water reference stations presented in Table 6, includes HN-Ds.

³TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

⁴A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

⁵A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 24. Summary of surface-water chemistry data showing the 95th percentile data for the Lower Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)															Lower Spring River Sub-basin	
	Willow Creek			Spring Brook			Beaver Creek			Warren Branch			Lost Creek			n	COC ⁵
	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴		
<i>Metals (µg/L)</i>																	
Aluminum, total	5	897	N	3	689	N	40	12200	Y	5	983	N	23	650	N	146	Y
Cadmium, total	0	ND	U	3	14.9	U	9	4.68	U	0	ND	U	10	0.0468	U	33	U
Copper, total	2	44.6	U	0	ND	U	10	33.3	U	0	ND	U	1	50.1	U	21	U
Iron, total	5	1960	N	3	668	N	58	10400	Y	5	961	N	23	491	N	192	Y
Lead, total	0	ND	U	0	ND	U	14	50.1	U	0	ND	U	11	6.21	U	44	U
Nickel, total	5	20.0	N	3	20.0	N	55	20.0	N	5	20.0	N	23	20.0	N	189	N
Zinc, total	5	966	Y	3	3720	Y	58	958	Y	5	91.9	N	33	110	N	215	Y
Cadmium, dissolved	0	ND	U	2	14.6	U	1	0.150	U	0	ND	U	0	ND	U	4	U
Iron, dissolved	5	1210	Y	3	101	N	47	62.6	N	5	50.0	N	23	50.0	N	180	Y
Mercury, dissolved	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Nickel, dissolved	1	20.0	N	1	20.0	N	40	5.00	N	0	ND	U	1	20.0	N	85	Y
Zinc, dissolved	5	1250	Y	3	3710	Y	99	1000	N	3	30.0	N	16	71.8	N	223	Y
<i>Nutrients/Inorganics/Conventionals</i>																	
Ammonia	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Chlorine, dissolved	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹The 95th percentile was calculated excluding data less than the analytical detection limit, but greater than the TRV. These excluded data are referred to as high non-detects (HN-Ds).

²The 95th percentile for surface water reference stations excludes HN-Ds; the 95th percentile for surface water reference stations presented in Table 6, includes HN-Ds.

³TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

⁴A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

⁵A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 25. Summary of surface-water chemistry data showing the 95th percentile data for the Neosho River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ³	Area of Interest (AoI)											
	n	95th Percentile ^{1,2}		Neosho River			Upper Tar Creek			Middle Tar Creek			Lytle Creek		
				n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴
<i>Metals (µg/L)</i>															
Aluminum, total	19	1420	87	41	33100	Y	3	4070	Y	7	760	N	16	1710	N
Cadmium, total	0	ND	0.25	0	ND	U	4	30.9	U	67	41.3	U	5	16.7	U
Copper, total	0	ND	4.17	23	44.7	U	5	33.5	U	18	6.24	U	2	48.9	U
Iron, total	19	1520	887	42	19500	Y	6	3750	Y	100	24400	Y	21	2940	N
Lead, total	0	ND	1.16	5	19.0	U	5	125	U	51	75.7	U	19	83.3	U
Mercury, total	0	ND	0.182	0	ND	U	0	ND	U	1	0.0250	U	0	ND	U
Nickel, total	19	22.1	52	39	20.2	N	3	20.0	N	84	231	Y	20	40.0	N
Zinc, total	19	333	60.8	43	278	N	6	7250	Y	100	11300	Y	21	7710	Y
Cadmium, dissolved	0	ND	0.25	0	ND	U	4	18.3	U	58	42.0	U	4	8.76	U
Iron, dissolved	18	110	887	42	112	N	6	703	N	81	22100	Y	5	5950	Y
Mercury, dissolved	0	ND	0.182	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Nickel, dissolved	7	20.0	52	32	5.00	N	1	20.0	N	65	232	Y	3	362	Y
Zinc, dissolved	17	622	60.8	38	35.9	N	6	6690	Y	99	10500	Y	5	14700	Y
<i>Nutrients/Inorganics/Conventionals</i>															
Ammonia	0	ND	ND	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Chlorine, dissolved	0	ND	10.1	0	ND	U	0	ND	U	0	ND	U	0	ND	U

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹The 95th percentile was calculated excluding data less than the analytical detection limit, but greater than the TRV. These excluded data are referred to as high non-detects (HN-Ds).

²The 95th percentile for surface water reference stations excludes HN-Ds; the 95th percentile for surface water reference stations presented in Table 6, includes HN-Ds.

³TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

⁴A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

⁵A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 25. Summary of surface-water chemistry data showing the 95th percentile data for the Neosho River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)						Neosho River Sub-basin	
	Lower Tar Creek			Elm Creek			n	COC ⁵
	n	95th Percentile	COC ⁴	n	95th Percentile	COC ⁴		
<i>Metals (µg/L)</i>								
Aluminum, total	69	19200	Y	8	1730	N	144	Y
Cadmium, total	80	15.3	U	15	112	U	171	U
Copper, total	48	37.0	U	13	28.2	U	109	U
Iron, total	182	18700	Y	19	1920	N	370	Y
Lead, total	68	126	U	17	424	U	165	U
Mercury, total	3	0.192	U	0	ND	U	4	U
Nickel, total	146	387	Y	19	20.5	N	311	Y
Zinc, total	182	6540	Y	20	20400	Y	372	Y
Cadmium, dissolved	40	16.5	U	1	87.6	U	107	U
Iron, dissolved	163	7190	Y	4	121	N	301	Y
Mercury, dissolved	0	ND	U	0	ND	U	0	U
Nickel, dissolved	123	384	Y	3	20.0	N	227	Y
Zinc, dissolved	176	6170	Y	5	8560	Y	329	Y
<i>Nutrients/Inorganics/Conventionals</i>								
Ammonia	0	ND	U	0	ND	U	0	U
Chlorine, dissolved	0	ND	U	0	ND	U	0	U

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹The 95th percentile was calculated excluding data less than the analytical detection limit, but greater than the TRV. These excluded data are referred to as high non-detects (HN-Ds).

²The 95th percentile for surface water reference stations excludes HN-Ds; the 95th percentile for surface water reference stations presented in Table 6, includes HN-Ds.

³TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

⁴A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

⁵A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 26. Summary of sediment chemistry data showing the 95th percentile data for the Upper/Middle Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ¹	Area of Interest (AoI)											
	n	95th Percentile		Upper Spring River			North Fork Spring River			Middle Spring River			Cow Creek		
				n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²
Metals (mg/kg)															
Aluminum, total	8	11700	58000	10	12900	N	15	10200	N	47	52000	N	11	52800	N
Arsenic, total	8	8.81	33	10	8.94	N	15	7.44	N	47	12.3	N	11	39.1	Y
Barium, total	8	149.3	130.1	10	237	N	15	281	N	47	517	Y	11	453	Y
Cadmium, total	8	2.34	4.98	18	7.33	Y	27	0.925	N	109	27.2	Y	34	15.6	Y
Chromium, total	8	35.1	111	10	61.7	N	15	28.3	N	47	63.8	N	11	222	Y
Copper, total	8	11.3	149	16	121	N	21	25.3	N	95	29.4	N	29	35.7	N
Iron, total	8	33500	250000	10	30100	N	15	19500	N	47	46000	N	11	322000	Y
Lead, total	8	27.9	128	18	221	Y	27	32.6	N	111	258	Y	34	111	N
Mercury, total	8	0.100	1.06	10	0.957	N	15	0.551	N	32	1.35	Y	11	0.355	N
Molybdenum	0	ND	NB	0	ND	U	0	ND	U	24	1	U	4	1.97	U
Nickel, total	8	19.4	48.6	10	29.8	N	15	14.2	N	47	47.7	N	11	219	Y
Zinc, total	8	258	459	18	1210	Y	27	257	N	111	4270	Y	34	2950	Y
Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)															
Anthracene	8	18.9	845	5	18.2	N	5	16.7	N	3	16.8	N	2	15.5	N
Benz(a)anthracene	8	43.5	1050	5	50.2	N	5	16.7	N	3	16.8	N	2	15.5	N
Benzo(a)pyrene	8	50.6	1450	5	65.8	N	5	16.7	N	3	32.6	N	2	15.5	N
Benzo(g,h,i)perylene	8	39.8	250	5	41.6	N	5	16.7	N	3	16.8	N	2	15.5	N
Benzo(k)fluoranthene	8	48.0	240	5	53.4	N	5	16.7	N	3	16.8	N	2	15.5	N
Chrysene	8	77.3	1290	5	69.8	N	5	16.7	N	3	35.9	N	2	35.9	N
Dibenz(a,h)anthracene	8	18.9	135	5	18.2	N	5	16.7	N	3	16.8	N	2	15.5	N
Fluoranthene	8	108	2230	5	95.8	N	5	16.7	N	3	49.7	N	2	15.5	N
Indeno(1,2,3-c,d)pyrene	8	38.1	240	5	39.6	N	5	16.7	N	3	16.8	N	2	15.5	N
Phenanthrene	8	62.1	1170	5	33.2	N	5	23.5	N	3	16.8	N	2	125	N
Pyrene	8	111	1520	5	83.8	N	5	16.7	N	3	51.6	N	2	22.4	N
Total HMW PAHs	8	403	2300	5	379	N	5	100	N	3	204	N	2	102	N
Total LMW PAHs	8	157	1200	5	128	N	5	117	N	3	118	N	2	211	N
Total PAHs	8	550	22800	5	494	N	5	217	N	3	321	N	2	314	N

Table 26. Summary of sediment chemistry data showing the 95th percentile data for the Upper/Middle Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ¹	Area of Interest (AoI)											
	n	95th Percentile		Upper Spring River			North Fork Spring River			Middle Spring River			Cow Creek		
				n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²
<i>Semi-Volatile Compounds (µg/kg DW)</i>															
Butylbenzyl phthalate	8	189	11000	5	182	N	5	167	N	3	909	N	2	155	N

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; PEC = probable effect concentration. HMW = high molecular weight; LMW = low molecular weight.

¹ TRV = PEC or equivalent sediment quality guideline (see Table 32 for a complete list of selected TRVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 26. Summary of sediment chemistry data showing the 95th percentile data for the Upper/Middle Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)											Upper/Middle Spring River Sub-basin		
	Center Creek			Turkey Creek			Shawnee Creek			Short Creek		n	COC ³	
	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile			COC ²
Metals (mg/kg)														
Aluminum, total	45	11800	N	32	38400	N	19	60200	Y	26	52800	N	205	Y
Arsenic, total	45	13.6	N	32	18.2	N	19	22.9	N	26	22.6	N	205	Y
Barium, total	44	375	Y	32	395	Y	19	503	Y	26	563	Y	204	Y
Cadmium, total	79	100	Y	48	101	Y	27	10.6	Y	44	430	Y	386	Y
Chromium, total	45	215	Y	32	241	Y	19	196	Y	26	76.4	N	205	Y
Copper, total	63	24.1	N	38	56.2	N	25	23.6	N	32	599	Y	319	Y
Iron, total	45	51200	N	32	77300	N	19	94200	N	26	38500	N	205	Y
Lead, total	79	735	Y	48	1140	Y	27	124	N	44	7400	Y	388	Y
Mercury, total	45	1.01	N	32	6.4	Y	19	0.178	N	26	5.8	Y	190	Y
Molybdenum	1	0.5	U	3	1	U	13	1.82	U	17	2.92	U	62	U
Nickel, total	45	40.9	N	32	34.9	N	19	110	Y	26	67.5	Y	205	Y
Zinc, total	79	14700	Y	48	15400	Y	27	1810	Y	44	59600	Y	388	Y
Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)														
Anthracene	9	33.9	N	10	166	N	2	11.9	N	3	103	N	39	N
Benz(a)anthracene	9	172	N	10	700	N	2	11.9	N	3	222	N	39	N
Benzo(a)pyrene	9	193	N	10	720	N	2	11.9	N	3	211	N	39	N
Benzo(g,h,i)perylene	9	112	N	10	377	Y	2	11.9	N	3	109	N	39	Y
Benzo(k)fluoranthene	9	161	N	10	628	Y	2	11.9	N	3	137	N	39	Y
Chrysene	9	257	N	10	751	N	2	24.7	N	3	226	N	39	N
Dibenz(a,h)anthracene	9	49.1	N	10	155	Y	2	11.9	N	3	42.1	N	39	Y
Fluoranthene	9	383	N	10	1620	N	2	47.8	N	3	486	N	39	N
Indeno(1,2,3-c,d)pyrene	9	129	N	10	390	Y	2	11.9	N	3	104	N	39	Y
Phenanthrene	9	308	N	10	972	N	2	69.4	N	3	417	N	39	N
Pyrene	9	371	N	10	1360	N	2	33.7	N	3	441	N	39	N
Total HMW PAHs	9	1410	N	10	5300	Y	2	141	N	3	1630	N	39	Y
Total LMW PAHs	9	425	N	10	1380	Y	2	139	N	3	634	N	39	Y
Total PAHs	9	1830	N	10	6680	N	2	280	N	3	2260	N	39	N

Table 26. Summary of sediment chemistry data showing the 95th percentile data for the Upper/Middle Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)											Upper/Middle Spring River Sub-basin		
	Center Creek			Turkey Creek			Shawnee Creek			Short Creek		n	COC ³	
	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile			COC ²
<i>Semi-Volatile Compounds (µg/kg DW)</i>														
Butylbenzyl phthalate	9	913	N	10	434	N	2	1480	N	3	124	N	39	N

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; PEC = probable effect concentration. HMW = high molecular weight; LMW = low molecular weight.

¹ TRV = PEC or equivalent sediment quality guideline (see Table 32 for a complete list of selected TRVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 27. Summary of sediment chemistry data showing the 95th percentile data for the Lower Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ¹	Area of Interest (AoI)											
	n	95th Percentile		Empire Lake			Lower Spring River			Shoal Creek			Brush Creek		
				n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²
Metals (mg/kg)															
Aluminum, total	8	11700	58000	39	60100	Y	40	37500	N	81	50000	N	13	78200	Y
Arsenic, total	8	8.81	33	39	11.1	N	40	10.6	N	81	11.5	N	13	26.6	N
Barium, total	8	149	130.1	39	560	Y	35	463	Y	81	620	Y	13	510	Y
Cadmium, total	8	2.34	4.98	41	73.0	Y	66	19.0	Y	112	35.9	Y	14	11.0	Y
Chromium, total	8	35.1	111	39	75.2	N	40	54.7	N	81	71.9	N	13	104	N
Copper, total	8	11.3	149	39	56.3	N	46	26.3	N	99	33.4	N	13	29.8	N
Iron, total	8	33500	250000	39	31100	N	40	25000	N	81	33400	N	13	65400	N
Lead, total	8	27.9	128	41	620	Y	66	190	Y	112	517	Y	14	717	Y
Mercury, total	8	0.100	1.06	10	5.10	Y	20	0.864	N	63	0.350	N	13	0.0785	N
Molybdenum, total	0	ND	NB	36	1.25	U	12	49.2	U	29	1.00	U	12	1.19	U
Nickel, total	8	19.4	48.6	39	56.7	Y	40	30.4	N	81	25.5	N	13	55.2	Y
Zinc, total	8	258	459	41	12000	Y	66	2810	Y	112	6550	Y	14	2480	Y
Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)															
Anthracene	8	18.9	845	1	24.1	N	2	16.8	N	7	16.0	N	0	ND	U
Benz(a)anthracene	8	43.5	1050	1	91.1	N	2	34.3	N	7	53.4	N	0	ND	U
Benzo(a)pyrene	8	50.6	1450	1	87.7	N	2	44.7	N	7	73.7	N	0	ND	U
Benzo(g,h,i)perylene	8	39.8	250	1	50.7	N	2	40.9	N	7	59.8	N	0	ND	U
Benzo(k)fluoranthene	8	48.0	240	1	58.5	N	2	42.1	N	7	58.7	N	0	ND	U
Chrysene	8	77.3	1290	1	114	N	2	56.4	N	7	80.1	N	0	ND	U
Dibenz(a,h)anthracene	8	18.9	135	1	10.8	N	2	16.8	N	7	24.7	N	0	ND	U
Fluoranthene	8	108	2230	1	202	N	2	71.3	N	7	109	N	0	ND	U
Indeno(1,2,3-c,d)pyrene	8	38.1	240	1	47.3	N	2	40.2	N	7	58.9	N	0	ND	U
Phenanthrene	8	62.1	1170	1	258	N	2	39.8	N	7	39.9	N	0	ND	U
Pyrene	8	111	1520	1	201	N	2	71.3	N	7	114	N	0	ND	U
Total HMW PAHs	8	403	2300	1	707	N	2	295	N	7	448	N	0	ND	U
Total LMW PAHs	8	157	1200	1	425	N	2	141	N	7	116	N	0	ND	U
Total PAHs	8	550	22800	1	1130	N	2	436	N	7	562	N	0	ND	U

Table 27. Summary of sediment chemistry data showing the 95th percentile data for the Lower Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ¹	Area of Interest (AoI)											
	n	95th Percentile		Empire Lake			Lower Spring River			Shoal Creek			Brush Creek		
				n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²
<i>Semi-Volatile Compounds (µg/kg DW)</i>															
Butylbenzyl phthalate	8	189	11000	1	108	N	2	168	N	7	160	N	0	ND	U

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; PEC = probable effect concentration. HMW = high molecular weight; LMW = low molecular weight.

¹ TRV = PEC or equivalent sediment quality guideline (see Table 32 for a complete list of selected TRVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 27. Summary of sediment chemistry data showing the 95th percentile data for the Lower Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)												Lower Spring River Sub-basin				
	Willow Creek			Spring Brook			Beaver Creek			Warren Branch			Lost Creek			n	COC ³
	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²		
Metals (mg/kg)																	
Aluminum, total	15	74600	Y	7	66100	Y	60	18000	N	6	9310	N	26	11800	N	287	Y
Arsenic, total	15	37.6	Y	7	26.4	N	60	31.2	N	6	11.6	N	26	8.04	N	287	Y
Barium, total	15	522	Y	7	520	Y	52	216	N	6	140	N	32	267	N	274	Y
Cadmium, total	30	29.0	Y	15	180	Y	65	57.3	Y	9	6.30	Y	33	18.9	Y	385	Y
Chromium, total	15	118	Y	7	88.5	N	60	84.4	N	6	123	Y	26	102	N	287	Y
Copper, total	21	42.9	N	7	123	N	60	31	N	6	17.6	N	26	20.3	N	317	N
Iron, total	15	120000	N	7	63600	N	60	66500	N	6	45000	N	26	29700	N	287	N
Lead, total	30	605	Y	15	810	Y	65	483	Y	9	139	Y	33	1280	Y	385	Y
Mercury, total	15	0.144	N	7	0.248	N	37	0.355	N	6	0.131	N	26	1.74	Y	197	Y
Molybdenum, total	8	3.13	U	4	1.29	U	23	83.1	U	0	ND	U	0	ND	U	124	U
Nickel, total	15	88.7	Y	7	45.7	N	60	58.1	Y	6	9.69	N	26	19.4	N	287	Y
Zinc, total	30	6370	Y	15	16000	Y	65	10800	Y	9	1470	Y	33	2760	Y	385	Y
Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)																	
Anthracene	2	11.5	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Benz(a)anthracene	2	11.5	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Benzo(a)pyrene	2	11.5	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Benzo(g,h,i)perylene	2	21.8	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Benzo(k)fluoranthene	2	11.5	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Chrysene	2	11.5	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Dibenz(a,h)anthracene	2	11.5	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Fluoranthene	2	11.5	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Indeno(1,2,3-c,d)pyrene	2	11.5	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Phenanthrene	2	55.5	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Pyrene	2	11.5	N	0	ND	U	1	10.5	N	0	ND	U	3	12.3	N	16	U
Total HMW PAHs	2	69.0	N	0	ND	U	1	62.7	N	0	ND	U	3	74.0	N	16	U
Total LMW PAHs	2	134	N	0	ND	U	1	73.2	N	0	ND	U	3	86.3	N	16	U
Total PAHs	2	199	N	0	ND	U	1	136	N	0	ND	U	3	160	N	16	U

Table 27. Summary of sediment chemistry data showing the 95th percentile data for the Lower Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)															Lower Spring River Sub-basin	
	Willow Creek			Spring Brook			Beaver Creek		Warren Branch			Lost Creek			n	COC ³	
	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile			COC ²
<i>Semi-Volatile Compounds (µg/kg DW)</i>																	
Butylbenzyl phthalate	2	115	N	0	ND	U	1	105	N	0	ND	U	3	429	N	16	U

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; PEC = probable effect concentration. HMW = high molecular weight; LMW = low molecular weight.

¹ TRV = PEC or equivalent sediment quality guideline (see Table 32 for a complete list of selected TRVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 28. Summary of sediment chemistry data showing the 95th percentile data for the Neosho River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ¹	Area of Interest (AoI)											
	n	95th Percentile		Neosho River			Upper Tar Creek			Middle Tar Creek			Lytle Creek		
				n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²
Metals (mg/kg)															
Aluminum, total	8	11700	58000	52	30500	N	34	45100	N	47	20100	N	38	3080	N
Arsenic, total	8	8.81	33	105	17.9	N	34	14	N	47	32.8	N	38	17.3	N
Barium, total	8	149	130.1	47	250	N	34	457	Y	46	216	N	38	344	Y
Cadmium, total	8	2.34	4.98	111	4.09	N	39	107	Y	52	1370	Y	41	327	Y
Chromium, total	8	35.1	111	52	42.9	N	34	56	N	47	33.5	N	38	44.3	N
Copper, total	8	11.3	149	106	40.0	N	34	54	N	47	409	Y	38	234	Y
Iron, total	8	33500	250000	106	62500	N	34	42600	N	47	90000	N	38	64800	N
Lead, total	8	27.9	128	117	123	N	39	1930	Y	52	7180	Y	41	5890	Y
Mercury, total	8	0.100	1.06	38	0.141	N	34	0.384	N	47	1.39	Y	38	1.09	Y
Molybdenum, total	0	ND	NB	27	6.75	U	29	1.50	U	25	35.8	U	16	23.3	U
Nickel, total	8	19.4	48.6	52	37.9	N	34	28.3	N	47	224	Y	38	102	Y
Zinc, total	8	258	459	117	2930	Y	39	26000	Y	52	71300	Y	41	62100	Y
Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)															
Anthracene	8	18.9	845	4	13.8	N	2	11.6	N	2	10.7	N	2	15.4	N
Benz(a)anthracene	8	43.5	1050	4	43.1	N	2	11.6	N	2	10.7	N	2	15.4	N
Benzo(a)pyrene	8	50.6	1450	4	40.7	N	2	11.6	N	2	10.7	N	2	15.4	N
Benzo(g,h,i)perylene	8	39.8	250	4	30.1	N	2	11.6	N	2	10.7	N	2	15.4	N
Benzo(k)fluoranthene	8	48.0	240	4	43.6	N	2	11.6	N	2	10.7	N	2	15.4	N
Chrysene	8	77.3	1290	4	81.5	N	2	11.6	N	2	10.7	N	2	15.4	N
Dibenz(a,h)anthracene	8	18.9	135	4	13.8	N	2	11.6	N	2	10.7	N	2	15.4	N
Fluoranthene	8	108	2230	4	108	N	2	11.6	N	2	10.7	N	2	15.4	N
Indeno(1,2,3-c,d)pyrene	8	38.1	240	4	29.7	N	2	11.6	N	2	10.7	N	2	15.4	N
Phenanthrene	8	62.1	1170	4	81.8	N	2	11.6	N	2	10.7	N	2	15.4	N
Pyrene	8	111	1520	4	122	N	2	11.6	N	2	10.7	N	2	15.4	N
Total HMW PAHs	8	403	2300	4	408	N	2	69.8	N	2	64.4	N	2	92.5	N
Total LMW PAHs	8	157	1200	4	163	N	2	81.5	N	2	75.1	N	2	108	N
Total PAHs	8	550	22800	4	566	N	2	151	N	2	140	N	2	200	N

Table 28. Summary of sediment chemistry data showing the 95th percentile data for the Neosho River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ¹	Area of Interest (AoI)											
	95th Percentile			Neosho River			Upper Tar Creek			Middle Tar Creek			Lytle Creek		
	n			n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²
<i>Semi-Volatile Compounds (µg/kg DW)</i>															
Butylbenzyl phthalate	8	189	11000	4	411	N	2	116	N	2	107	N	2	1150	N

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; PEC = probable effect concentration. HMW = high molecular weight; LMW = low molecular weight.

¹ TRV = PEC or equivalent sediment quality guideline (see Table 32 for a complete list of selected TRVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 28. Summary of sediment chemistry data showing the 95th percentile data for the Neosho River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)						Neosho River Sub-basin	
	Lower Tar Creek			Elm Creek			n	COC ³
	n	95th Percentile	COC ²	n	95th Percentile	COC ²		
Metals (mg/kg)								
Aluminum, total	100	33800	N	21	17200	N	292	N
Arsenic, total	104	99.9	Y	21	38.5	Y	349	Y
Barium, total	89	222	N	21	341	Y	275	Y
Cadmium, total	108	104	Y	26	170	Y	377	Y
Chromium, total	100	248	Y	21	56.4	N	292	Y
Copper, total	105	86	N	21	1150	Y	351	Y
Iron, total	105	338000	Y	21	63700	N	351	Y
Lead, total	108	1330	Y	26	46600	Y	383	Y
Mercury, total	43	0.289	N	21	1.72	Y	221	Y
Molybdenum, total	27	87.9	U	1	0.500	U	125	U
Nickel, total	100	224	Y	21	106	Y	292	Y
Zinc, total	108	18100	Y	26	114000	Y	383	Y
Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)								
Anthracene	4	58.0	N	1	13.8	N	15	N
Benz(a)anthracene	4	268	N	1	13.8	N	15	N
Benzo(a)pyrene	4	288	N	1	13.8	N	15	N
Benzo(g,h,i)perylene	4	208	N	1	13.8	N	15	N
Benzo(k)fluoranthene	4	273	Y	1	13.8	N	15	Y
Chrysene	4	325	N	1	13.8	N	15	N
Dibenz(a,h)anthracene	4	71.6	N	1	13.8	N	15	N
Fluoranthene	4	484	N	1	13.8	N	15	N
Indeno(1,2,3-c,d)pyrene	4	212	N	1	13.8	N	15	N
Phenanthrene	4	257	N	1	13.8	N	15	N
Pyrene	4	592	N	1	13.8	N	15	N
Total HMW PAHs	4	2030	N	1	82.5	N	15	N
Total LMW PAHs	4	381	N	1	96.3	N	15	N
Total PAHs	4	2410	N	1	179	N	15	N

Table 28. Summary of sediment chemistry data showing the 95th percentile data for the Neosho River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)						Neosho River Sub-basin	
	Lower Tar Creek			Elm Creek			n	COC ³
	n	95th Percentile	COC ²	n	95th Percentile	COC ²		
<i>Semi-Volatile Compounds (µg/kg DW)</i>								
Butylbenzyl phthalate	4	111	N	1	138	N	15	N

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; PEC = probable effect concentration. HMW = high molecular weight; LMW = low molecular weight.

¹ TRV = PEC or equivalent SQG (see Table 32 for a complete list of selected TRVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 29. Summary of pore-water chemistry data showing the 95th percentile data for the Upper/Middle Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ¹	Area of Interest (AoI)											
	n	95th Percentile		Upper Spring River			North Fork Spring River			Middle Spring River			Cow Creek		
				n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²
<i>Metals (µg/L)</i>															
Aluminum, total	0	ND	87	0	ND	U	0	ND	U	1	783	U	0	ND	U
Cadmium, total	0	ND	0.25	0	ND	U	0	ND	U	0	ND	U	1	42.0	U
Chromium, total	0	ND	2	0	ND	U	2	5.00	U	3	5.00	U	3	5.00	U
Cobalt, total	0	ND	5	0	ND	U	2	25.0	U	3	25.0	U	3	25.0	U
Copper, total	0	ND	4.17	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Iron, total	0	ND	887	0	ND	U	2	113	U	3	668	U	3	50.0	U
Lead, total	0	ND	1.16	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Mercury, total	0	ND	0.182	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Molybdenum, total	0	ND	395	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Selenium, total	0	ND	4.96	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Silver, total	0	ND	0.098	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Zinc, total	0	ND	60.8	0	ND	U	2	92.9	U	3	139	U	3	14000	U
Cadmium, dissolved	8	0.0800	0.25	5	0.0300	N	5	0.0300	N	3	0.0800	N	2	0.0300	N
Cobalt, dissolved	8	10.0	5	5	18.0	N	5	18.0	N	3	3.90	N	2	67.0	Y
Lead, dissolved	8	0.160	1.16	5	0.578	N	5	0.165	N	3	0.0950	N	2	0.215	N
Mercury, dissolved	0	ND	0.182	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Zinc, dissolved	8	2.85	60.8	5	26.0	N	5	1.20	N	3	3.94	N	2	34.1	N

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 29. Summary of pore-water chemistry data showing the 95th percentile data for the Upper/Middle Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)												Upper/Middle Spring River Sub-basin	
	Center Creek			Turkey Creek			Shawnee Creek			Short Creek			n	COC ³
	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²		
<i>Metals (µg/L)</i>														
Aluminum, total	3	4520	U	1	551	U	0	ND	U	0	ND	U	5	U
Cadmium, total	2	13.9	U	0	ND	U	0	ND	U	0	ND	U	3	U
Chromium, total	4	5.00	U	2	5.00	U	0	ND	U	0	ND	U	14	U
Cobalt, total	4	25.0	U	2	25.0	U	0	ND	U	0	ND	U	14	U
Copper, total	2	31.7	U	0	ND	U	0	ND	U	0	ND	U	2	U
Iron, total	4	4000	U	2	6110	U	0	ND	U	0	ND	U	14	U
Lead, total	3	111	U	0	ND	U	0	ND	U	0	ND	U	3	U
Mercury, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Molybdenum, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Selenium, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Silver, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Zinc, total	4	2340	U	2	2970	U	0	ND	U	0	ND	U	14	U
Cadmium, dissolved	9	0.289	Y	10	2.41	Y	2	0.0300	N	3	18.6	Y	39	Y
Cobalt, dissolved	9	16.0	N	10	30.0	Y	2	19.4	N	3	38.0	Y	39	Y
Lead, dissolved	9	4.36	Y	10	12.3	Y	2	0.440	N	3	62.6	Y	39	Y
Mercury, dissolved	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Zinc, dissolved	9	893	Y	10	540	Y	2	1.20	N	3	6530	Y	39	Y

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 30. Summary of pore-water chemistry data showing the 95th percentile data for the Lower Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ¹	Area of Interest (AoI)											
	n	95th Percentile		Empire Lake			Lower Spring River			Shoal Creek			Brush Creek		
				n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²
<i>Metals (µg/L)</i>															
Aluminum, total	0	ND	87	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Cadmium, total	0	ND	0.25	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Chromium, total	0	ND	2	0	ND	U	2	5.00	U	4	5.00	U	0	ND	U
Cobalt, total	0	ND	5	0	ND	U	2	25.0	U	4	25.0	U	0	ND	U
Copper, total	0	ND	4.17	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Iron, total	0	ND	887	0	ND	U	2	50.0	U	4	290	U	0	ND	U
Lead, total	0	ND	1.16	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Mercury, total	0	ND	0.182	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Molybdenum, total	0	ND	395	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Selenium, total	0	ND	4.96	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Silver, total	0	ND	0.098	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Zinc, total	0	ND	60.8	0	ND	U	2	643	U	4	146	U	0	ND	U
Cadmium, dissolved	8	0.0800	0.25	1	0.0800	N	2	0.0800	N	7	0.241	N	0	ND	U
Cobalt, dissolved	8	10.0	5	1	2.00	N	2	9.95	N	7	10.0	N	0	ND	U
Lead, dissolved	8	0.160	1.16	1	0.0950	N	2	0.0950	N	7	0.482	N	0	ND	U
Mercury, dissolved	0	ND	0.182	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Zinc, dissolved	8	2.85	60.8	1	10.7	N	2	29.2	N	7	45.7	N	0	ND	U

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 30. Summary of pore-water chemistry data showing the 95th percentile data for the Lower Spring River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)															Lower Spring River Sub-basin	
	Willow Creek			Spring Brook			Beaver Creek			Warren Branch			Lost Creek			n	COC ³
	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²		
<i>Metals (µg/L)</i>																	
Aluminum, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Cadmium, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Chromium, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	1	5.00	U	7	U
Cobalt, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	1	25.0	U	7	U
Copper, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Iron, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	1	50.0	U	7	U
Lead, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Mercury, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Molybdenum, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Selenium, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Silver, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Zinc, total	0	ND	U	0	ND	U	0	ND	U	0	ND	U	1	30.0	U	7	U
Cadmium, dissolved	2	0.185	N	0	ND	U	1	0.0800	N	0	ND	U	3	0.0750	N	16	U
Cobalt, dissolved	2	4.95	N	0	ND	U	1	8.00	N	0	ND	U	3	7.90	N	16	U
Lead, dissolved	2	0.400	N	0	ND	U	1	0.0950	N	0	ND	U	3	1.18	Y	16	Y
Mercury, dissolved	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	ND	U	0	U
Zinc, dissolved	2	39.5	N	0	ND	U	1	349	Y	0	ND	U	3	2.69	N	16	Y

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹TRV = TSV, either a water quality criteria, or draft freshwater benchwater (see Table 3 for a complete list of selected TSVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 31. Summary of pore-water chemistry data showing the 95th percentile data for the Neosho River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Reference		TRV ¹	Area of Interest (AoI)											
	n	95th Percentile		Neosho River			Upper Tar Creek			Middle Tar Creek			Lytle Creek		
				n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²	n	95th Percentile	COC ²
<i>Metals (µg/L)</i>															
Aluminum, total	0	ND	87	0	ND	U	1	550	U	0	ND	U	0	ND	U
Cadmium, total	0	ND	0.25	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Chromium, total	0	ND	2	2	5.00	U	1	5.00	U	0	ND	U	0	ND	U
Cobalt, total	0	ND	5	2	25.0	U	1	25.0	U	0	ND	U	0	ND	U
Copper, total	0	ND	4.17	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Iron, total	0	ND	887	2	50.0	U	1	432	U	0	ND	U	0	ND	U
Lead, total	0	ND	1.16	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Mercury, total	0	ND	0.182	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Molybdenum, total	0	ND	395	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Selenium, total	0	ND	4.96	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Silver, total	0	ND	0.098	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Zinc, total	0	ND	60.8	2	30.0	U	1	30.0	U	0	ND	U	0	ND	U
Cadmium, dissolved	8	0.0800	0.25	4	0.0800	N	2	0.0775	N	2	12.9	Y	2	0.361	Y
Cobalt, dissolved	8	10.0	5	4	7.70	N	2	29.5	Y	2	5.80	N	2	4.77	N
Lead, dissolved	8	0.160	1.16	4	0.0950	N	2	0.102	N	2	3.79	Y	2	16.3	Y
Mercury, dissolved	0	ND	0.182	0	ND	U	0	ND	U	0	ND	U	0	ND	U
Zinc, dissolved	8	2.85	60.8	4	3.16	N	2	4.51	N	2	5320	Y	2	943	Y

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 31. Summary of pore-water chemistry data showing the 95th percentile data for the Neosho River Sub-basin of the Tri-State Mining District (2002 - 2009).

Chemical of Potential Concern (COPC)	Area of Interest (AoI)						Neosho River Sub-basin	
	Lower Tar Creek			Elm Creek			n	COC ³
	n	95th Percentile	COC ²	n	95th Percentile	COC ²		
<i>Metals (µg/L)</i>								
Aluminum, total	0	ND	U	0	ND	U	1	U
Cadmium, total	0	ND	U	0	ND	U	0	U
Chromium, total	1	5.00	U	1	5.00	U	5	U
Cobalt, total	1	25.0	U	1	25.0	U	5	U
Copper, total	0	ND	U	0	ND	U	0	U
Iron, total	1	50.0	U	1	50.0	U	5	U
Lead, total	0	ND	U	0	ND	U	0	U
Mercury, total	0	ND	U	0	ND	U	0	U
Molybdenum, total	0	ND	U	0	ND	U	0	U
Selenium, total	0	ND	U	0	ND	U	0	U
Silver, total	0	ND	U	0	ND	U	0	U
Zinc, total	1	790	U	1	1840	U	5	U
Cadmium, dissolved	4	3.72	Y	1	0.0725	N	15	Y
Cobalt, dissolved	4	38.5	Y	1	4.00	N	15	Y
Lead, dissolved	4	0.345	N	1	1.52	Y	15	Y
Mercury, dissolved	0	ND	U	0	ND	U	0	U
Zinc, dissolved	4	1930	Y	1	13.0	N	15	Y

Y = Yes; N = No; U = Uncertain; n = number of samples; COC = contaminant of concern; ND = no data; NB = no benchmark; TRV = toxicity reference value; TSV = toxicity screening value.

¹TRV = TSV, either a water quality criteria, or draft freshwater benchmark (see Table 3 for a complete list of selected TSVs).

² A substance was identified as a COC for individual AoIs if the 95th percentile concentration for the AoI exceeded both the TRV, as well as exceeded the reference 95th percentile concentration by a factor of 2 or more. If either the the 95th percentile concentration for an AoI or reference area could not be calculated, or no benchmark existed for the COPC, then the COPC was retained as an uncertain COC.

³ A substance was identified as a COC for the sub-basin if it was identified as a COC in any one or more AoIs within that sub-basin. A substance was identified as an uncertain COC for the sub-basin if it was identified as an uncertain COC in any one or more (or all) AoIs and was eliminated as a COC in all other AoIs.

Table 32. Sources for selected toxicity reference values for sediment.

Chemical of Potential Concern	TRV	Sediment Quality Guideline-Type	Source
Metals (mg/kg)			
Aluminum, total	58000	ERM	Ingersoll <i>et al.</i> 1996
Arsenic, total	33	PEC	MacDonald <i>et al.</i> 2000a
Barium, total	130.1	HC5	Leung <i>et al.</i> 2005
Cadmium, total	4.98	PEC	MacDonald <i>et al.</i> 2000a
Chromium, total	111	PEC	MacDonald <i>et al.</i> 2000a
Copper, total	149	PEC	MacDonald <i>et al.</i> 2000a
Iron, total	250000	PEL	Ingersoll <i>et al.</i> 1996
Lead, total	128	PEC	MacDonald <i>et al.</i> 2000a
Mercury, total	1.06	PEC	MacDonald <i>et al.</i> 2000a
Molybdenum, total	NB	NA	NA
Nickel, total	48.6	PEC	MacDonald <i>et al.</i> 2000a
Zinc, total	459	PEC	MacDonald <i>et al.</i> 2000a
Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)			
Anthracene	845	PEC	MacDonald <i>et al.</i> 2000a
Benz(<i>a</i>)anthracene	1050	PEC	MacDonald <i>et al.</i> 2000a
Benzo(<i>a</i>)pyrene	1450	PEC	MacDonald <i>et al.</i> 2000a
Benzo(<i>g,h,i</i>)perylene	250	PEL	Ingersoll <i>et al.</i> 1996
Benzo(<i>k</i>)fluoranthene	240	LEL	Persaud <i>et al.</i> 1993
Chrysene	1290	PEC	MacDonald <i>et al.</i> 2000a
Dibenz(<i>a,h</i>)anthracene	135	PEL	Ingersoll <i>et al.</i> 1996
Fluoranthene	2230	PEC	MacDonald <i>et al.</i> 2000a
Fluorene	536	PEC	MacDonald <i>et al.</i> 2000a
Indeno(1,2,3- <i>c,d</i>)pyrene	240	PEL	Ingersoll <i>et al.</i> 1996
Phenanthrene	1170	PEC	MacDonald <i>et al.</i> 2000a
Pyrene	1520	PEC	MacDonald <i>et al.</i> 2000a
Total High Molecular Weight PAHs	2300	PEL	Ingersoll <i>et al.</i> 1996
Total Low Molecular Weight PAHs	1200	PEL	Ingersoll <i>et al.</i> 1996
Total PAHs	22800	PEC	MacDonald <i>et al.</i> 2000a
Semi-Volatile Compounds (µg/kg DW)			
Butylbenzyl phthalate	11000	LEL	USEPA 2004

TRVs = toxicity reference values; ERM = effect range median; PEL = probable effect level;
 LEL = lowest effect level; PEC = probable effect concentration; HC5 = hazardous concentration for 5% of the species;
 NB = no benchmark; NA = not applicable.

Table 33. Summary of surface-water chemistry data showing the overall contaminants of concern for the sub-basins within the Tri-State Mining District.

Chemical of Potential Concern	Upper/Middle Spring River Sub-basin		Lower Spring River Sub-basin		Neosho River Sub-basin	
	n	COC	n	COC	n	COC
<i>Metals (µg/L)</i>						
Aluminum, total	107	N	146	Y	144	Y
Cadmium, total	10	U	33	U	171	U
Copper, total	12	U	21	U	109	U
Iron, total	107	N	192	Y	370	Y
Lead, total	17	U	44	U	165	U
Nickel, total	107	N	189	N	311	Y
Zinc, total	107	Y	215	Y	372	Y
Cadmium, dissolved	8	U	4	U	107	U
Iron, dissolved	106	N	180	Y	301	Y
Mercury, dissolved	0	U	0	U	0	U
Nickel, dissolved	53	U	85	Y	227	Y
Zinc, dissolved	100	Y	223	Y	329	Y
<i>Nutrients/Inorganics/Conventionals</i>						
Ammonia	0	U	0	U	0	U
Chlorine, dissolved	0	U	0	U	0	U

n = number of samples; COC = contaminant of concern; Y = Yes; N = No; U = Uncertain.

Table 34. Summary of pore-water chemistry data showing the overall contaminants of concern for the sub-basins within the Tri-State Mining District.

Chemical of Potential Concern	Upper/Middle Spring River Sub-basin		Lower Spring River Sub-basin		Neosho River Sub-basin	
	n	COC	n	COC	n	COC
<i>Metals (µg/L)</i>						
Aluminum, total	5	U	0	U	1	U
Cadmium, total	3	U	0	U	0	U
Chromium, total	14	U	7	U	5	U
Cobalt, total	14	U	7	U	5	U
Copper, total	2	U	0	U	0	U
Iron, total	14	U	7	U	5	U
Lead, total	3	U	0	U	0	U
Mercury, total	0	U	0	U	0	U
Molybdenum, total	0	U	0	U	0	U
Selenium, total	0	U	0	U	0	U
Silver, total	0	U	0	U	0	U
Zinc, total	14	U	7	U	5	U
Cadmium, dissolved	39	Y	16	U	15	Y
Cobalt, dissolved	39	Y	16	U	15	Y
Lead, dissolved	39	Y	16	Y	15	Y
Mercury, dissolved	0	U	0	U	0	U
Zinc, dissolved	39	Y	16	Y	15	Y

n = number of samples; COC = contaminant of concern; Y = Yes; N = No; U = Uncertain.

Table 35. Summary of sediment chemistry data showing the overall contaminants of concern for the sub-basins within the Tri-State Mining District.

Chemical of Potential Concern	Upper/Middle Spring River Sub-basin		Lower Spring River Sub-basin		Neosho River Sub-basin	
	n	COC	n	COC	n	COC
<i>Metals (mg/kg)</i>						
Aluminum, total	205	Y	287	Y	292	N
Arsenic, total	205	Y	287	Y	349	Y
Barium, total	204	Y	274	Y	275	Y
Cadmium, total	386	Y	385	Y	377	Y
Chromium, total	205	Y	287	Y	292	Y
Copper, total	319	Y	317	N	351	Y
Iron, total	205	Y	287	N	351	Y
Lead, total	388	Y	385	Y	383	Y
Mercury, total	190	Y	197	Y	221	Y
Molybdenum	62	U	124	U	125	U
Nickel, total	205	Y	287	Y	292	Y
Zinc, total	388	Y	385	Y	383	Y
<i>Polycyclic Aromatic Hydrocarbons (PAHs; µg/kg DW)</i>						
Anthracene	39	N	16	U	15	N
Benz(a)anthracene	39	N	16	U	15	N
Benzo(a)pyrene	39	N	16	U	15	N
Benzo(g,h,i)perylene	39	Y	16	U	15	N
Benzo(k)fluoranthene	39	Y	16	U	15	Y
Chrysene	39	N	16	U	15	N
Dibenz(a,h)anthracene	39	Y	16	U	15	N
Fluoranthene	39	N	16	U	15	N
Indeno(1,2,3-c,d)pyrene	39	Y	16	U	15	N
Phenanthrene	39	N	16	U	15	N
Pyrene	39	N	16	U	15	N
Total HMW PAHs	39	Y	16	U	15	N
Total LMW PAHs	39	Y	16	U	15	N
Total PAHs	39	N	16	U	15	N
<i>Semi-Volatile Compounds</i>						
Butylbenzyl phthalate	39	N	16	U	15	N

n = number of samples; COC = contaminant of concern; Y = Yes; N = No; U = Uncertain; HMW = high molecular weight; LMW = low molecular weight.

Table 36. Summary of the available invertebrate-tissue chemistry data for the Tri-State Mining District.

Chemical Class/Analyte	n	n Detects	% Non-Detect	Distribution							Mean	Standard Deviation	Geometric Mean	Min	Max
				5th	10th	25th	50th	75th	90th	95th					
<i>Metals (mg/kg DW)</i>															
Aluminum, total	21	21	0%	321	607	665	1520	3160	5330	5860	2350	1950	1570	142	6340
Arsenic, total	21	21	0%	2.60	2.70	3.30	4.30	6.80	9.00	9.90	5.21	2.35	4.75	2.4	9.9
Cadmium, total	239	218	9%	0.500	0.520	0.695	1.10	3.85	7.37	9.73	3.13	5.21	1.62	<0.5	44.98
Calcium, total	21	21	0%	1340	1480	1630	1940	2910	4540	5030	2560	1430	2270	1230	6560
Chromium, total	21	21	0%	2.40	2.40	3.40	4.50	6.00	7.00	7.40	4.76	1.82	4.43	2.3	8.8
Copper, total	239	239	0%	3.79	4.20	5.85	9.60	16.0	27.0	35.0	13.8	14.9	10.2	2.9	111
Iron, total	21	21	0%	1690	1820	2190	3470	5830	11300	12500	4820	3590	3880	1620	13800
Lead, total	239	221	8%	0.500	0.570	0.790	1.60	4.85	13.0	31.7	15.2	112	2.30	<0.5	1702
Nickel, total	21	21	0%	1.90	2.53	3.55	4.70	6.13	9.42	10.8	5.22	2.82	4.59	1.771	12.6
Silver, total	21	2	90%	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.233	0.153	0.215	0.2	0.9
Zinc, total	239	239	0%	140	158	235	323	620	1500	3100	698	1010	421	130	7100

n = sample size; ND = no data; min = minimum; max = maximum.

Table 37. Frequency of exceedance of site-specific toxicity thresholds for divalent metals in surface water (i.e., Σ SW-TU_{DIVALENT METALS}) in the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ SW-TU _{DIVALENT METALS}	Number of Samples Predicted to be Toxic ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
Upper/Middle Spring River Sub-basin							
Upper Spring River AoI	5	0.408	0 (0%)	5	0	0	Low
North Fork Spring River AoI	8	0.556	0 (0%)	8	0	0	Low
Middle Spring River AoI	20	0.857	9 (45%)	11	4	5	High
Cow Creek AoI	5	0.919	1 (20%)	4	0	1	Moderate
Center Creek AoI	36	1.02	14 (39%)	22	0	14	High
Turkey Creek AoI	19	1.51	16 (84%)	3	3	13	High
Shawnee Creek AoI	7	0.635	2 (29%)	5	1	1	High
Short Creek AoI	6	50.6	6 (100%)	0	0	6	High
<i>Sub-basin Subtotal</i>	<i>106</i>	<i>1.16</i>	<i>48 (45%)</i>	<i>58</i>	<i>8</i>	<i>40</i>	<i>High</i>
Lower Spring River Sub-basin							
Empire Lake AoI	2	0.954	1 (50%)	1	1	0	High
Lower Spring River AoI	32	0.543	3 (9%)	29	3	0	Low
Shoal Creek AoI	50	0.623	8 (16%)	42	3	5	Moderate
Brush Creek AoI	1	NC	1 (100%)	0	1	0	High
Willow Creek AoI	5	3.74	5 (100%)	0	1	4	High
Spring Brook AoI	3	31.6	3 (100%)	0	0	3	High
Beaver Creek AoI	87	0.998	39 (45%)	48	10	29	High
Warren Branch AoI	5	0.500	0 (0%)	5	0	0	Low
Lost Creek AoI	23	0.617	1 (4%)	22	0	1	Low
<i>Sub-basin Subtotal</i>	<i>208</i>	<i>0.820</i>	<i>61 (29%)</i>	<i>147</i>	<i>19</i>	<i>42</i>	<i>High</i>
Neosho River Sub-basin							
Neosho River AoI	37	0.433	3 (8%)	34	2	1	Low
Upper Tar Creek AoI	3	6.19	3 (100%)	0	1	2	High
Middle Tar Creek AoI	53	5.97	44 (83%)	9	2	42	High
Lytle Creek AoI	4	16.7	4 (100%)	0	0	4	High
Lower Tar Creek AoI	121	3.66	101 (83%)	20	2	99	High
Elm Creek AoI	5	8.38	4 (80%)	1	0	4	High
<i>Sub-basin Subtotal</i>	<i>223</i>	<i>3.04</i>	<i>159 (71%)</i>	<i>64</i>	<i>7</i>	<i>152</i>	<i>High</i>

Table 37. Frequency of exceedance of site-specific toxicity thresholds for divalent metals in surface water (i.e., Σ SW-TU_{DIVALENT METALS}) in the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ SW-TU _{DIVALENT METALS}	Number of Samples Predicted to be Toxic ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
<i>Study Area as a Whole</i>	537	1.52	268 (50%)	269	34	234	<i>High</i>
Reference Surface Water Samples	18	0.54	1 (6%)	17	0	1	Low

Σ SW-TUs = sum of surface water toxic units; Divalent metals = dissolved copper, dissolved cadmium, dissolved lead, dissolved nickel, dissolved silver, dissolved zinc;

SSTT = site-specific toxicity threshold; AoI = area of interest; n = sample size; ND = no data; NC = not calculated.

¹ Surface water samples were predicted to be toxic to benthic invertebrates if the SSTT was exceeded: i.e., Σ SW-TU_{DIVALENT METALS} \geq 1.03.

² Risk classification: Low if Σ SW-TUs < 1.03; Moderate if Σ SW-TUs = 1.03 to 1.41; and High if Σ SW-TUs > 1.41.

³ Based on frequency of exceedance of the SSTT of 1.03: Low if <10%; Moderate if 10 to 20%; and High if >20% (i.e. based on 20% increase in frequency of exceedance compared to that for surface water samples from the selected reference area).

Table 38. Frequency of exceedance of the site-specific toxicity thresholds for sediment that were developed for the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of ΣPEC-Q _{Cd,Pb,Zn}	Number of Samples Predicted to be Toxic ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
Upper/Middle Spring River Sub-basin							
Upper Spring River AoI	18	1.07	1 (6%)	17	1	0	Low
North Fork Spring River AoI	27	0.54	0 (0%)	27	0	0	Low
Middle Spring River AoI	115	2.29	27 (23%)	88	15	12	High
Cow Creek AoI	34	1.87	5 (15%)	29	2	3	Moderate
Center Creek AoI	81	5.39	37 (46%)	44	7	30	High
Turkey Creek AoI	48	18.1	40 (83%)	8	5	35	High
Shawnee Creek AoI	27	1.37	2 (7%)	25	2	0	Low
Short Creek AoI	44	74.2	44 (100%)	0	2	42	High
<i>Sub-basin Subtotal</i>	<i>394</i>	<i>4.30</i>	<i>156 (40%)</i>	<i>238</i>	<i>34</i>	<i>122</i>	<i>High</i>
Lower Spring River Sub-basin							
Empire Lake AoI	41	20.9	38 (93%)	3	2	36	High
Lower Spring River AoI	66	5.04	32 (48%)	34	20	12	High
Shoal Creek AoI	112	5.56	55 (49%)	57	24	31	High
Brush Creek AoI	14	1.47	2 (14%)	12	1	1	Moderate
Willow Creek AoI	30	6.79	14 (47%)	16	8	6	High
Spring Brook AoI	15	27.3	14 (93%)	1	0	14	High
Beaver Creek AoI	65	7.51	33 (51%)	32	7	26	High
Warren Branch AoI	9	1.23	0 (0%)	9	0	0	Low
Lost Creek AoI	33	1.49	4 (12%)	29	1	3	Moderate
<i>Sub-basin Subtotal</i>	<i>385</i>	<i>5.87</i>	<i>192 (50%)</i>	<i>193</i>	<i>63</i>	<i>129</i>	<i>High</i>
Neosho River Sub-basin							
Neosho River AoI	117	1.26	9 (8%)	108	5	4	Low
Upper Tar Creek AoI	39	3.12	8 (21%)	31	0	8	High
Middle Tar Creek AoI	52	79.9	52 (100%)	0	1	51	High
Lytle Creek AoI	41	62.5	39 (95%)	2	2	37	High
Lower Tar Creek AoI	108	13.6	88 (81%)	20	3	85	High
Elm Creek AoI	26	34.1	22 (85%)	4	2	20	High
<i>Sub-basin Subtotal</i>	<i>383</i>	<i>8.41</i>	<i>218 (57%)</i>	<i>165</i>	<i>13</i>	<i>205</i>	<i>High</i>

Table 38. Frequency of exceedance of the site-specific toxicity thresholds for sediment that were developed for the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Samples Predicted to be Toxic ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
<i>Study Area as a Whole</i>	<i>1162</i>	<i>6.09</i>	<i>566 (49%)</i>	<i>596</i>	<i>110</i>	<i>456</i>	<i>High</i>
Reference Sediment Samples	10	0.46	0 (0%)	10	0	0	Low

Σ PEC-Q = sum probable effect concentration quotient; Cd = cadmium; Pb = lead; Zn = zinc; d = day; n = sample size; AoI = area of interest; SSTT = site-specific toxicity thresholds.

¹ Sediment samples were predicted to be toxic to benthic invertebrates if the SSTT was exceeded: i.e., if Σ PEC-Q_{Cd,Pb,Zn} \geq 6.47.

² Risk classification: Low if Σ PEC-Q_{Cd,Pb,Zn} < 6.47; Moderate if Σ PEC-Q_{Cd,Pb,Zn} = 6.47 to 10.04; and High if Σ PEC-Q_{Cd,Pb,Zn} > 10.04.

³ Based on frequency of exceedance of the SSTT of 6.47: Low if <10%; Moderate if 10 to 20%; and High if >20% (i.e. based on 20% increase in frequency of toxicity compared to that for reference sediment samples).

Table 39. Frequency of exceedance of the site-specific toxicity thresholds for pore water that were developed for the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of PW-TU _{Zn}	Number of Samples Predicted to be Toxic ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
Upper/Middle Spring River Sub-basin							
Upper Spring River AoI	5	0.010	0 (0%)	5	0	0	Low
North Fork Spring River AoI	7	0.017	1 (14%)	6	1	0	Moderate
Middle Spring River AoI	6	0.066	1 (17%)	5	0	1	Moderate
Cow Creek AoI	5	0.198	1 (20%)	4	0	1	Moderate
Center Creek AoI	13	0.469	8 (62%)	5	1	7	High
Turkey Creek AoI	12	0.560	6 (50%)	6	1	5	High
Shawnee Creek AoI	2	0.007	0 (0%)	2	0	0	Low
Short Creek AoI	3	9.59	3 (100%)	0	0	3	High
<i>Sub-basin Subtotal</i>	<i>53</i>	<i>0.163</i>	<i>20 (38%)</i>	<i>33</i>	<i>3</i>	<i>17</i>	<i>High</i>
Lower Spring River Sub-basin							
Empire Lake AoI	1	NC	0 (0%)	1	0	0	Low
Lower Spring River AoI	4	0.160	1 (25%)	3	0	1	High
Shoal Creek AoI	11	0.114	1 (9%)	10	0	1	Low
Brush Creek AoI	ND	ND	ND	ND	ND	ND	ND
Willow Creek AoI	2	0.051	0 (0%)	2	0	0	Low
Spring Brook AoI	ND	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	1	NC	1 (100%)	0	0	1	High
Warren Branch AoI	ND	ND	ND	ND	ND	ND	ND
Lost Creek AoI	4	0.021	0 (0%)	4	0	0	Low
<i>Sub-basin Subtotal</i>	<i>23</i>	<i>0.0859</i>	<i>3 (13%)</i>	<i>20</i>	<i>0</i>	<i>3</i>	<i>Moderate</i>
Neosho River Sub-basin							
Neosho River AoI	6	0.026	0 (0%)	6	0	0	Low
Upper Tar Creek AoI	3	0.028	0 (0%)	3	0	0	Low
Middle Tar Creek AoI	2	0.904	1 (50%)	1	0	1	High
Lytle Creek AoI	2	0.634	1 (50%)	1	0	1	High
Lower Tar Creek AoI	5	0.816	3 (60%)	2	1	2	High
Elm Creek AoI	2	0.553	1 (50%)	1	0	1	High
<i>Sub-basin Subtotal</i>	<i>20</i>	<i>0.166</i>	<i>6 (30%)</i>	<i>14</i>	<i>1</i>	<i>5</i>	<i>High</i>

Table 39. Frequency of exceedance of the site-specific toxicity thresholds for pore water that were developed for the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of PW-TU _{Zn}	Number of Samples Predicted to be Toxic ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
<i>Study Area as a Whole</i>	96	0.141	29 (30%)	67	4	25	High
Reference Sediment Samples	8	0.006	0 (0%)	8	0	0	Low

PW-TU = pore-water toxic units; Zn = zinc; n = sample size; SSTT = site-specific toxicity threshold; ND = no data; NC = not calculated.

AoI = area of interest

¹ Pore-water samples were predicted to be toxic to benthic invertebrates if the SSTT was exceeded: i.e., PW-TU_{Zn} ≥ 0.581.

² Risk classification: Low if PW-TU_{Zn} < 0.581; Moderate if PW-TU_{Zn} = 0.581 to 0.867; and High if PW-TU_{Zn} > 0.867.

³ Based on frequency of exceedance of the SSTT of 0.581: Low if <10%; Moderate if 10 to 20%; and High if >20% (i.e. based on 20% increase in frequency of toxicity compared to that for reference pore-water samples).

Table 40. Incidence of toxicity to amphipods, midges, and mussels exposed to sediment samples from the Tri-State Mining District.

Area of Interest (AoI)	Incidence of Toxicity (IOT) to Benthic Invertebrates						Overall Toxicity for Amphipod, Midge, or Mussel ²	
	Amphipod (<i>H. azteca</i>) ¹		Midge (<i>C. dilutus</i>) ¹		Mussel (<i>L. siliquoidea</i>) ¹			
	IOT	Number Toxic	IOT	Number Toxic	IOT	Number Toxic	IOT	Number Toxic
Upper/Middle Spring River Sub-basin								
Upper Spring River AoI	0%	0 of 5	40%	2 of 5	0%	0 of 3	40%	2 of 5
North Fork Spring River AoI	0%	0 of 5	0%	0 of 5	0%	0 of 2	0%	0 of 5
Middle Spring River AoI	0%	0 of 7	33%	1 of 3	33%	2 of 6	43%	3 of 7
Cow Creek AoI	0%	0 of 2	100%	2 of 2	0%	0 of 1	100%	2 of 2
Center Creek AoI	36%	4 of 11	44%	4 of 9	40%	4 of 10	64%	7 of 9
Turkey Creek AoI	60%	6 of 10	80%	8 of 10	57%	4 of 7	90%	9 of 10
Shawnee Creek AoI	0%	0 of 2	0%	0 of 2	0%	0 of 2	0%	0 of 2
Short Creek AoI	100%	3 of 3	100%	3 of 3	100%	2 of 2	100%	3 of 3
<i>Sub-basin Subtotal</i>	<i>29%</i>	<i>13 of 45</i>	<i>51%</i>	<i>20 of 39</i>	<i>36%</i>	<i>12 of 33</i>	<i>58%</i>	<i>26 of 45</i>
Lower Spring River Sub-basin								
Empire Lake AoI	0%	0 of 1	0%	0 of 1	ND	ND	0%	0 of 1
Lower Spring River AoI	0%	0 of 2	50%	1 of 2	ND	ND	50%	1 of 2
Shoal Creek AoI	0%	0 of 7	29%	2 of 7	0%	0 of 2	29%	2 of 7
Brush Creek AoI	ND	ND	ND	ND	ND	ND	ND	ND
Willow Creek AoI	0%	0 of 2	50%	1 of 2	0%	0 of 2	50%	1 of 2
Spring Brook AoI	ND	ND	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	100%	1 of 1	100%	1 of 1	100%	1 of 1	100%	1 of 1
Warren Branch AoI	ND	ND	ND	ND	ND	ND	ND	ND
Lost Creek AoI	0%	0 of 3	33%	1 of 3	0%	0 of 2	33%	1 of 3
<i>Sub-basin Subtotal</i>	<i>6%</i>	<i>1 of 16</i>	<i>38%</i>	<i>6 of 16</i>	<i>14%</i>	<i>1 of 7</i>	<i>38%</i>	<i>6 of 16</i>
Neosho River Sub-basin								
Neosho River AoI	25%	1 of 4	25%	1 of 4	0%	0 of 3	25%	1 of 4
Upper Tar Creek AoI	0%	0 of 2	50%	1 of 2	50%	1 of 2	50%	1 of 2
Middle Tar Creek AoI	100%	2 of 2	100%	2 of 2	ND	ND	100%	2 of 2
Lytle Creek AoI	50%	1 of 2	50%	1 of 2	0%	0 of 1	50%	1 of 2

Table 40. Incidence of toxicity to amphipods, midges, and mussels exposed to sediment samples from the Tri-State Mining District.

Area of Interest (AoI)	Incidence of Toxicity (IOT) to Benthic Invertebrates						Overall Toxicity for Amphipod, Midge, or Mussel ²	
	Amphipod (<i>H. azteca</i>) ¹		Midge (<i>C. dilutus</i>) ¹		Mussel (<i>L. siliquoides</i>) ¹		IOT	Number Toxic
	IOT	Number Toxic	IOT	Number Toxic	IOT	Number Toxic		
Neosho River Sub-basin (cont.)								
Lower Tar Creek AoI	75%	3 of 4	75%	3 of 4	100%	2 of 2	100%	4 of 4
Elm Creek AoI	100%	1 of 1	100%	1 of 1	ND	ND	100%	1 of 1
<i>Sub-basin Subtotal</i>	<i>53%</i>	<i>8 of 15</i>	<i>60%</i>	<i>9 of 15</i>	<i>38%</i>	<i>3 of 8</i>	<i>67%</i>	<i>10 of 15</i>
Study Area as a Whole	29%	22 of 76	50%	35 of 70	33%	16 of 48	55%	42 of 76
Reference Sediment Samples	0%	0 of 10	0%	0 of 8	0%	0 of 5	0%	0 of 10

ND = no data; AoI = area of interest; IOT = incidence of toxicity.

¹ Sediment samples were designated as toxic if the sample was designated as toxic based on the survival or biomass endpoints.

² Sediment samples were designated as toxic if the sample was designated as toxic for one or more endpoints (survival or biomass) for any species.

Table 41. Frequency of exceedance of selected toxicity thresholds for evaluating invertebrate-tissue chemistry data from the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ Metal-TUs ¹	Number of Samples with Σ Metal-TUs \geq 6.01 ¹	Number of Samples Predicted to be Toxic ²	Number of Samples/Risk Category ³			Risk to Benthic Community ⁴
					Low	Moderate	High	
Upper/Middle Spring River Sub-basin								
Upper Spring River AoI	13	1.80	0	0 (0%)	13	0	0	Low
North Fork Spring River AoI	16	1.95	0	0 (0%)	16	0	0	Low
Middle Spring River AoI	130	4.34	38	38 (29%)	92	7	31	High
Cow Creek AoI	21	2.49	0	0 (0%)	21	0	0	Low
Center Creek AoI	7	3.49	1	1 (14%)	6	0	1	Moderate
Turkey Creek AoI	6	7.46	5	5 (83%)	1	1	4	High
Shawnee Creek AoI	1	NC	0	0 (0%)	1	0	0	Low
Short Creek AoI	1	NC	1	1 (100%)	0	0	1	High
<i>Sub-basin Subtotal</i>	<i>195</i>	<i>3.67</i>	<i>45</i>	<i>45 (23%)</i>	<i>150</i>	<i>8</i>	<i>37</i>	<i>High</i>
Lower Spring River Sub-basin								
Lower Spring River AoI	11	3.06	1	1 (9%)	10	0	1	Low
Shoal Creek AoI	26	3.96	6	6 (23%)	20	4	2	High
Willow Creek AoI	1	NC	0	0 (0%)	1	0	0	Low
Beaver Creek AoI	1	NC	1	1 (100%)	0	0	1	High
Lost Creek AoI	1	NC	0	0 (0%)	1	0	0	Low
<i>Sub-basin Subtotal</i>	<i>40</i>	<i>3.26</i>	<i>8</i>	<i>8 (20%)</i>	<i>32</i>	<i>4</i>	<i>4</i>	<i>High</i>
Neosho River Sub-basin								
Middle Tar Creek AoI	1	NC	1	1 (100%)	0	0	1	High
Lytle Creek AoI	1	NC	1	1 (100%)	0	0	1	High
Lower Tar Creek AoI	2	13.1	2	2 (100%)	0	0	2	High
<i>Sub-basin Subtotal</i>	<i>4</i>	<i>20.9</i>	<i>4</i>	<i>4 (100%)</i>	<i>0</i>	<i>0</i>	<i>4</i>	<i>High</i>
Study Area as a Whole	239	3.81	57	57 (24%)	182	12	45	High

Table 41. Frequency of exceedance of selected toxicity thresholds for evaluating invertebrate-tissue chemistry data from the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ Metal-TUs ¹	Number of Samples with Σ Metal-TUs \geq 6.01 ¹	Number of Samples Predicted to be Toxic ²	Number of Samples/Risk Category ³			Risk to Benthic Community ⁴
					Low	Moderate	High	
Reference Sediment Samples	2	2.85	0	0 (0%)	2	0	0	Low

Σ Metal-TUs = sum of metal toxic units; Cd = cadmium; Cu = copper; Hg = Mercury; Pb = lead; Zn = zinc; n = sample size; NC = not calculated; TT = toxicity threshold.

¹ Σ Metal-TUs calculated by summing the hazard quotients for Cd, Cu, Pb, Hg, and Zn.

² Tissue samples were designated as having metal concentrations sufficient to adversely affect benthic invertebrates if the selected TT was exceeded: i.e., Σ Metal-TUs \geq 6.01.

³ Risk classification: Low if Σ Metal-TUs <6.01; Moderate if Σ Metal-TUs = 6.01 to 7.45; and High if Σ Metal-TUs >7.45.

⁴ Based on predicted frequency of toxicity: Low if <10%; Moderate if 10 to 20%; and High if >20%.

Table 42. Frequency of exceedance of the site-specific toxicity thresholds for freshwater mussels derived based on the results of field studies conducted in the Tri-State Mining District (Angelo *et al.* 2007).

Area of Interest (AoI)	n	Geometric Mean of ΣPEC-Q _{Cd,Pb,Zn}	Number of Exceedances of TTs ¹	Number of Samples/Risk Category ²			Risk to the Mussel Community ³
				Low	Moderate	High	
Upper/Middle Spring River Sub-basin							
Upper Spring River AoI	18	1.07	16 (89%)	2	13	3	High
North Fork Spring River AoI	27	0.54	12 (44%)	15	12	0	High
Middle Spring River AoI	115	2.29	91 (79%)	24	36	55	High
Cow Creek AoI	34	1.87	34 (100%)	0	28	6	High
Center Creek AoI	81	5.39	80 (99%)	1	34	46	High
Turkey Creek AoI	48	18.1	48 (100%)	0	2	46	High
Shawnee Creek AoI	27	1.37	27 (100%)	0	25	2	High
Short Creek AoI	44	74.2	44 (100%)	0	0	44	High
<i>Sub-basin Subtotal</i>	<i>394</i>	<i>4.30</i>	<i>352 (89%)</i>	<i>42</i>	<i>150</i>	<i>202</i>	<i>High</i>
Lower Spring River Sub-basin							
Empire Lake AoI	41	20.9	41 (100%)	0	0	41	High
Lower Spring River AoI	66	5.04	66 (100%)	0	13	53	High
Shoal Creek AoI	112	5.56	112 (100%)	0	36	76	High
Brush Creek AoI	14	1.47	12 (86%)	2	10	2	High
Willow Creek AoI	30	6.79	30 (100%)	0	5	25	High
Spring Brook AoI	15	27.3	15 (100%)	0	0	15	High
Beaver Creek AoI	65	7.51	65 (100%)	0	10	55	High
Warren Branch AoI	9	1.23	5 (56%)	4	2	3	High
Lost Creek AoI	33	1.49	24 (73%)	9	15	9	High
<i>Sub-basin Subtotal</i>	<i>385</i>	<i>5.87</i>	<i>370 (96%)</i>	<i>15</i>	<i>91</i>	<i>279</i>	<i>High</i>
Neosho River Sub-basin							
Neosho River AoI	117	1.26	83 (71%)	34	62	21	High
Upper Tar Creek AoI	39	3.12	36 (92%)	3	25	11	High
Middle Tar Creek AoI	52	79.9	52 (100%)	0	0	52	High
Lytle Creek AoI	41	62.5	41 (100%)	0	0	41	High
Lower Tar Creek AoI	108	13.6	105 (97%)	3	15	90	High
Elm Creek AoI	26	34.1	25 (96%)	1	0	25	High
<i>Sub-basin Subtotal</i>	<i>383</i>	<i>8.41</i>	<i>342 (89%)</i>	<i>41</i>	<i>102</i>	<i>240</i>	<i>High</i>

Table 42. Frequency of exceedance of the site-specific toxicity thresholds for freshwater mussels derived based on the results of field studies conducted in the Tri-State Mining District (Angelo *et al.* 2007).

Area of Interest (AoI)	n	Geometric Mean of Σ PEC- $Q_{Cd,Pb,Zn}$	Number of Exceedances of TTs ¹	Number of Samples/Risk Category ²			Risk to the Mussel Community ³
				Low	Moderate	High	
<i>Study Area as a Whole</i>	<i>1162</i>	<i>6.09</i>	<i>1064 (92%)</i>	<i>98</i>	<i>343</i>	<i>721</i>	<i>High</i>
Reference Sediment Samples	10	0.46	5 (50%)	5	5	0	High

Σ PEC- $Q_{Cd,Pb,Zn}$ = sum probable effect concentration quotients for cadmium, lead and zinc; TT = toxicity threshold; n = sample size; AoI = area of interest.

¹ A site-specific TT of 0.6 was developed for Σ PEC- $Q_{Cd,Pb,Zn}$ using the data from Angelo *et al.* (2007).

² Risk classification: Low if Σ PEC- $Q_{Cd,Pb,Zn}$ <0.6; Moderate if Σ PEC- $Q_{Cd,Pb,Zn}$ = 0.6 to 3.0; and High if Σ PEC- $Q_{Cd,Pb,Zn}$ >3.0.

³ Based on frequency of exceedance of TT: Low if <10%; Moderate if 10 to 20%; and High if >20%

Table 43. Frequency of exceedance of the site-specific toxicity thresholds for freshwater mussels derived based on results of laboratory toxicity tests with the mussel, *Lampsilis siliquoidea* (Endpoint: Survival) conducted in the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Exceedances of TTs ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
Upper/Middle Spring River Sub-basin							
Upper Spring River AoI	18	1.07	0 (0%)	18	0	0	Low
North Fork Spring River AoI	27	0.543	0 (0%)	27	0	0	Low
Middle Spring River AoI	115	2.29	0 (0%)	115	0	0	Low
Cow Creek AoI	34	1.87	0 (0%)	34	0	0	Low
Center Creek AoI	81	5.39	8 (10%)	73	6	2	Low
Turkey Creek AoI	48	18.1	7 (15%)	41	5	2	Moderate
Shawnee Creek AoI	27	1.37	0 (0%)	27	0	0	Low
Short Creek AoI	44	74.2	31 (70%)	13	7	24	High
<i>Sub-basin Subtotal</i>	<i>394</i>	<i>4.30</i>	<i>46 (12%)</i>	<i>348</i>	<i>18</i>	<i>28</i>	<i>Moderate</i>
Lower Spring River Sub-basin							
Empire Lake AoI	41	20.9	6 (15%)	35	6	0	Moderate
Lower Spring River AoI	66	5.04	0 (0%)	66	0	0	Low
Shoal Creek AoI	112	5.56	0 (0%)	112	0	0	Low
Brush Creek AoI	14	1.47	0 (0%)	14	0	0	Low
Willow Creek AoI	30	6.79	0 (0%)	30	0	0	Low
Spring Brook AoI	15	27.3	7 (47%)	8	5	2	High
Beaver Creek AoI	65	7.51	4 (6%)	61	2	2	Low
Warren Branch AoI	9	1.23	0 (0%)	9	0	0	Low
Lost Creek AoI	33	1.49	1 (3%)	32	1	0	Low
<i>Sub-basin Subtotal</i>	<i>385</i>	<i>5.87</i>	<i>18 (5%)</i>	<i>367</i>	<i>14</i>	<i>4</i>	<i>Low</i>
Neosho River Sub-basin							
Neosho River AoI	117	1.26	1 (1%)	116	1	0	Low
Upper Tar Creek AoI	39	3.12	8 (21%)	31	3	5	High
Middle Tar Creek AoI	52	79.9	39 (75%)	13	5	34	High
Lytle Creek AoI	41	62.5	28 (68%)	13	7	21	High
Lower Tar Creek AoI	108	13.6	19 (18%)	89	15	4	Moderate
Elm Creek AoI	26	34.1	10 (38%)	16	1	9	High
<i>Sub-basin Subtotal</i>	<i>383</i>	<i>8.41</i>	<i>105 (27%)</i>	<i>278</i>	<i>32</i>	<i>73</i>	<i>High</i>

Table 43. Frequency of exceedance of the site-specific toxicity thresholds for freshwater mussels derived based on results of laboratory toxicity tests with the mussel, *Lampsilis siliquoidea* (Endpoint: Survival) conducted in the Tri-State Mining District.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Exceedances of TTs ¹	Number of Samples/Risk Category ²			Risk to Benthic Community ³
				Low	Moderate	High	
<i>Study Area as a Whole</i>	<i>1162</i>	<i>6.09</i>	<i>169 (15%)</i>	<i>993</i>	<i>64</i>	<i>105</i>	<i>Moderate</i>
Reference Sediment Samples	10	0.464	0 (0%)	10	0	0	Low

Σ PEC-Q_{Cd,Pb,Zn} = sum probable effect concentration quotient for cadmium, lead, and zinc; TT = toxicity threshold; n = sample size.

¹ A site-specific TT of 39.7 was developed for Σ PEC-Q_{Cd,Pb,Zn}, using the matching sediment chemistry and toxicity data from the Tri-State Mining District.

² Risk classification: Low if Σ PEC-Q_{Cd,Pb,Zn} ≤ 39.7; Moderate if Σ PEC-Q_{Cd,Pb,Zn} > 39.7 to 72.6; and High if Σ PEC-Q_{Cd,Pb,Zn} > 72.6.

³ Based on frequency of exceedance of TT of 39.7: Low if <10%; Moderate if 10 to 20%; and High if >20%.

Table 44. Survival, weight, and biomass of amphipods (*H. azteca*), midges (*C. dilutus*), and mussels (*L. siliquoidea*) exposed to surface-water samples from the Tri-State Mining District that were classified into reference, low risk, moderate risk, and high risk categories using the selected surface-water toxicity thresholds of 1.03 and 1.41 for $\Sigma TU_{\text{Divalent Metals}}$ (control-adjusted results are reported for each endpoint).

Toxicity Test Organism	Test Duration	Endpoint Measured	Control-Adjusted Survival, Weight, or Biomass			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
<i>H. azteca</i>	28-d	Survival	98.8% ± 6.3% (8)	98.6% ± 10.% (49)	93.1% ± 13.7% (6)	25.1% ± 34.6% (15)
		Weight	115.% ± 49.6% (8)	93.9% ± 28.9% (49)	99.1% ± 16.8% (6)	82.1% ± 72.% (15)
		Biomass	115.9% ± 54.5% (8)	93.8% ± 33.1% (49)	92.4% ± 13.1% (6)	27.7% ± 40.5% (15)
<i>C. dilutus</i>	10-d	Survival	99.2% ± 3.9% (3)	98.8% ± 4.2% (30)	94.9% ± 3.6% (4)	71.7% ± 30.8% (8)
		Weight	79.9% ± 20.4% (3)	88.6% ± 16.2% (30)	95.3% ± 4.9% (4)	64.3% ± 24.7% (8)
		Biomass	79.1% ± 19.8% (3)	87.3% ± 16.% (30)	90.1% ± 2.6% (4)	50.6% ± 30.5% (8)
<i>L. siliquoidea</i>	28-d	Survival	104.7% ± 7.4% (8)	101.4% ± 9.7% (49)	97.7% ± 4.7% (6)	84.2% ± 11.9% (15)
		Weight	99.5% ± 18.% (8)	81.9% ± 25.6% (49)	86.9% ± 13.9% (6)	64.1% ± 29.2% (15)
		Biomass	105.7% ± 21.8% (8)	83.3% ± 25.4% (49)	83.3% ± 12.3% (6)	54.3% ± 25.3% (15)

d = day; n = sample size; divalent metals include Cadmium (Cd), Copper (Cu), Lead (Pb), Nickel (Ni), Silver (As), and Zinc (Zn); TSV = toxicity screening value (see Table 3).

$$^1 \Sigma TU_{\text{Divalent Metals}} < 1.03, \text{ where } \Sigma TU_{\text{Divalent Metals}} = \frac{[\text{Cd}]}{\text{TSV}_{\text{Cd}}} + \frac{[\text{Cu}]}{\text{TSV}_{\text{Cu}}} + \frac{[\text{Pb}]}{\text{TSV}_{\text{Pb}}} + \frac{[\text{Ni}]}{\text{TSV}_{\text{Ni}}} + \frac{[\text{As}]}{\text{TSV}_{\text{As}}} + \frac{[\text{Zn}]}{\text{TSV}_{\text{Zn}}}$$

$$^2 \Sigma TU_{\text{Divalent Metals}} = 1.03 \text{ to } 1.41.$$

$$^3 \Sigma TU_{\text{Divalent Metals}} > 1.41.$$

Note: TSVs for divalent metals were calculated by assuming a water hardness of 100 mg/L.

Table 45. Survival, weight, and biomass of amphipods (*H. azteca*), midges (*C. dilutus*), and mussels (*L. siliquoidea*) exposed to sediment samples from the Tri-State Mining District that were classified into reference, low risk, moderate risk, and high risk categories using the selected sediment toxicity thresholds of 6.47 and 10.04 for Σ PEC-Q_{Cd,Pb,Zn} (control-adjusted results are repeated for each endpoint).

Toxicity Test Organism	Test Duration	Endpoint Measured	Control-Adjusted Survival, Weight, or Biomass			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
<i>H. azteca</i>	28-d	Survival	98.5% ± 5.6% (10)	100.5% ± 5.6% (46)	92.2% ± 13.4% (6)	49.1% ± 42.8% (24)
		Weight	112.8% ± 45.% (10)	97.6% ± 31.4% (46)	94.6% ± 20.0% (6)	86.6% ± 58.3% (24)
		Biomass	112.9% ± 49.3% (10)	99.0% ± 33.7% (46)	87.4% ± 22.0% (6)	49.1% ± 45.7% (24)
<i>C. dilutus</i>	10-d	Survival	104.7% ± 7.4% (8)	100.3% ± 10.2% (41)	104.6% ± 8.3% (6)	90.4% ± 13.0% (23)
		Weight	99.5% ± 18.% (8)	85.2% ± 25.4% (41)	64.1% ± 26.8% (6)	70.4% ± 25.5% (23)
		Biomass	105.7% ± 21.8% (8)	85.9% ± 26.0% (41)	65.6% ± 19.8% (6)	64.5% ± 25.2% (23)
<i>L. siliquoidea</i>	28-d	Survival	100.7% ± 3.9% (5)	97.8% ± 9.4% (28)	98.1% ± 4.4% (4)	83.9% ± 24.7% (16)
		Weight	82.6% ± 18.6% (5)	94.1% ± 21.8% (28)	93.0% ± 13.2% (4)	76.7% ± 23.6% (16)
		Biomass	83.4% ± 20.5% (5)	91.2% ± 19.1% (28)	91.5% ± 14.3% (4)	68.1% ± 29.1% (16)
			Average Number of Taxa ⁴			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
Mussels	NA	Number of Live Mussel Taxa	ND (0)	8.17 ± 6.12 (12)	3.75 ± 4.35 (4)	ND (0)
	NA	Number of Live Mussel Taxa	ND (0)	8.17 ± 6.12 (12)	3.75 ± 4.35 (4)	ND (0)
	NA	Classified as Threatened, Endangered, or of Special Concern	ND (0)	3.25 ± 3.52 (12)	0.25 ± 0.5 (4)	ND (0)
NA	Total Number of Mussel Taxa	ND (0)	11.3 ± 7.94 (12)	5.75 ± 6.13 (4)	ND (0)	

Σ PEC-Q_{Cd,Pb,Zn} = sum probable effect concentration quotient for cadmium, lead, and zinc; d = day; n = sample size; ND = no data or limited data.

¹ Σ PEC-Q_{Cd,Pb,Zn} < 6.47

² Σ PEC-Q_{Cd,Pb,Zn} = 6.47 to 10.04

³ Σ PEC-Q_{Cd,Pb,Zn} > 10.04

⁴ Includes data for sampling sites that had matching mussel taxa abundance and sediment chemistry data only.

Table 46. Survival, weight, and biomass of amphipods (*H. azteca*), midges (*C. dilutus*), and mussels (*L. siliquoidea*) exposed to pore-water samples from the Tri-State Mining District that were classified into reference, low risk, moderate risk, and high risk categories using the selected pore-water toxicity thresholds of 0.581 and 0.867 for PW-TU_{Zn} (control-adjusted results are repeated for each endpoint).

Toxicity Test Organism	Test Duration	Endpoint Measured	Control-Adjusted Survival, Weight, or Biomass			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
<i>H. azteca</i>	28-d	Survival	98.8% ± 6.3% (8)	98.8% ± 9.7% (52)	80.6% ± 15.8% (2)	29.4% ± 37.8% (16)
		Weight	115.% ± 49.6% (8)	93.8% ± 28.1% (52)	131.7% ± 33.1% (2)	80.4% ± 67.8% (16)
		Biomass	115.9% ± 54.5% (8)	93.8% ± 32.2% (52)	110.8% ± 48.3% (2)	29.1% ± 35.7% (16)
<i>C. dilutus</i>	10-d	Survival	104.7% ± 7.4% (8)	101.2% ± 9.5% (52)	93.4% ± 13.% (2)	85.6% ± 12.1% (16)
		Weight	99.5% ± 18.% (8)	81.8% ± 24.9% (52)	111.7% ± 28.% (2)	63.7% ± 25.4% (16)
		Biomass	105.7% ± 21.8% (8)	83.% ± 24.8% (52)	97.5% ± 5.3% (2)	55.4% ± 24.6% (16)
<i>L. siliquoidea</i>	28-d	Survival	99.2% ± 3.9% (3)	98.8% ± 4.1% (31)	94.9% (1)	75.9% ± 28.5% (10)
		Weight	79.9% ± 20.4% (3)	88.6% ± 15.9% (31)	98.9% (1)	70.8% ± 25.8% (10)
		Biomass	79.1% ± 19.8% (3)	87.4% ± 15.7% (31)	93.9% (1)	58.4% ± 31.5% (10)

PW-TU_{Zn} = pore-water toxic unit for zinc; d = day; n = sample size.

¹ PW-TU_{Zn} < 0.581

² PW-TU_{Zn} = 0.581 to 0.867

³ PW-TU_{Zn} > 0.867

Table 47. Survival, weight, and biomass of amphipods (*H. azteca*), midges (*C. dilutus*), and mussels (*L. siliquoidea*) exposed to sediment samples from the Tri-State Mining District that were classified into reference, low risk, moderate risk, and high risk categories using the selected toxicity thresholds for invertebrate tissues (i.e., Σ Metal-TUs of 6.01 and 7.45; i.e., using oligochaete-tissue residue data from the 28-d bioaccumulation tests).

Toxicity Test Organism	Test Duration	Endpoint Measured	Control-Adjusted Survival, Weight, or Biomass			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
<i>H. azteca</i>	28-d	Survival	107% ± 5.9% (2)	101.4% ± 7.2% (9)	89.7% (1)	55.8% ± 42.4% (11)
		Weight	170% ± 47.6% (2)	98.2% ± 46.4% (9)	66.1% (1)	79.2% ± 42.1% (11)
		Biomass	182% ± 39.7% (2)	101.7% ± 51.3% (9)	59.9% (1)	52.5% ± 40.4% (11)
<i>C. dilutus</i>	10-d	Survival	101% ± 1.8% (2)	102.4% ± 6.5% (9)	117% (1)	95.0% ± 8.8% (11)
		Weight	112% ± 1.1% (2)	85.1% ± 25.1% (9)	39.8% (1)	68.1% ± 26.1% (11)
		Biomass	112% ± 5.5% (2)	86.9% ± 22.7% (9)	49.2% (1)	65.0% ± 26.1% (11)
<i>L. siliquoidea</i>	28-d	Survival	101% ± 1.8% (2)	99.7% ± 2.5% (8)	97.5% (1)	86.2% ± 20.7% (8)
		Weight	81.4% ± 27.2% (2)	85.2% ± 13.6% (8)	90.0% (1)	74.3% ± 22.1% (8)
		Biomass	81.9% ± 27.2% (2)	84.5% ± 12.1% (8)	87.9% (1)	67.5% ± 28.2% (8)
			Average Number of Taxa ⁴			
			Reference Samples (n)	Low Risk Samples (n) ¹	Moderate Risk Samples (n) ²	High Risk Samples (n) ³
Mussels	NA	Number of Live Mussel Taxa	ND (0)	7.64 ± 6.31 (11)	6.0 (1)	10.5 ± 4.95 (2)
	NA	Number of Live Mussel Taxa	ND (0)	7.64 ± 6.31 (11)	6.0 (1)	10.5 ± 4.95 (2)
	NA	Classified as Threatened, Endangered, or of Special Concern	ND (0)	2.64 ± 3.59 (11)	3.0 (1)	3.5 ± 4.95 (2)
	NA	Number of Total Mussel Taxa	ND (0)	11.18 ± 8.33 (11)	7.0 (1)	13.0 ± 4.24 (2)

Σ Metal-TUs = sum of metal toxic units for cadmium, copper, mercury, lead, and zinc; d = day; n = sample size; ND = no data; HQ = hazard quotient; NA = not applicable.

Σ Metal-TUs calculated by summing the HQs for Cd, Cu, Pb, Hg, and Zn.

Σ Metal-TUs based on concentrations of metals in tissues were calculated on a wet weight basis. Concentrations of metals in tissues that were reported in dry weight were converted to a wet weight equivalent for the Σ Metal-TUs calculation by dividing the dry weight concentration by 0.2.

¹ Σ Metal-TUs < 6.01

² Σ Metal-TUs = 6.01 to 7.45

³ Σ Metal-TUs > 7.45

⁴ Includes data for sampling sites that had matching mussel taxa abundance and tissue chemistry data only

Table 48. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted survival of the amphipod, *Hyalella azteca*, in 28-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of ΣPEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control- Adjusted Survival (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
Upper/Middle Spring River Sub-basin								
Upper Spring River AoI	5	1.28	0 (0%)	99.0	5	0	0	Low
North Fork Spring River AoI	5	0.312	0 (0%)	95.4	5	0	0	Low
Middle Spring River AoI	7	0.764	0 (0%)	101.3	7	0	0	Low
Cow Creek AoI	2	1.71	0 (0%)	101.3	2	0	0	Low
Center Creek AoI	11	8.16	4 (36%)	75.1	7	0	4	High
Turkey Creek AoI	10	13.9	6 (60%)	68.6	4	2	4	High
Shawnee Creek AoI	2	0.848	0 (0%)	98.7	2	0	0	Low
Short Creek AoI	3	39.8	3 (100%)	2.6	0	0	3	High
<i>Sub-basin Subtotal</i>	<i>45</i>	<i>3.38</i>	<i>13 (29%)</i>	<i>80.0</i>	<i>32</i>	<i>2</i>	<i>11</i>	<i>High</i>
Lower Spring River Sub-basin								
Empire Lake AoI	1	NC	0 (0%)	94.4	1	0	0	Low
Lower Spring River AoI	2	3.09	0 (0%)	109.7	2	0	0	Low
Shoal Creek AoI	7	2.85	0 (0%)	100.1	7	0	0	Low
Brush Creek AoI	0	ND	ND	ND	ND	ND	ND	ND
Willow Creek AoI	2	3.48	0 (0%)	100.0	2	0	0	Low
Spring Brook AoI	0	ND	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	1	NC	1 (100%)	83.3	0	1	0	Moderate
Warren Branch AoI	0	ND	ND	ND	ND	ND	ND	ND
Lost Creek AoI	3	2.07	0 (0%)	105.4	3	0	0	Low
<i>Sub-basin Subtotal</i>	<i>16</i>	<i>3.10</i>	<i>1 (6%)</i>	<i>101</i>	<i>15</i>	<i>1</i>	<i>0</i>	<i>Low</i>
Neosho River Sub-basin								
Neosho River AoI	4	0.701	1 (25%)	101.4	3	1	0	Low
Upper Tar Creek AoI	2	1.17	0 (0%)	104.1	2	0	0	Low
Middle Tar Creek AoI	2	14.5	2 (100%)	27.1	0	0	2	High
Lytle Creek AoI	2	36.6	1 (50%)	50.0	1	0	1	High
Lower Tar Creek AoI	4	15.4	3 (75%)	75.3	1	2	1	High
Elm Creek AoI	1	NC	1 (100%)	71.8	0	0	1	High
<i>Sub-basin Subtotal</i>	<i>15</i>	<i>5.17</i>	<i>8 (53%)</i>	<i>76.0</i>	<i>7</i>	<i>3</i>	<i>5</i>	<i>High</i>

Table 48. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted survival of the amphipod, *Hyalella azteca*, in 28-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Survival (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
<i>Study Area as a Whole</i>	76	3.61	22(29%)	83.6	54	6	16	Moderate
Reference Sediment Samples	10	0.464	0 (0%)	98.5	10	0	0	Low

Σ PEC-Q_{Cd,Pb,Zn} = sum probable effect concentration quotient based on cadmium, lead, and zinc; d = day; n = sample size, SE = simultaneously extracted; ND = no data; NC = not calculated.

Where only SE-Cd, SE-Pb, and SE-Zn data available, these concentrations were used in calculation of the Σ PEC-Q_{Cd,Pb,Zn} as if equivalent to total Cd, total Pb, and total Zn concentrations.

¹ Sediment samples were designated as toxic if control-adjusted survival was <92.3%

² Risk classification: Low if survival \geq 92.3%; Moderate if survival 83.1 to 92.3%; and High if survival <83.1%

³ Based on average control-adjusted response: Low if \geq 92.3% survival; Moderate if 83.1 to 92.3% survival; and High if <83.1% survival.

Table 49. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted biomass of the amphipod, *Hyaella azteca*, in 28-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Biomass (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
Upper/Middle Spring River Sub-basin								
Upper Spring River AoI	5	1.28	0 (0%)	95.0	5	0	0	Low
North Fork Spring River AoI	5	0.312	0 (0%)	86.3	5	0	0	Low
Middle Spring River AoI	7	0.764	0 (0%)	111.5	7	0	0	Low
Cow Creek AoI	2	1.71	0 (0%)	75.3	2	0	0	Low
Center Creek AoI	11	8.16	3 (27%)	92.5	8	0	3	Low
Turkey Creek AoI	10	13.9	5 (50%)	57.0	5	2	3	Moderate
Shawnee Creek AoI	2	0.848	0 (0%)	73.7	2	0	0	Low
Short Creek AoI	3	39.8	3 (100%)	2.2	0	0	3	High
<i>Sub-basin Subtotal</i>	<i>45</i>	<i>3.38</i>	<i>11 (24%)</i>	<i>79.5</i>	<i>34</i>	<i>2</i>	<i>9</i>	<i>Low</i>
Lower Spring River Sub-basin								
Empire Lake AoI	1	NC	0 (0%)	88.1	1	0	0	Low
Lower Spring River AoI	2	3.09	0 (0%)	131.3	2	0	0	Low
Shoal Creek AoI	7	2.85	0 (0%)	107.1	7	0	0	Low
Brush Creek AoI	0	ND	ND	ND	ND	ND	ND	ND
Willow Creek AoI	2	3.48	0 (0%)	75.0	2	0	0	Low
Spring Brook AoI	0	ND	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	1	NC	0 (0%)	106.0	1	0	0	Low
Warren Branch AoI	0	ND	ND	ND	ND	ND	ND	ND
Lost Creek AoI	3	2.07	0 (0%)	82.8	3	0	0	Low
<i>Sub-basin Subtotal</i>	<i>16</i>	<i>3.10</i>	<i>0 (0%)</i>	<i>100.3</i>	<i>16</i>	<i>0</i>	<i>0</i>	<i>Low</i>
Neosho River Sub-basin								
Neosho River AoI	4	0.701	0 (0%)	91.3	4	0	0	Low
Upper Tar Creek AoI	2	1.17	0 (0%)	66.8	2	0	0	Low
Middle Tar Creek AoI	2	14.5	2 (100%)	26.6	0	0	2	High
Lytle Creek AoI	2	36.6	1 (50%)	41.9	1	0	1	High
Lower Tar Creek AoI	4	15.4	1 (25%)	92.8	3	0	1	Low
Elm Creek AoI	1	NC	0 (0%)	66.2	1	0	0	Low
<i>Sub-basin Subtotal</i>	<i>15</i>	<i>5.17</i>	<i>4 (27%)</i>	<i>71.5</i>	<i>11</i>	<i>0</i>	<i>4</i>	<i>Low</i>

Table 49. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted biomass of the amphipod, *Hyaella azteca*, in 28-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Biomass (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
<i>Study Area as a Whole</i>	76	3.61	15(20%)	82.3	61	2	13	Low
Reference Sediment Samples	10	0.464	0 (0%)	112.9	10	0	0	Low

Σ PEC-Q_{Cd,Pb,Zn} = sum probable effect concentration quotient based on cadmium, lead, and zinc; d = day; n = sample size, SE = simultaneously extracted; ND = no data; NC = not calculated.

Where only SE-Cd, SE-Pb, and SE-Zn data available, these concentrations were used in calculation of the Σ PEC-Q_{Cd,Pb,Zn} as if equivalent to total Cd, total Pb, and total Zn concentrations.

¹ Sediment samples were designated as toxic if control-adjusted biomass was <60.0%

² Risk classification: Low if biomass \geq 60.0%; Moderate if biomass 54.0 to 60.0%; and High if biomass <54%

³ Based on average control-adjusted response: Low if \geq 60.0% biomass; Moderate if 54 to 60.0% biomass; and High if <54% biomass.

Table 50. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted survival of the midge, *Chironomus dilutus*, in 10-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of ΣPEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Survival (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
Upper/Middle Spring River Sub-basin								
Upper Spring River AoI	5	1.28	0 (0%)	112.2	5	0	0	Low
North Fork Spring River AoI	5	0.31	0 (0%)	109.8	5	0	0	Low
Middle Spring River AoI	3	1.36	0 (0%)	99.1	3	0	0	Low
Cow Creek AoI	2	1.71	0 (0%)	111.0	2	0	0	Low
Center Creek AoI	9	9.38	3(33%)	94.1	6	1	2	Moderate
Turkey Creek AoI	10	13.9	4 (40%)	98.1	6	4	0	Low
Shawnee Creek AoI	2	0.85	0 (0%)	105.0	2	0	0	Low
Short Creek AoI	3	39.8	3 (100%)	80.0	0	1	2	High
<i>Sub-basin Subtotal</i>	<i>39</i>	<i>4.06</i>	<i>10 (26%)</i>	<i>100.2</i>	<i>29</i>	<i>6</i>	<i>4</i>	<i>Low</i>
Lower Spring River Sub-basin								
Empire Lake AoI	1	NC	0 (0%)	100.0	1	0	0	Low
Lower Spring River AoI	2	3.09	1 (50%)	92.1	1	1	0	Moderate
Shoal Creek AoI	7	2.85	1 (14%)	98.1	6	1	0	Low
Brush Creek AoI	0	ND	ND	ND	ND	ND	ND	ND
Willow Creek AoI	2	3.48	0 (0%)	101.0	2	0	0	Low
Spring Brook AoI	0	ND	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	1	NC	1 (100%)	92.1	0	1	0	Moderate
Warren Branch AoI	0	ND	ND	ND	ND	ND	ND	ND
Lost Creek AoI	3	2.07	1 (33%)	90.2	2	0	1	Moderate
<i>Sub-basin Subtotal</i>	<i>16</i>	<i>3.10</i>	<i>4 (25%)</i>	<i>96.0</i>	<i>12</i>	<i>3</i>	<i>1</i>	<i>Low</i>
Neosho River Sub-basin								
Neosho River AoI	4	0.701	1 (25%)	92.1	3	0	1	Moderate
Upper Tar Creek AoI	2	1.17	1 (50%)	91.4	1	0	1	Moderate
Middle Tar Creek AoI	2	14.5	1 (50%)	80.2	1	0	1	High
Lytle Creek AoI	2	36.6	1 (50%)	96.2	1	1	0	Low
Lower Tar Creek AoI	4	15.4	2 (50%)	91.3	2	0	2	Moderate
Elm Creek AoI	1	NC	0 (0%)	105.0	1	0	0	Low
<i>Sub-basin Subtotal</i>	<i>15</i>	<i>5.17</i>	<i>6 (40%)</i>	<i>91.6</i>	<i>9</i>	<i>1</i>	<i>5</i>	<i>Moderate</i>

Table 50. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted survival of the midge, *Chironomus dilutus*, in 10-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Survival (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
<i>Study Area as a Whole</i>	70	4.02	20 (29%)	97.4	50	10	10	Low
Reference Sediment Samples	8	0.560	0 (0%)	104.7	8	0	0	Low

Σ PEC-Q_{Cd,Pb,Zn} = sum probable effect concentration quotient based on cadmium, lead, and zinc; d = day; n = sample size, SE = simultaneously extracted; ND = no data; NC = not calculated.

Where only SE-Cd, SE-Pb, and SE-Zn data available, these concentrations were used in calculation of the Σ PEC-Q_{Cd,Pb,Zn} as if equivalent to total Cd, total Pb, and total Zn concentrations.

¹ Sediment samples were designated as toxic if control-adjusted survival was <94.7%

² Risk classification: Low if survival \geq 94.7%; Moderate if survival 85.2 to 94.7%; and High if survival <85.2%

³ Based on average control-adjusted response: Low if \geq 94.7% survival; Moderate if 85.2 to 94.7% survival; and High if <85.2% survival.

Table 51. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted biomass of the midge, *Chironomus dilutus*, in 10-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of ΣPEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Biomass (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
Upper/Middle Spring River Sub-basin								
Upper Spring River AoI	5	1.28	2 (40%)	81.4	3	0	2	Low
North Fork Spring River AoI	5	0.312	0 (0%)	107.2	5	0	0	Low
Middle Spring River AoI	3	1.36	1 (33%)	81.9	2	0	1	Low
Cow Creek AoI	2	1.71	2 (100%)	40.8	0	0	2	High
Center Creek AoI	9	9.38	4 (44%)	77.8	5	2	2	Low
Turkey Creek AoI	10	13.9	6 (60%)	69.1	4	1	5	Moderate
Shawnee Creek AoI	2	0.848	0 (0%)	96.5	2	0	0	Low
Short Creek AoI	3	39.8	3 (100%)	39.4	0	1	2	High
<i>Sub-basin Subtotal</i>	<i>39</i>	<i>4.06</i>	<i>18 (46%)</i>	<i>76.2</i>	<i>21</i>	<i>4</i>	<i>14</i>	<i>Low</i>
Lower Spring River Sub-basin								
Empire Lake AoI	1	NC	0 (0%)	100.6	1	0	0	Low
Lower Spring River AoI	2	3.09	1 (50%)	79.6	1	0	1	Low
Shoal Creek AoI	7	2.85	2 (29%)	90.9	5	1	1	Low
Brush Creek AoI	0	ND	ND	ND	ND	ND	ND	ND
Willow Creek AoI	2	3.48	1 (50%)	84.7	1	0	1	Low
Spring Brook AoI	0	ND	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	1	NC	0 (0%)	96.5	1	0	0	Low
Warren Branch AoI	0	ND	ND	ND	ND	ND	ND	ND
Lost Creek AoI	3	2.07	1 (33%)	75.2	2	0	1	Low
<i>Sub-basin Subtotal</i>	<i>16</i>	<i>3.10</i>	<i>5 (31%)</i>	<i>86.7</i>	<i>11</i>	<i>1</i>	<i>4</i>	<i>Low</i>
Neosho River Sub-basin								
Neosho River AoI	4	0.701	0 (0%)	69.3	3	0	1	Moderate
Upper Tar Creek AoI	2	1.17	0 (0%)	89.7	2	0	0	Low
Middle Tar Creek AoI	2	14.5	2 (100%)	48.8	0	1	1	High
Lytle Creek AoI	2	36.6	1 (50%)	73.0	1	0	1	Moderate
Lower Tar Creek AoI	4	15.4	2 (50%)	69.2	2	1	1	Moderate
Elm Creek AoI	1	NC	1 (100%)	62.6	0	0	1	High
<i>Sub-basin Subtotal</i>	<i>15</i>	<i>5.17</i>	<i>7 (47%)</i>	<i>69.3</i>	<i>8</i>	<i>2</i>	<i>5</i>	<i>Moderate</i>

Table 51. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted biomass of the midge, *Chironomus dilutus*, in 10-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Biomass (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
<i>Study Area as a Whole</i>	70	4.02	30(43%)	77.1	40	7	23	Low
Reference Sediment Samples	8	0.560	0 (0%)	105.7	8	0	0	Low

Σ PEC-Q_{Cd,Pb,Zn} = sum probable effect concentration quotient based on cadmium, lead, and zinc; d = day; n = sample size, SE = simultaneously extracted; ND = no data; NC = not calculated.

Where only SE-Cd, SE-Pb, and SE-Zn data available, these concentrations were used in calculation of the Σ PEC-Q_{Cd,Pb,Zn} as if equivalent to total Cd, total Pb, and total Zn concentrations.

¹ Sediment samples were designated as toxic if control-adjusted biomass was <73.8%

² Risk classification: Low if biomass \geq 73.8%; Moderate if biomass 66.4 to 73.8%; and High if biomass <66.4%

³ Based on average control-adjusted response: Low if \geq 73.8% biomass; Moderate if 66.4 to 73.8% biomass; and High if <66.4% biomass.

Table 52. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted survival of the mussel, *Lampsilis siliquoidea*, in 28-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of ΣPEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Survival (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
Upper/Middle Spring River Sub-basin								
Upper Spring River AoI	3	0.900	0 (0%)	96.7	3	0	0	Low
North Fork Spring River AoI	2	0.294	0 (0%)	97.5	2	0	0	Low
Middle Spring River AoI	6	0.828	2 (33%)	93.8	4	1	1	Moderate
Cow Creek AoI	1	NC	0 (0%)	100.0	1	0	0	Low
Center Creek AoI	10	7.87	4 (40%)	96.4	6	3	1	Low
Turkey Creek AoI	7	18.8	4 (57%)	92.8	3	3	1	Moderate
Shawnee Creek AoI	2	0.848	0 (0%)	96.3	2	0	0	Low
Short Creek AoI	2	51.2	2 (100%)	23.8	0	0	2	High
<i>Sub-basin Subtotal</i>	<i>33</i>	<i>3.96</i>	<i>12 (36%)</i>	<i>90.9</i>	<i>21</i>	<i>7</i>	<i>5</i>	<i>Moderate</i>
Lower Spring River Sub-basin								
Empire Lake AoI	0	ND	ND	ND	ND	ND	ND	ND
Lower Spring River AoI	0	ND	ND	ND	ND	ND	ND	ND
Shoal Creek AoI	2	2.53	0 (0%)	100.0	2	0	0	Low
Brush Creek AoI	0	ND	ND	ND	ND	ND	ND	ND
Willow Creek AoI	2	3.48	0 (0%)	101.3	2	0	0	Low
Spring Brook AoI	0	ND	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	1	NC	1 (100%)	92.3	0	1	0	Moderate
Warren Branch AoI	0	ND	ND	ND	ND	ND	ND	ND
Lost Creek AoI	2	4.05	0 (0%)	101.3	2	0	0	Low
<i>Sub-basin Subtotal</i>	<i>7</i>	<i>3.73</i>	<i>1 (14%)</i>	<i>99.6</i>	<i>6</i>	<i>1</i>	<i>0</i>	<i>Low</i>
Neosho River Sub-basin								
Neosho River AoI	3	0.770	0 (0%)	101.7	3	0	0	Low
Upper Tar Creek AoI	2	1.17	1 (50%)	90.0	1	0	1	Moderate
Middle Tar Creek AoI	0	ND	ND	ND	ND	ND	ND	ND
Lytle Creek AoI	1	NC	0 (0%)	102.6	1	0	0	Low
Lower Tar Creek AoI	2	17.5	2 (100%)	93.6	0	2	0	Moderate
Elm Creek AoI	0	ND	ND	ND	ND	ND	ND	ND
<i>Sub-basin Subtotal</i>	<i>8</i>	<i>3.15</i>	<i>3 (38%)</i>	<i>96.9</i>	<i>5</i>	<i>2</i>	<i>1</i>	<i>Low</i>

Table 52. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted survival of the mussel, *Lampsilis siliquoidea*, in 28-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Survival (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
<i>Study Area as a Whole</i>	48	3.78	16 (33%)	93.2	32	10	6	Moderate
Reference Sediment Samples	5	0.528	0 (0%)	100.7	5	0	0	Low

Σ PEC-Q_{Cd,Pb,Zn} = sum probable effect concentration quotient based on cadmium, lead, and zinc; d = day; n = sample size, SE = simultaneously extracted; ND = no data; NC = not calculated.

Where only SE-Cd, SE-Pb, and SE-Zn data available, these concentrations were used in calculation of the Σ PEC-Q_{Cd,Pb,Zn} as if equivalent to total Cd, total Pb, and total Zn concentrations.

¹ Sediment samples were designated as toxic if control-adjusted survival was <95.0%

² Risk classification: Low if survival \geq 95.0%; Moderate if survival 85.5 to 95.0%; and High if survival <85.5%

³ Based on average control-adjusted response: Low if \geq 95.0% survival; Moderate if 85.5 to 95.0% survival; and High if <85.5% survival.

Table 53. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted biomass of the mussel, *Lampsilis siliquoidea*, in 28-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of ΣPEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Biomass (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
Upper/Middle Spring River Sub-basin								
Upper Spring River AoI	3	0.900	0 (0%)	73.8	3	0	0	Low
North Fork Spring River AoI	2	0.294	0 (0%)	82.8	2	0	0	Low
Middle Spring River AoI	6	0.828	0 (0%)	99.8	6	0	0	Low
Cow Creek AoI	1	NC	0 (0%)	87.2	1	0	0	Low
Center Creek AoI	10	7.87	2 (20%)	82.9	8	0	2	Low
Turkey Creek AoI	7	18.81	1 (14%)	82.2	6	0	1	Low
Shawnee Creek AoI	2	0.848	0 (0%)	108.4	2	0	0	Low
Short Creek AoI	2	51.24	2 (100%)	8.6	0	0	2	High
<i>Sub-basin Subtotal</i>	<i>33</i>	<i>3.96</i>	<i>5 (15%)</i>	<i>82.2</i>	<i>28</i>	<i>0</i>	<i>5</i>	<i>Low</i>
Lower Spring River Sub-basin								
Empire Lake AoI	0	ND	ND	ND	ND	ND	ND	ND
Lower Spring River AoI	0	ND	ND	ND	ND	ND	ND	ND
Shoal Creek AoI	2	2.53	0 (0%)	108.4	2	0	0	Low
Brush Creek AoI	0	ND	ND	ND	ND	ND	ND	ND
Willow Creek AoI	2	3.48	0 (0%)	83.6	2	0	0	Low
Spring Brook AoI	0	ND	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	1	NC	0 (0%)	88.9	1	0	0	Low
Warren Branch AoI	0	ND	ND	ND	ND	ND	ND	ND
Lost Creek AoI	2	4.05	0 (0%)	90.1	2	0	0	Low
<i>Sub-basin Subtotal</i>	<i>7</i>	<i>3.73</i>	<i>0 (0%)</i>	<i>93.3</i>	<i>7</i>	<i>0</i>	<i>0</i>	<i>Low</i>
Neosho River Sub-basin								
Neosho River AoI	3	0.770	0 (0%)	84.7	3	0	0	Low
Upper Tar Creek AoI	2	1.17	0 (0%)	83.5	2	0	0	Low
Middle Tar Creek AoI	0	ND	ND	ND	ND	ND	ND	ND
Lytle Creek AoI	1	NC	0 (0%)	92.0	1	0	0	Low
Lower Tar Creek AoI	2	17.49	1 (50%)	66.2	1	1	0	Low
Elm Creek AoI	0	ND	ND	ND	ND	ND	ND	ND
<i>Sub-basin Subtotal</i>	<i>8</i>	<i>3.15</i>	<i>1 (13%)</i>	<i>80.7</i>	<i>7</i>	<i>1</i>	<i>0</i>	<i>Low</i>

Table 53. Frequency of toxicity to benthic invertebrates exposed to sediment samples from the Tri-State Mining District, based on control-adjusted biomass of the mussel, *Lampsilis siliquoidea*, in 28-d toxicity tests.

Area of Interest (AoI)	n	Geometric Mean of Σ PEC-Q _{Cd,Pb,Zn}	Number of Toxic Samples ¹	Average Control-Adjusted Biomass (%)	Number of Samples/Risk Category ²			Risk to Benthic Community ³
					Low	Moderate	High	
<i>Study Area as a Whole</i>	48	3.78	6 (12.5%)	83.5	42	1	5	Low
Reference Sediment Samples	5	0.528	0(0%)	83.4	5	0	0	Low

Σ PEC-Q_{Cd,Pb,Zn} = sum probable effect concentration quotient based on cadmium, lead, and zinc; d = day; n = sample size, SE = simultaneously extracted; ND = no data; NC = not calculated.

Where only SE-Cd, SE-Pb, and SE-Zn data available, these concentrations were used in calculation of the Σ PEC-Q_{Cd,Pb,Zn} as if equivalent to total Cd, total Pb, and total Zn concentrations.

¹ Sediment samples were designated as toxic if control-adjusted biomass was <62.7%

² Risk classification: Low if biomass \geq 62.7%; Moderate if biomass 56.4 to 62.7%; and High if biomass <56.4%

³ Based on average control-adjusted response: Low if \geq 62.7% biomass; Moderate if 56.4 to 62.7% biomass; and High if <56.4% biomass.

Table 54. Evaluation of risks to benthic invertebrates exposed to chemicals of potential concern in the Tri-State Mining District, based on multiple lines-of-evidence.

Area of Interest (AoI)	Chemistry							Sediment Toxicity						
	Sediment		Pore-Water		Invertebrate-Tissue		Surface Water		Amphipod		Mussel		Midge	
	n	Number Predicted Toxic	n	Number Predicted Toxic	n	Number Predicted Toxic	n	Number of Exceedences	n	Observed Toxicity	n	Observed Toxicity	n	Observed Toxicity
Upper/Middle Spring River Sub-basin														
Upper Spring River AoI	18	1 (6%)	5	0 (0%)	13	0 (0%)	5	0 (0%)	5	0%	3	0%	5	40%
North Fork Spring River AoI	27	0 (0%)	7	1 (14%)	16	0 (0%)	8	0 (0%)	5	0%	2	0%	5	0%
Middle Spring River AoI	115	27 (23%)	6	1 (17%)	130	38 (29%)	20	9 (45%)	7	0%	6	33%	3	33%
Cow Creek AoI	34	5 (15%)	5	1 (20%)	21	0 (0%)	5	1 (20%)	2	0%	1	0%	2	100%
Center Creek AoI	81	37 (46%)	13	8 (62%)	7	1 (14%)	36	14 (39%)	11	36%	10	40%	9	44%
Turkey Creek AoI	48	40 (83%)	12	6 (50%)	6	5 (83%)	19	16 (84%)	10	60%	7	57%	10	80%
Shawnee Creek AoI	27	2 (7%)	2	0 (0%)	1	0 (0%)	7	2 (29%)	2	0%	2	0%	2	0%
Short Creek AoI	44	44 (100%)	3	3 (100%)	1	1 (100%)	6	6 (100%)	3	100%	2	100%	3	100%
<i>Sub-basin Subtotal</i>	<i>394</i>	<i>156 (40%)</i>	<i>53</i>	<i>20 (38%)</i>	<i>195</i>	<i>45 (23%)</i>	<i>106</i>	<i>48 (45%)</i>	<i>45</i>	<i>29%</i>	<i>33</i>	<i>36%</i>	<i>39</i>	<i>51%</i>
Lower Spring River Sub-basin														
Empire Lake AoI	41	38 (93%)	1	0 (0%)	ND	ND	2	1 (50%)	1	0%	ND	ND	1	0%
Lower Spring River AoI	66	32 (48%)	4	1 (25%)	11	1 (9%)	32	3 (9%)	2	0%	ND	ND	2	50%
Shoal Creek AoI	112	55 (49%)	11	1 (9%)	26	6 (23%)	50	8 (16%)	7	0%	2	0%	7	29%
Brush Creek AoI	14	2 (14%)	ND	ND	ND	ND	1	1 (100%)	ND	ND	ND	ND	ND	ND
Willow Creek AoI	30	14 (47%)	2	0 (0%)	1	0 (0%)	5	5 (100%)	2	0%	2	0%	2	50%
Spring Brook AoI	15	14 (93%)	ND	ND	ND	ND	3	3 (100%)	ND	ND	ND	ND	ND	ND
Beaver Creek AoI	65	33 (51%)	1	1 (100%)	1	1 (100%)	87	39 (45%)	1	100%	1	100%	1	100%
Warren Branch AoI	9	0 (0%)	ND	ND	ND	ND	5	0 (0%)	ND	ND	ND	ND	ND	ND
Lost Creek AoI	33	4 (12%)	4	0 (0%)	1	0 (0%)	23	1 (4%)	3	0%	2	0%	3	33%
<i>Sub-basin Subtotal</i>	<i>385</i>	<i>192 (50%)</i>	<i>23</i>	<i>3 (14%)</i>	<i>40</i>	<i>8 (20%)</i>	<i>208</i>	<i>61 (29%)</i>	<i>16</i>	<i>6%</i>	<i>7</i>	<i>14%</i>	<i>16</i>	<i>38%</i>
Neosho River Sub-basin														
Neosho River AoI	117	9 (8%)	6	0 (0%)	ND	ND	37	3 (8%)	4	25%	3	0%	4	25%
Upper Tar Creek AoI	39	8 (21%)	3	0 (0%)	ND	ND	3	3 (100%)	2	0%	2	50%	2	50%
Middle Tar Creek AoI	52	52 (100%)	2	1 (50%)	1	1 (100%)	53	44 (83%)	2	100%	ND	ND	2	100%
Lytle Creek AoI	41	39 (95%)	2	1 (50%)	1	1 (100%)	4	4 (100%)	2	50%	1	0%	2	50%

Table 54. Evaluation of risks to benthic invertebrates exposed to chemicals of potential concern in the Tri-State Mining District, based on multiple lines-of-evidence.

Area of Interest (AoI)	Chemistry								Sediment Toxicity					
	Sediment		Pore-Water		Invertebrate-Tissue		Surface Water		Amphipod		Mussel		Midge	
	n	Number Predicted Toxic	n	Number Predicted Toxic	n	Number Predicted Toxic	n	Number of Exceedences	n	Observed Toxicity	n	Observed Toxicity	n	Observed Toxicity
Neosho River Sub-basin (cont.)														
Lower Tar Creek AoI	108	88 (81%)	5	3 (60%)	2	2 (100%)	121	101 (83%)	4	75%	2	100%	4	75%
Elm Creek AoI	26	22 (85%)	2	1 (50%)	ND	ND	5	4 (80%)	1	100%	ND	ND	1	100%
<i>Sub-basin Subtotal</i>	<i>383</i>	<i>218 (57%)</i>	<i>20</i>	<i>6 (30%)</i>	<i>4</i>	<i>4 (100%)</i>	<i>223</i>	<i>159 (71%)</i>	<i>15</i>	<i>53%</i>	<i>8</i>	<i>38%</i>	<i>15</i>	<i>60%</i>
Study Area as a Whole	1162	566 (49%)	96	29 (31%)	239	57 (24%)	537	268 (50%)	76	29%	48	33%	70	50%
Reference Sediment Samples	10	0 (0%)	8	0 (0%)	2	0 (0%)	18	1 (6%)	10	0%	5	0%	8	0%

n = sample size; ND = no data or limited data.

Figures

Figure 1. Map of Study Area.

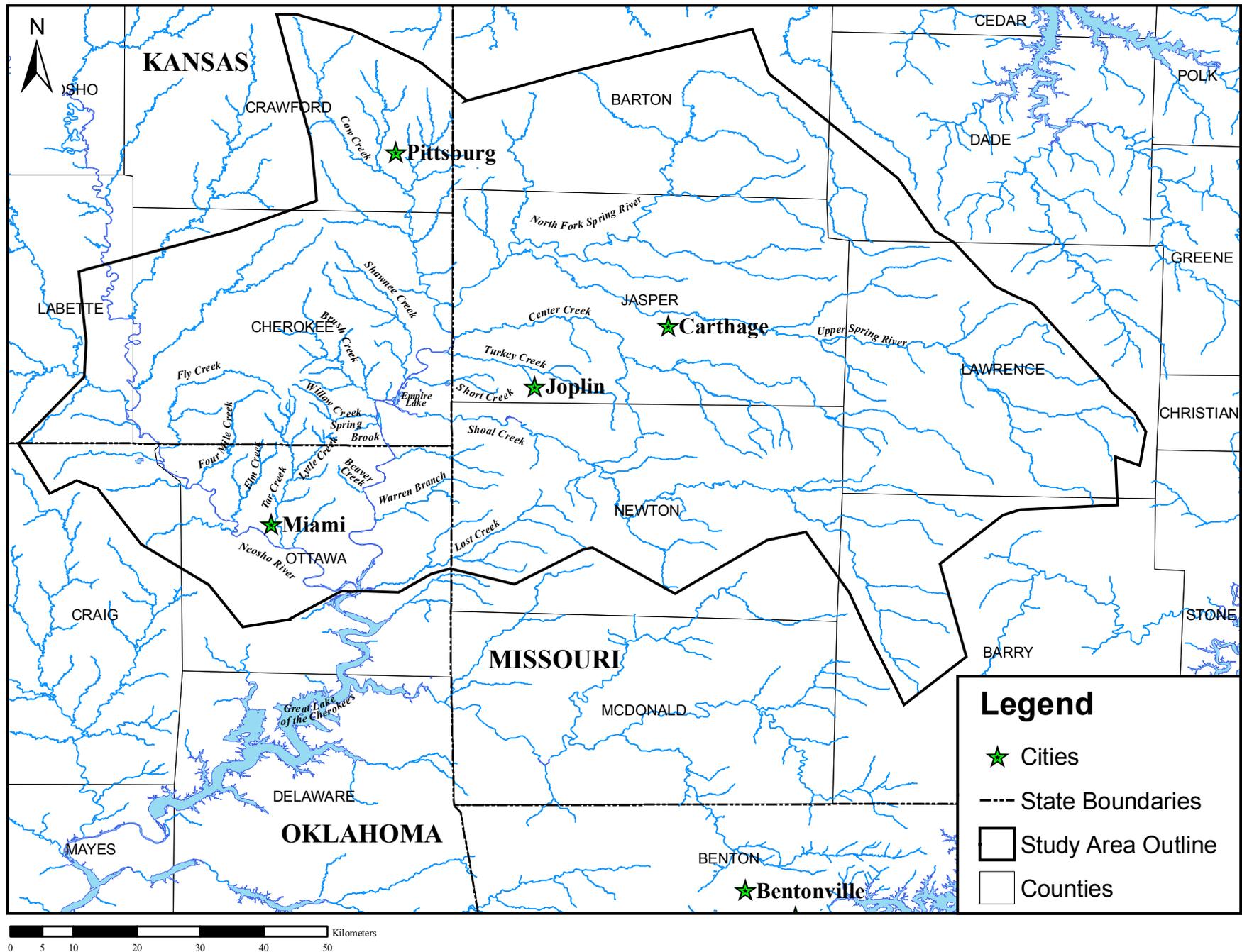
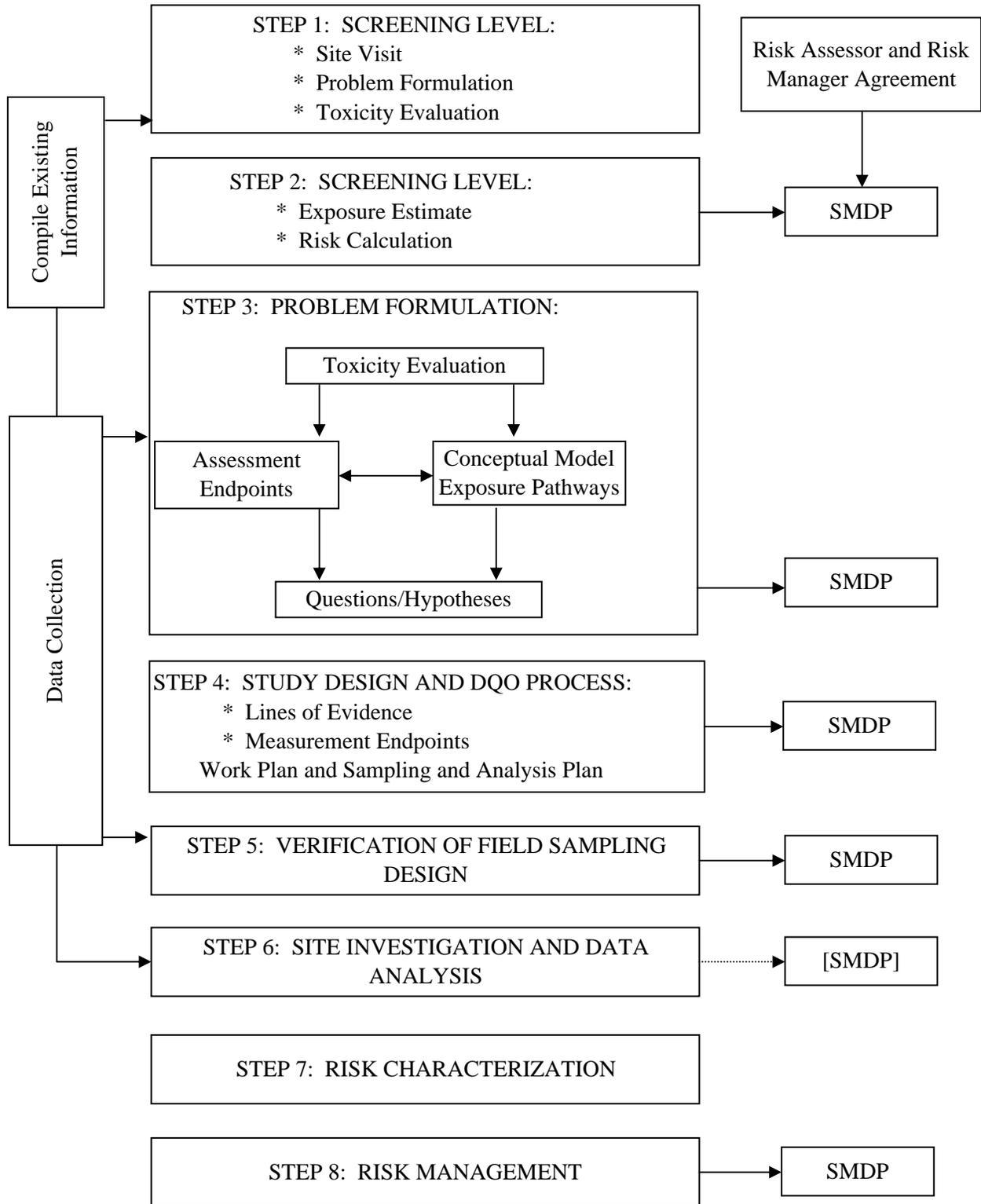


Figure 2. Eight-step ecological risk assessment process for Superfund (USEPA 1997a).



SMDP = Scientific/Management Decision Point

Figure 3. The framework for ecological risk assessment (modified from USEPA 1997a).

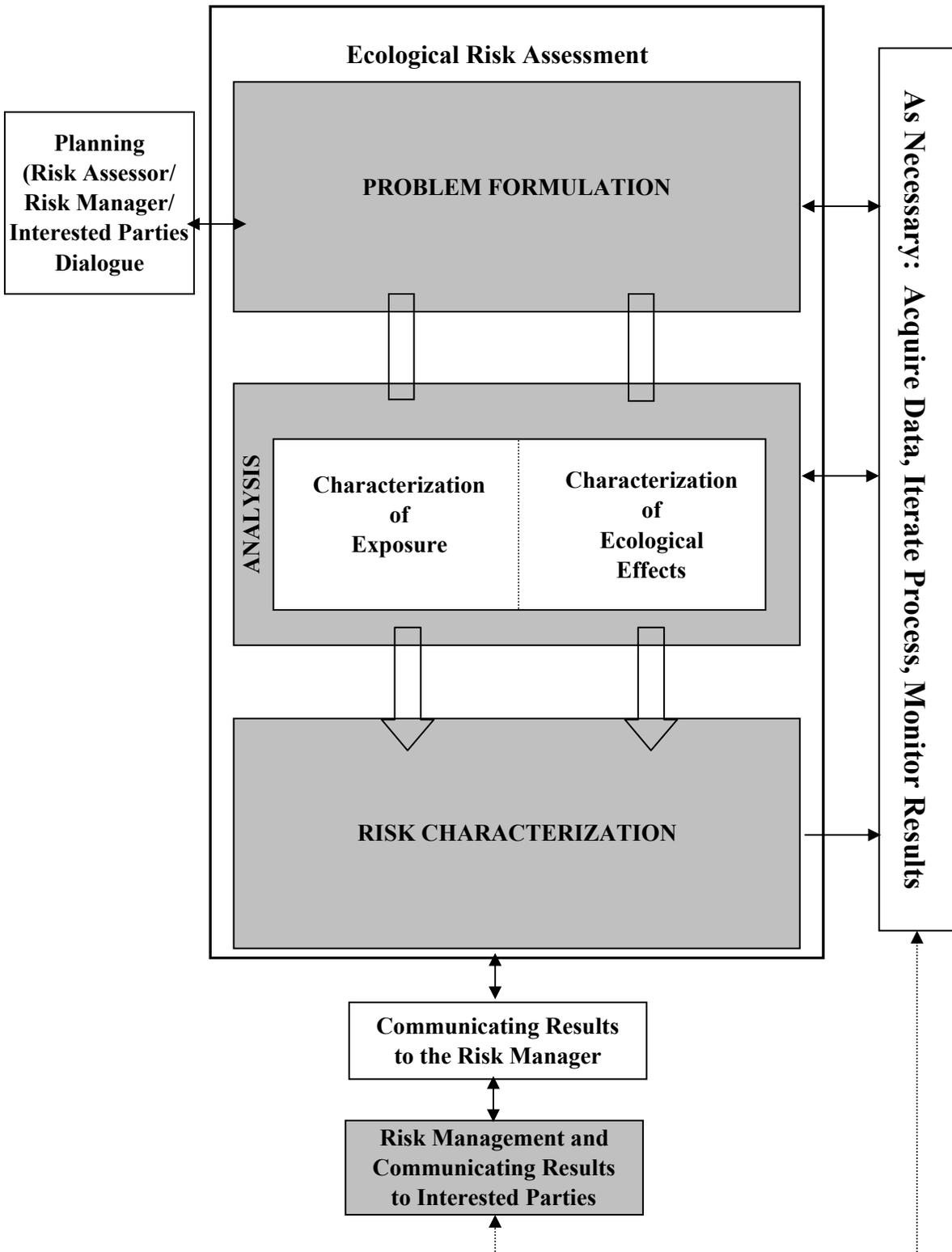


Figure 4. Map of Study Area, showing Areas of Interest (AoI).

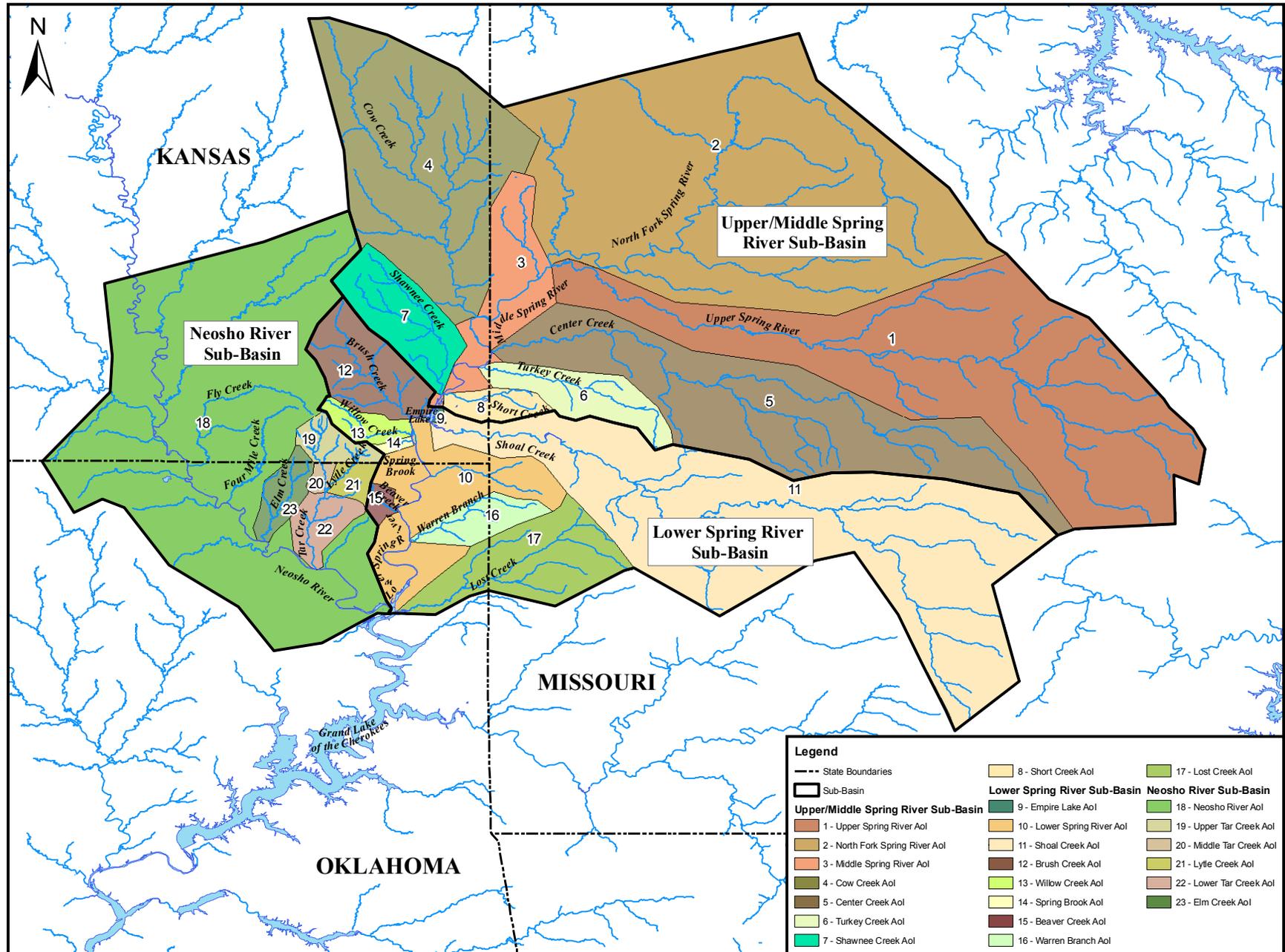


Figure 5. Map of Study Area, showing Areas of Interest (AoI) within Missouri.

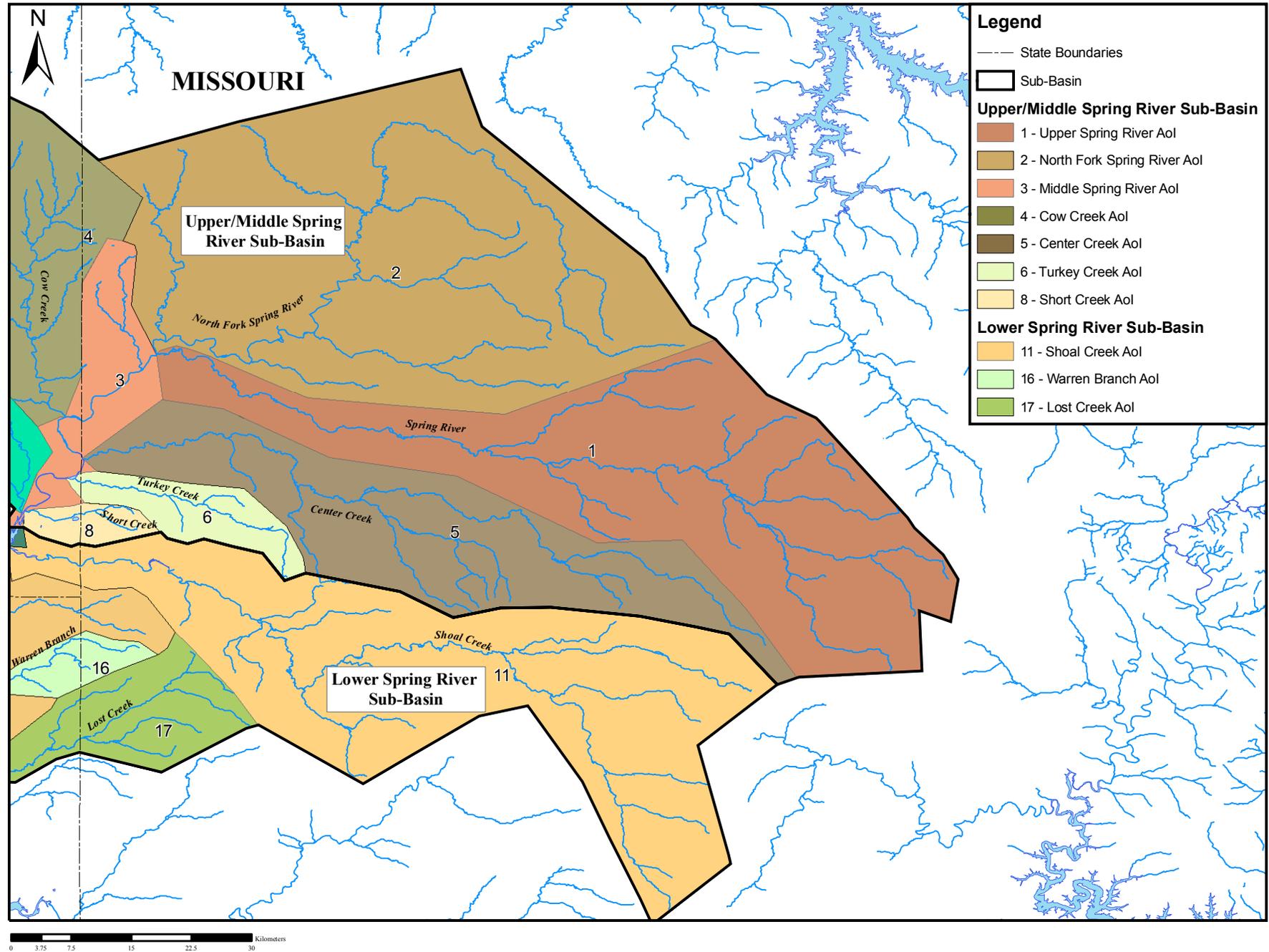


Figure 6. Map of Study Area, showing Areas of Interest (AoI) within Kansas.

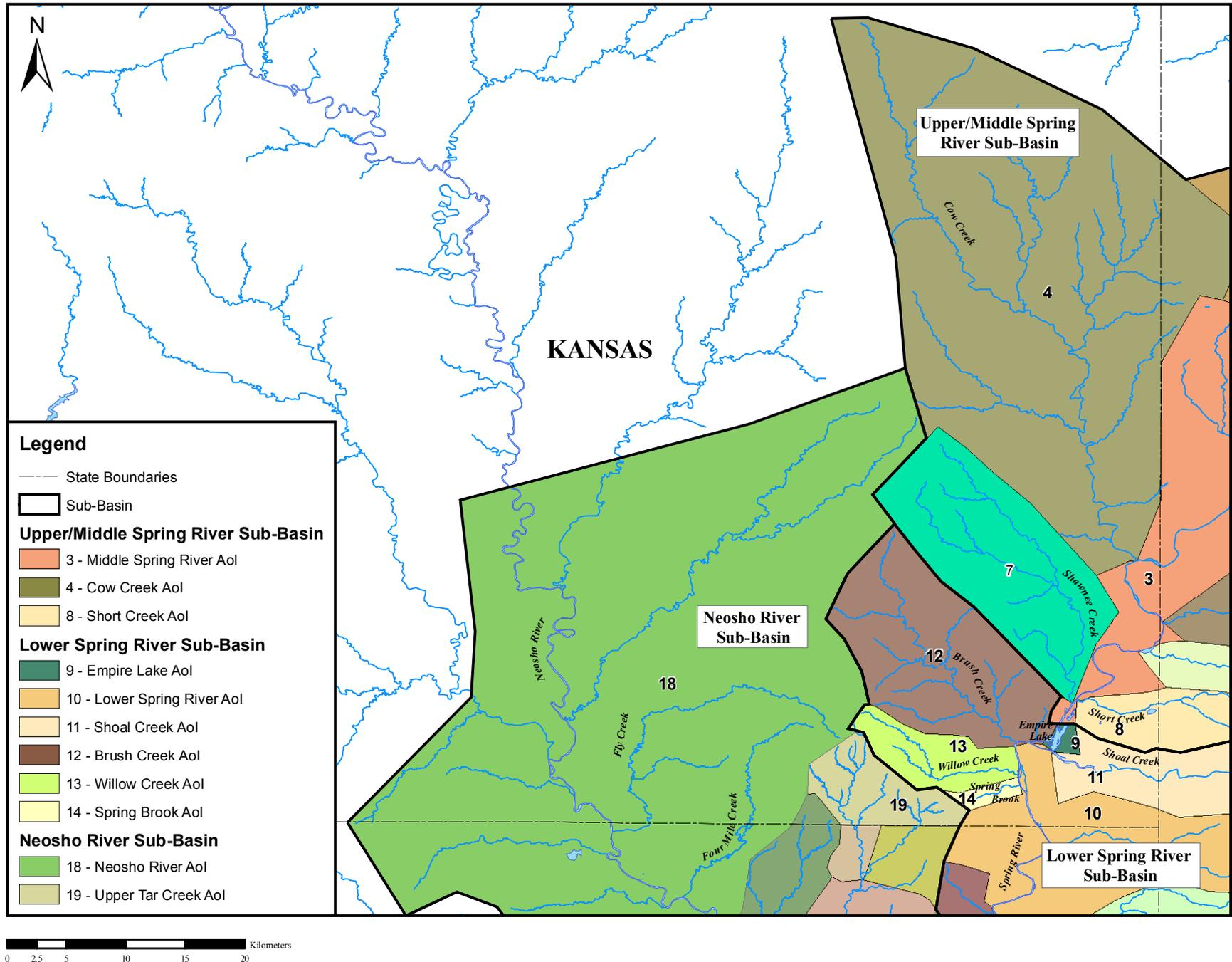


Figure 7. Map of Study Area, showing Areas of Interest (AoI) within Oklahoma.

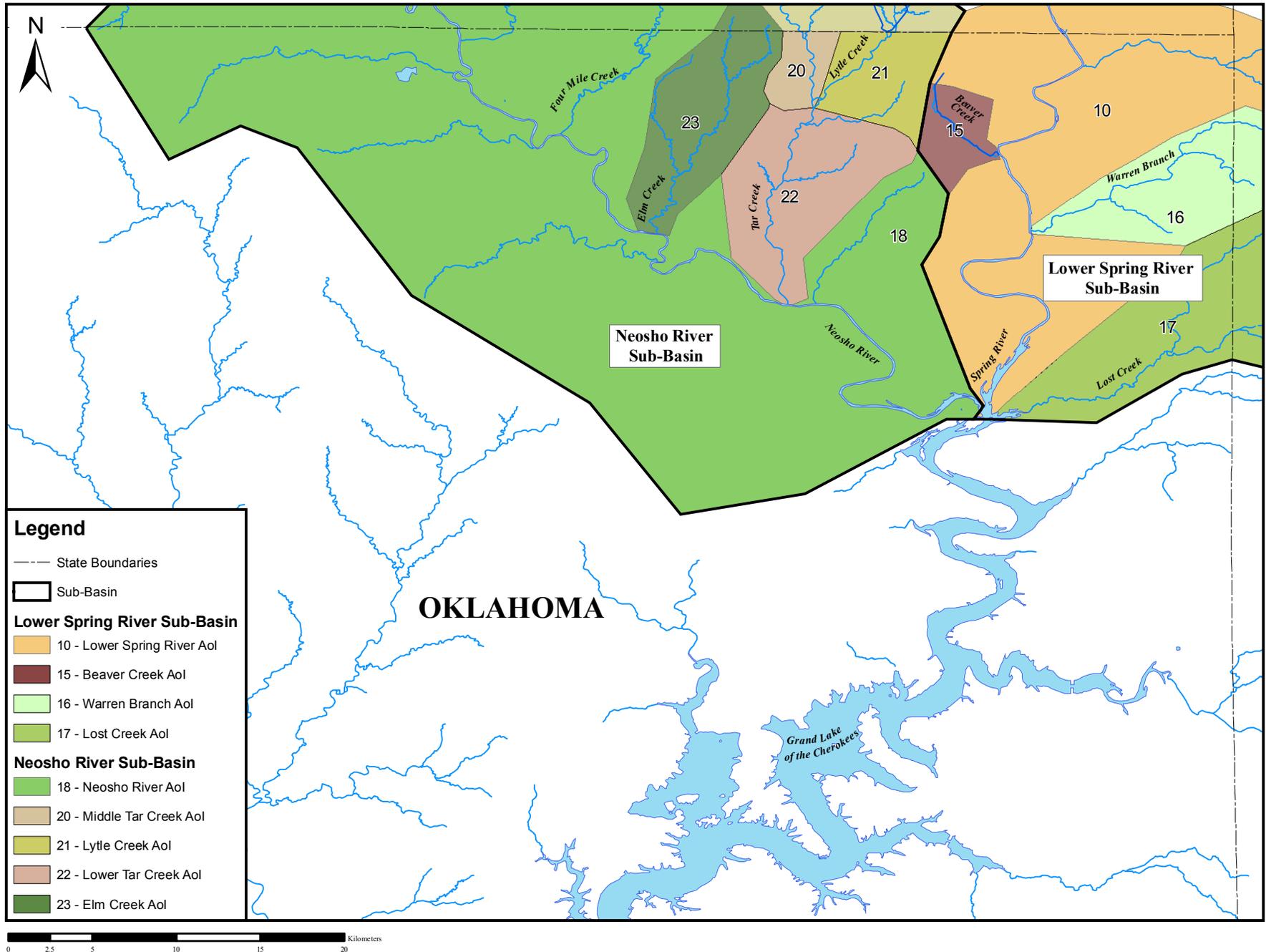


Figure 8. Map of Study Area showing mining locations.

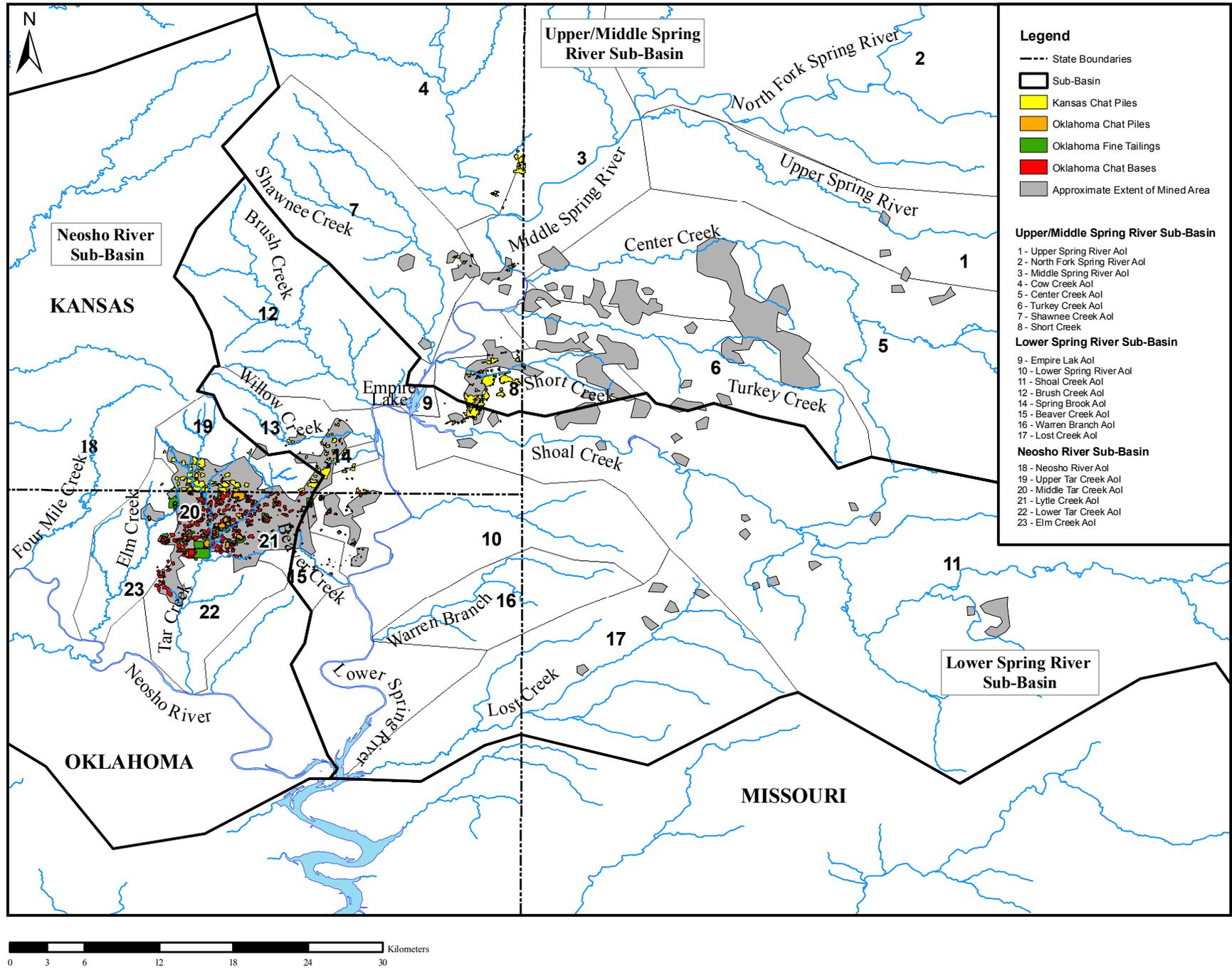
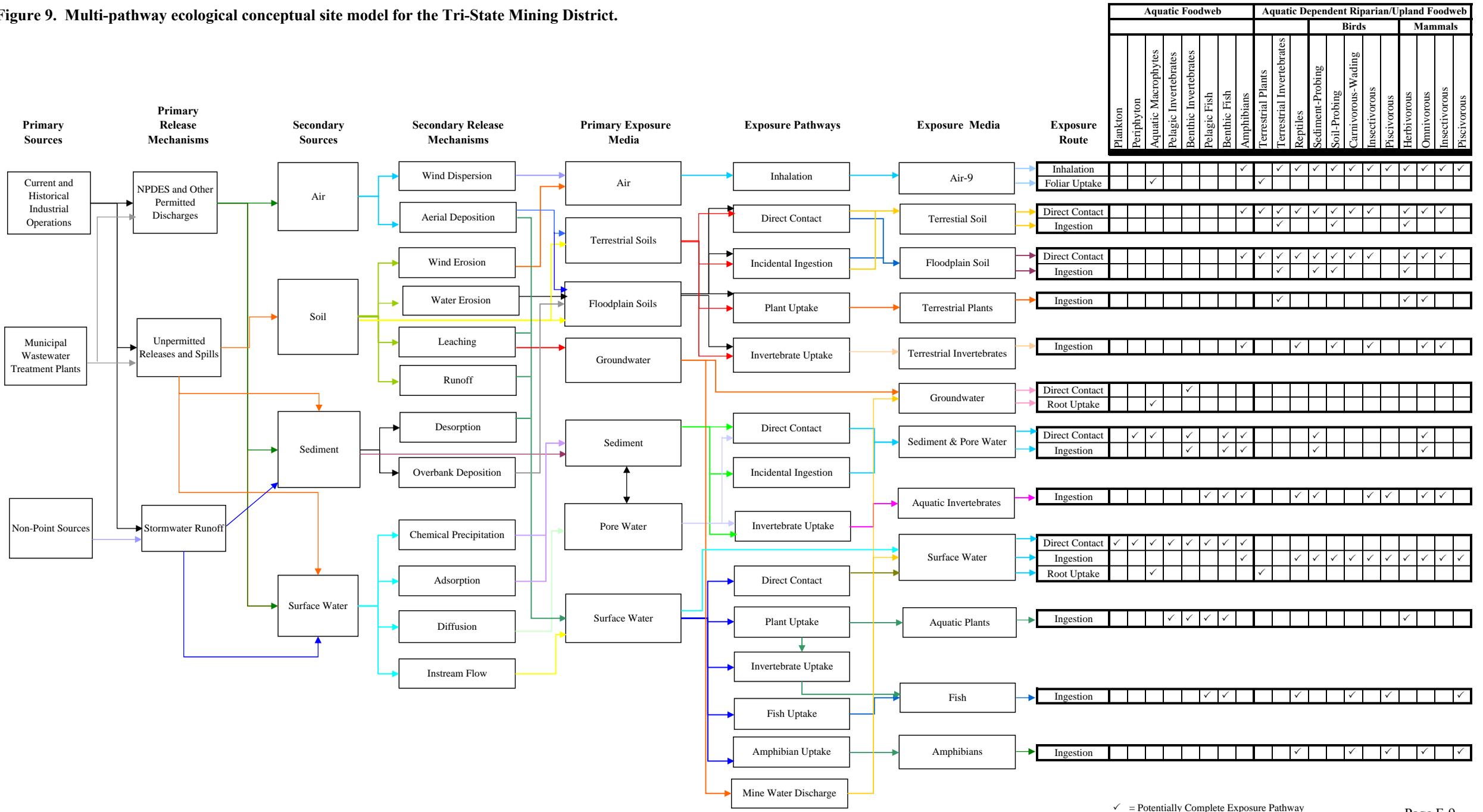


Figure 9. Multi-pathway ecological conceptual site model for the Tri-State Mining District.



✓ = Potentially Complete Exposure Pathway

Figure 10. Map of Study Area, showing the locations of surface-water sampling stations.

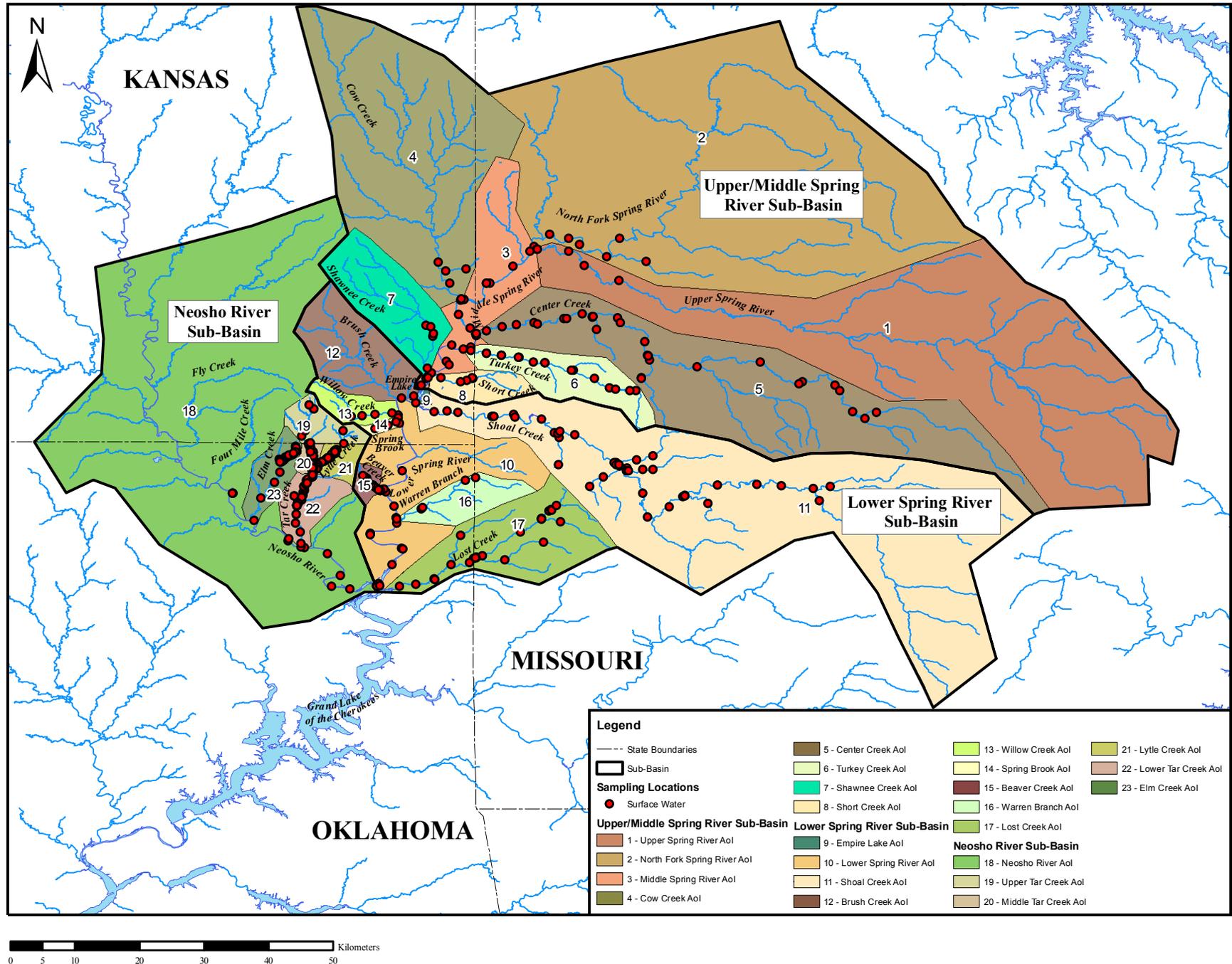


Figure 11. Map of Study Area, showing the locations of reference surface-water sampling stations.

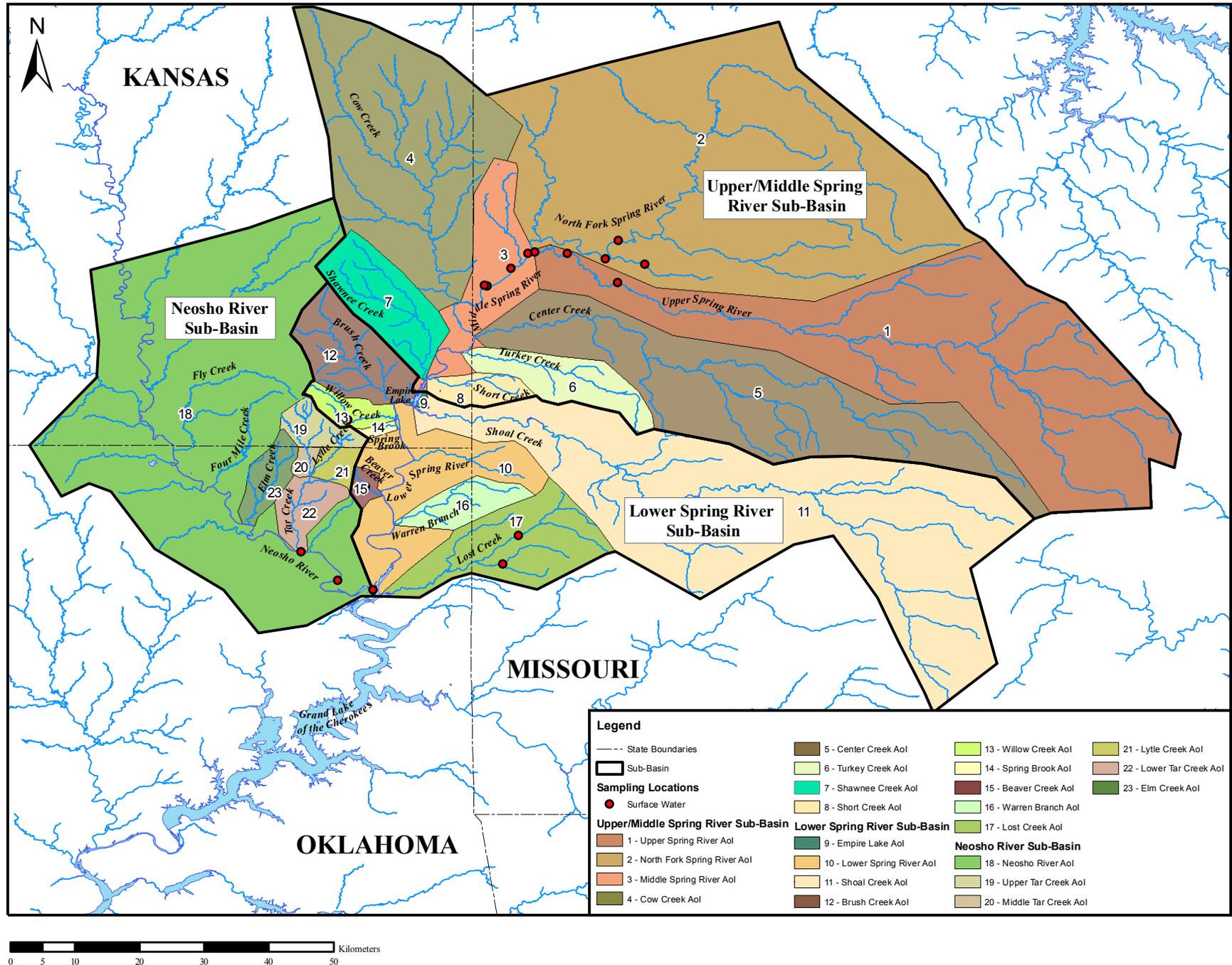


Figure 12. Map of Study Area, showing the locations of sediment sampling stations.

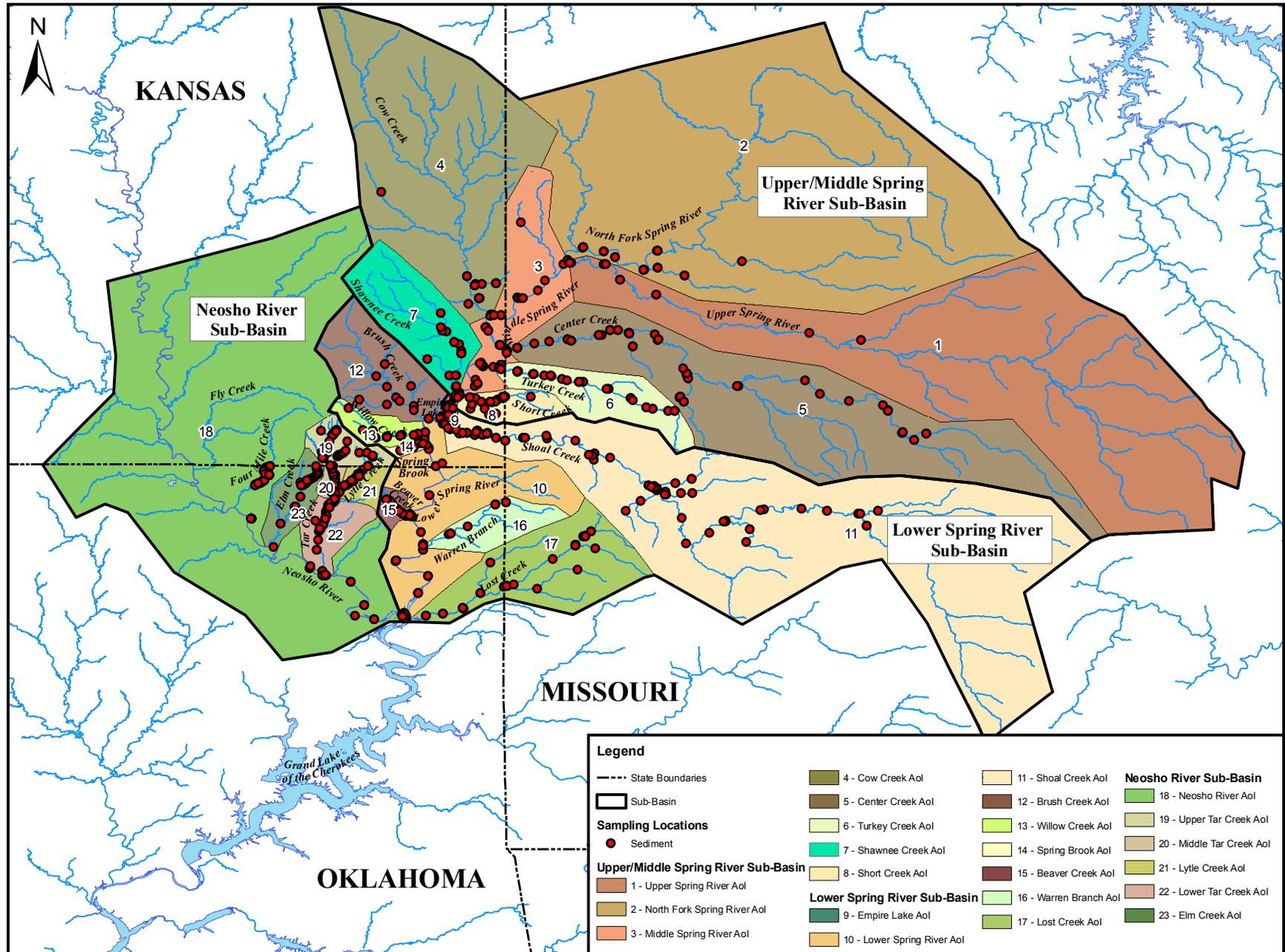


Figure 13. Map of Study Area, showing locations where reference samples for sediment and pore-water samples were collected.

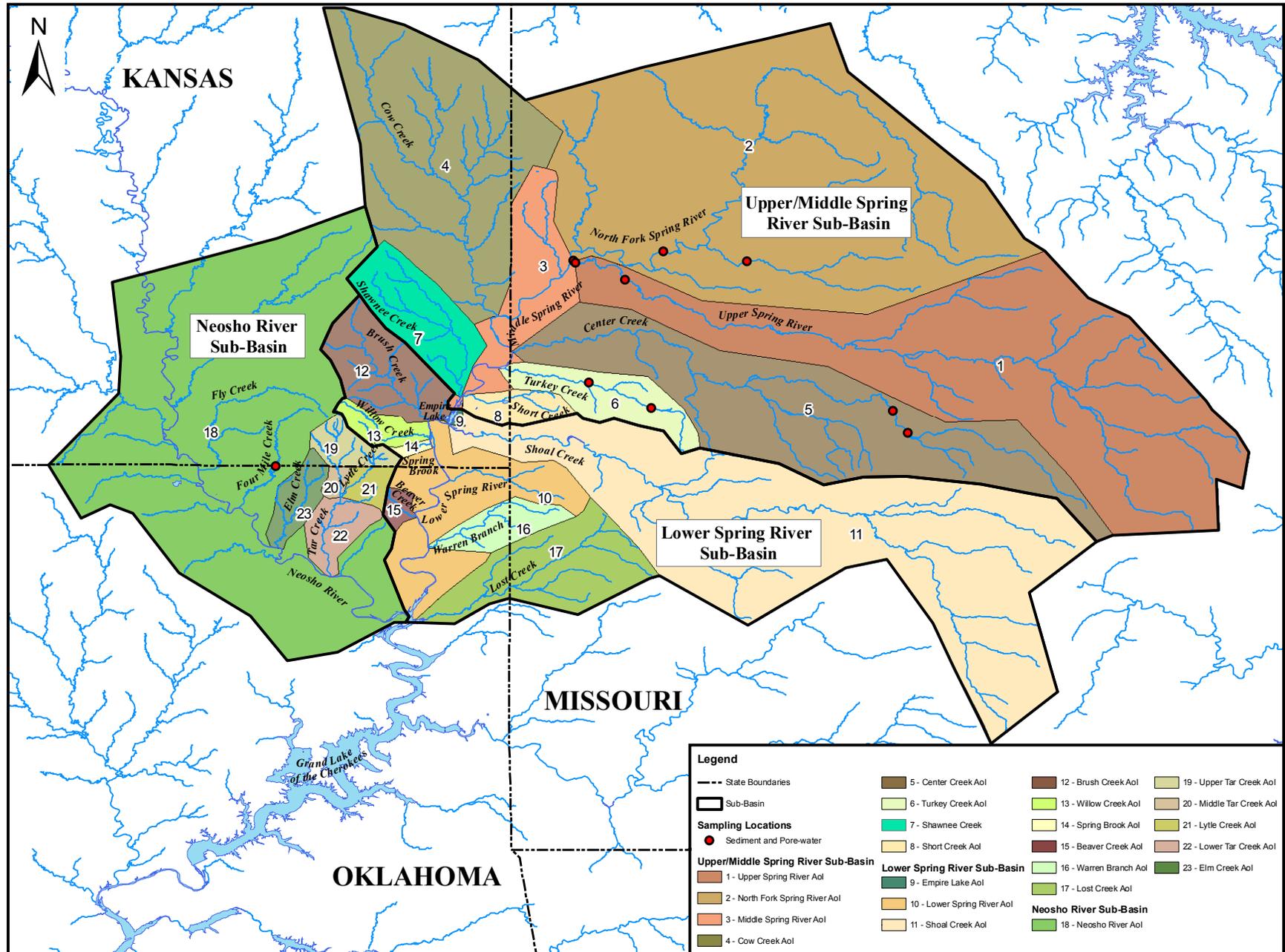


Figure 14. Map of Study Area, showing the locations of pore-water sampling stations.

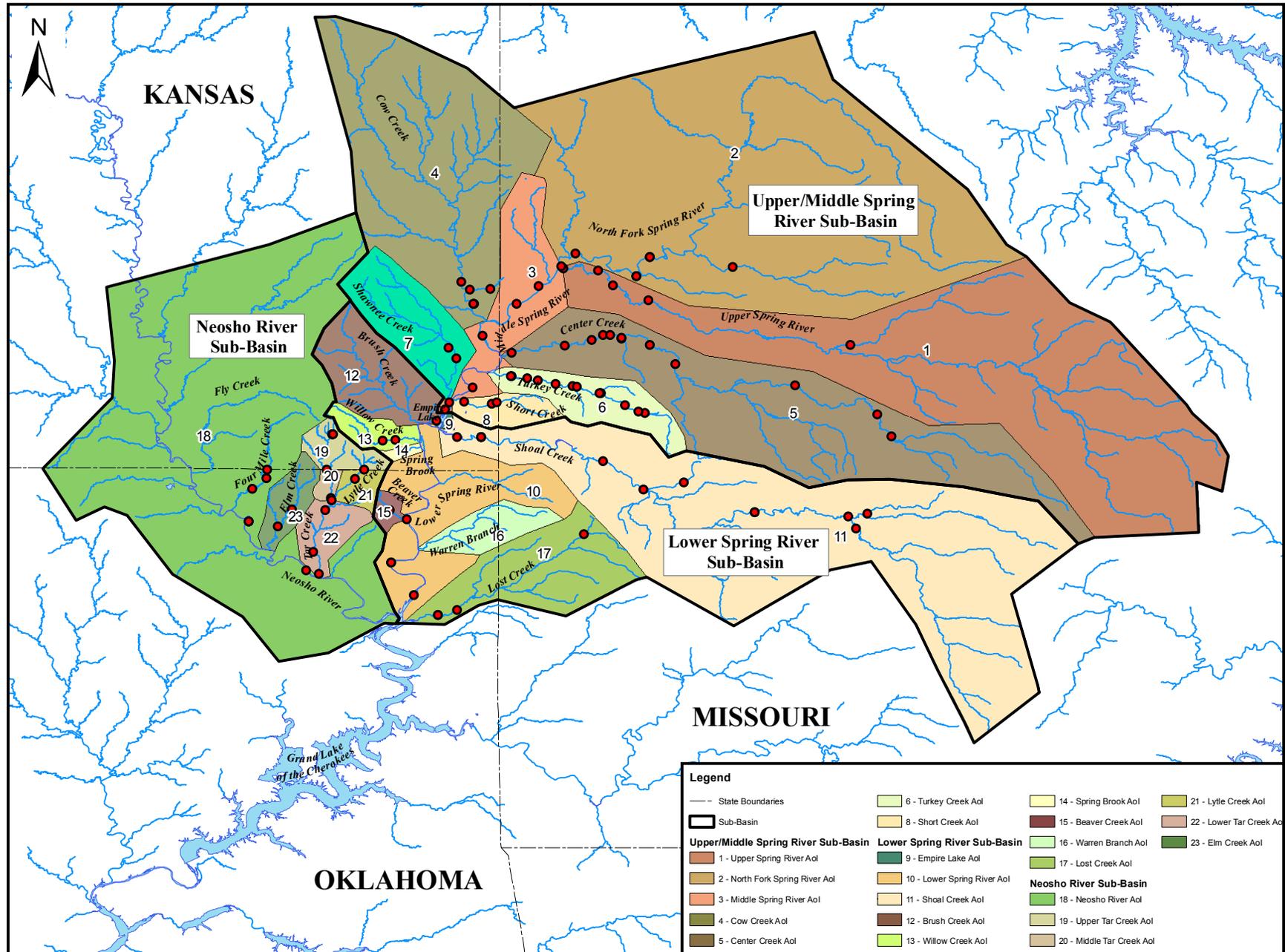


Figure 15. Relationship between $\Sigma\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ sediment concentrations and the control-adjusted survival of *Hyalella azteca* during 28-d exposure tests to <2 mm sediment from the Tri-State Mining District.

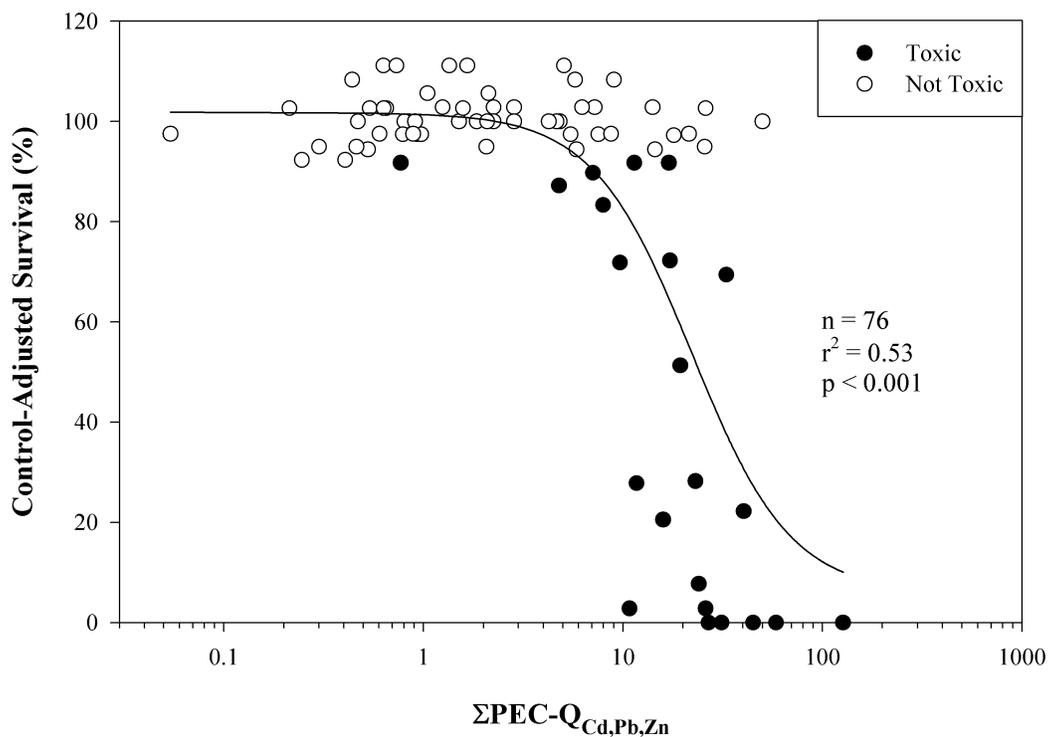


Figure 16. Relationship between $\Sigma\text{PEC-Q}_{\text{Cd,Cu,Pb,Hg,Ni,Zn}}$ sediment concentrations and the control-adjusted survival of *Hyalella azteca* during 28-d exposure tests to <2 mm sediment from the Tri-State Mining District.

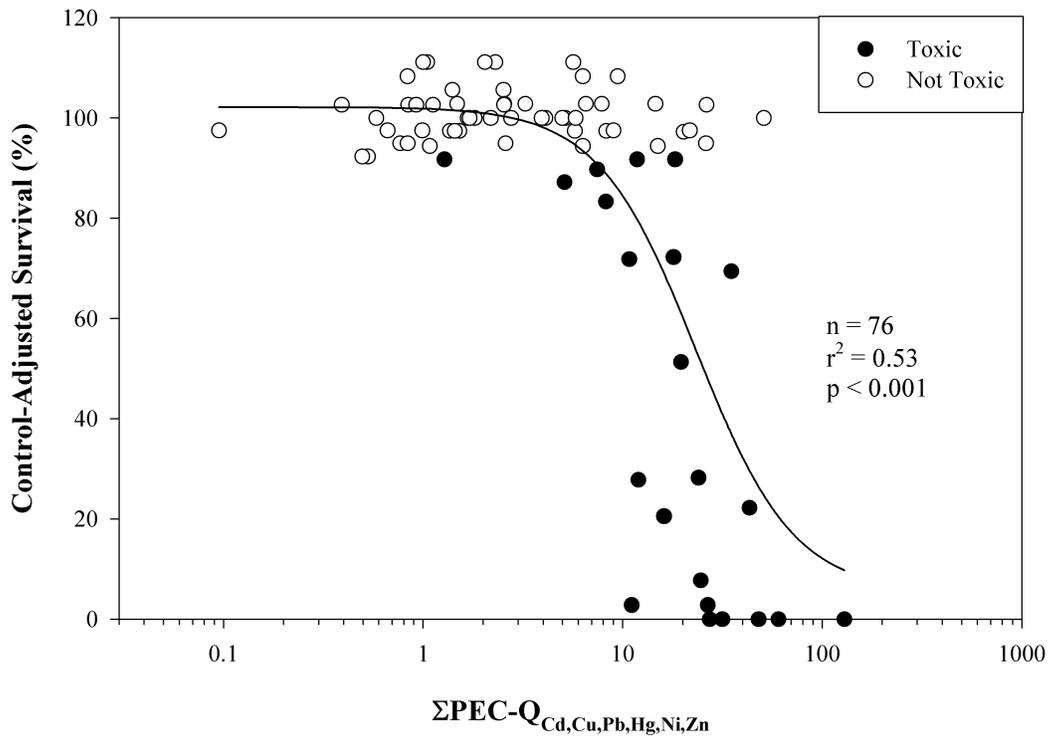


Figure 17. Relationship between $\Sigma\text{PEC-Q}_{\text{Cd,Pb,Zn}}$ sediment concentrations and the control-adjusted survival of *Hyalella azteca* during 28-d exposure tests to <2 mm sediment from the Tri-State Mining District. The T_{10} toxicity threshold corresponds to the minimum control-adjusted survival value of the reference envelope samples.

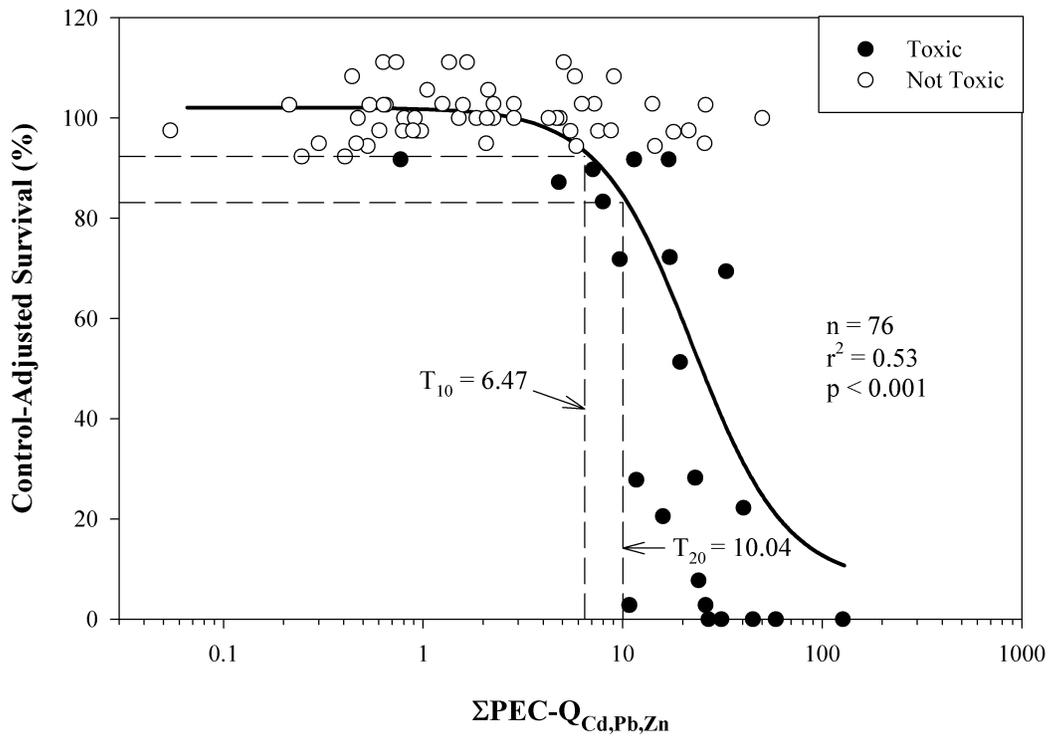


Figure 18: Relationship between the concentrations of metals in the tissues of the oligochaete *Lumbriculus variegatus* (expressed as Σ Metal-TUs) and the control-adjusted survival of amphipods, *Hyalella azteca*, in 28-d toxicity tests conducted with sediment samples from the Tri-State Mining District.

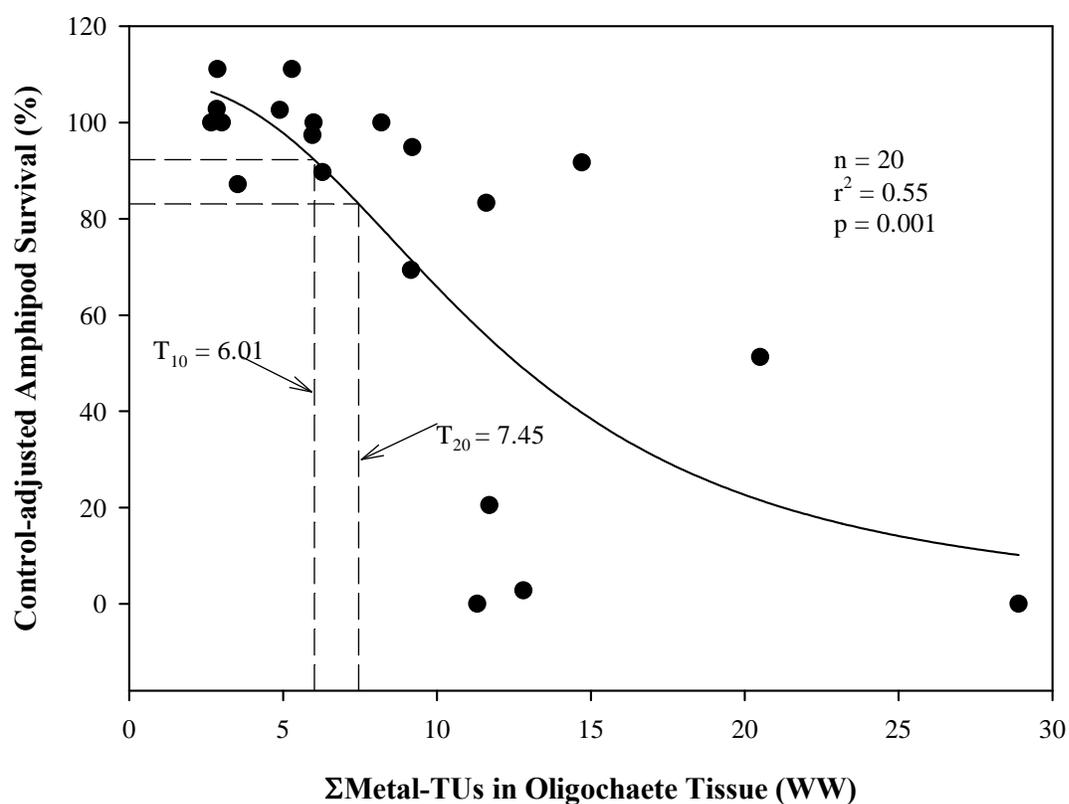
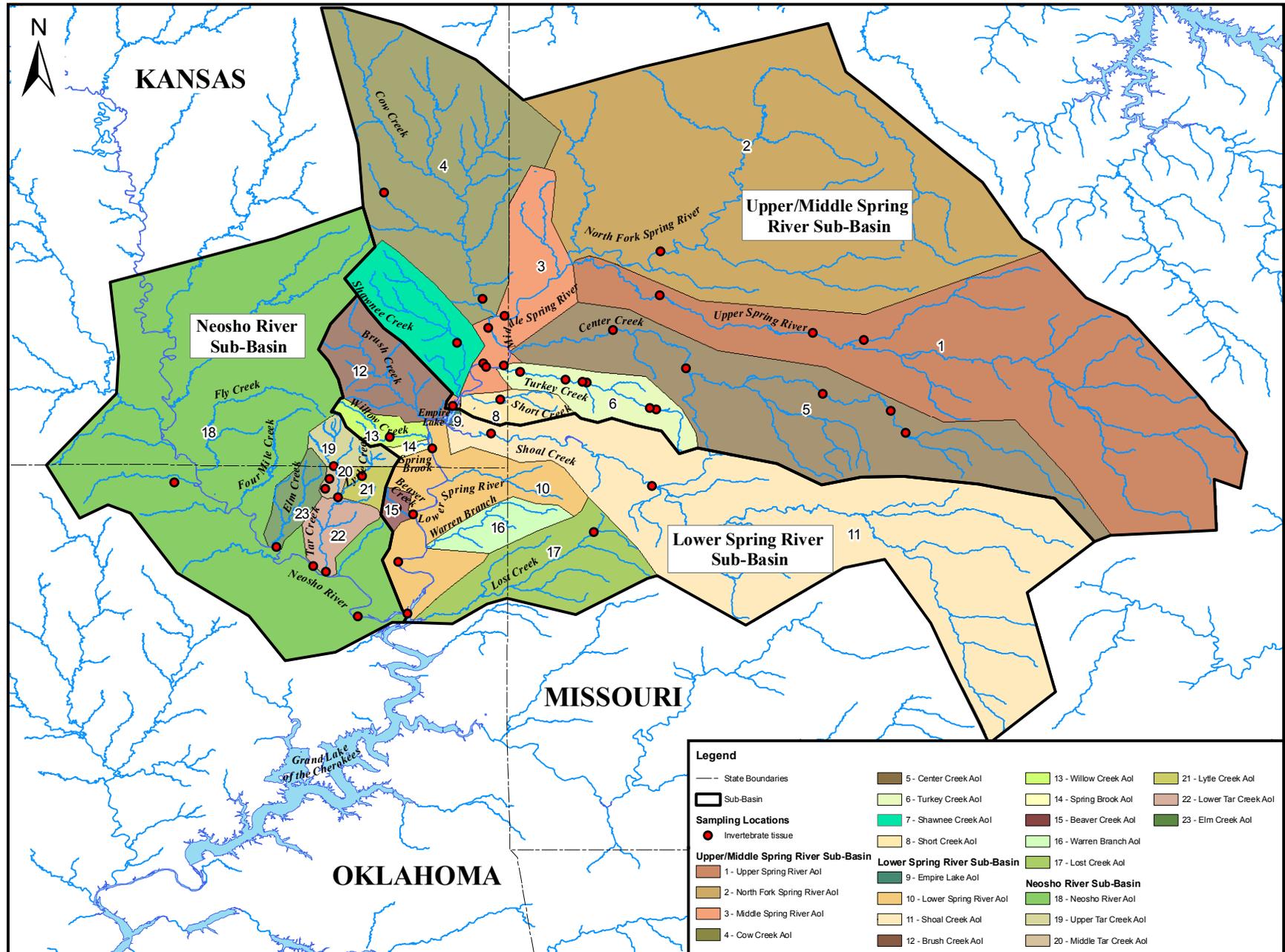


Figure 19. Map of Study Area, showing the locations of invertebrate-tissue sampling stations.



0 5 10 20 30 40 50 Kilometers

Figure 20. Map of Study Area, showing the locations of sampling stations selected for sediment toxicity testing.

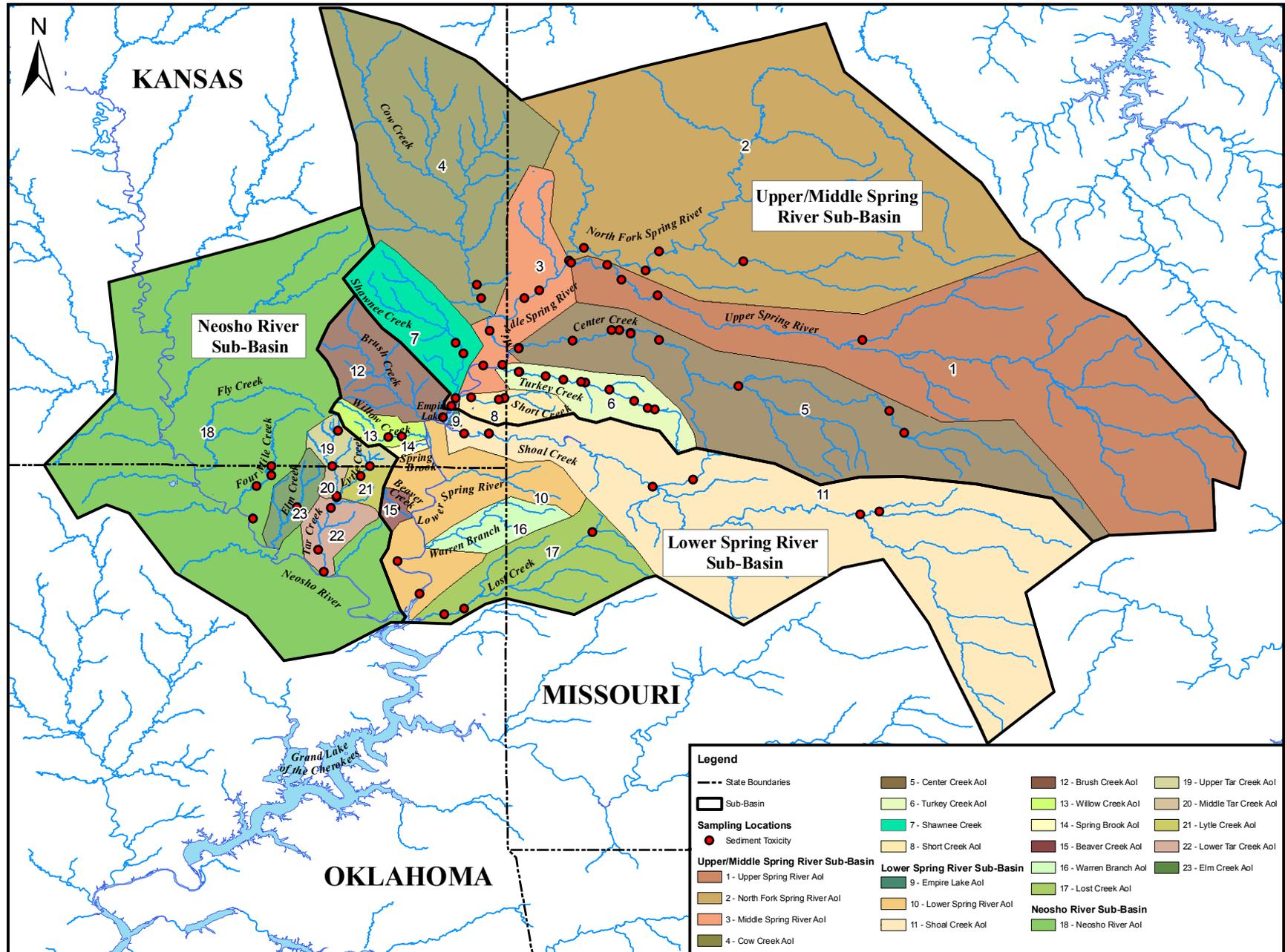


Figure 21. Map of Study Area, showing the locations of qualitative bivalve sampling stations (Angelo *et al.* 2007).

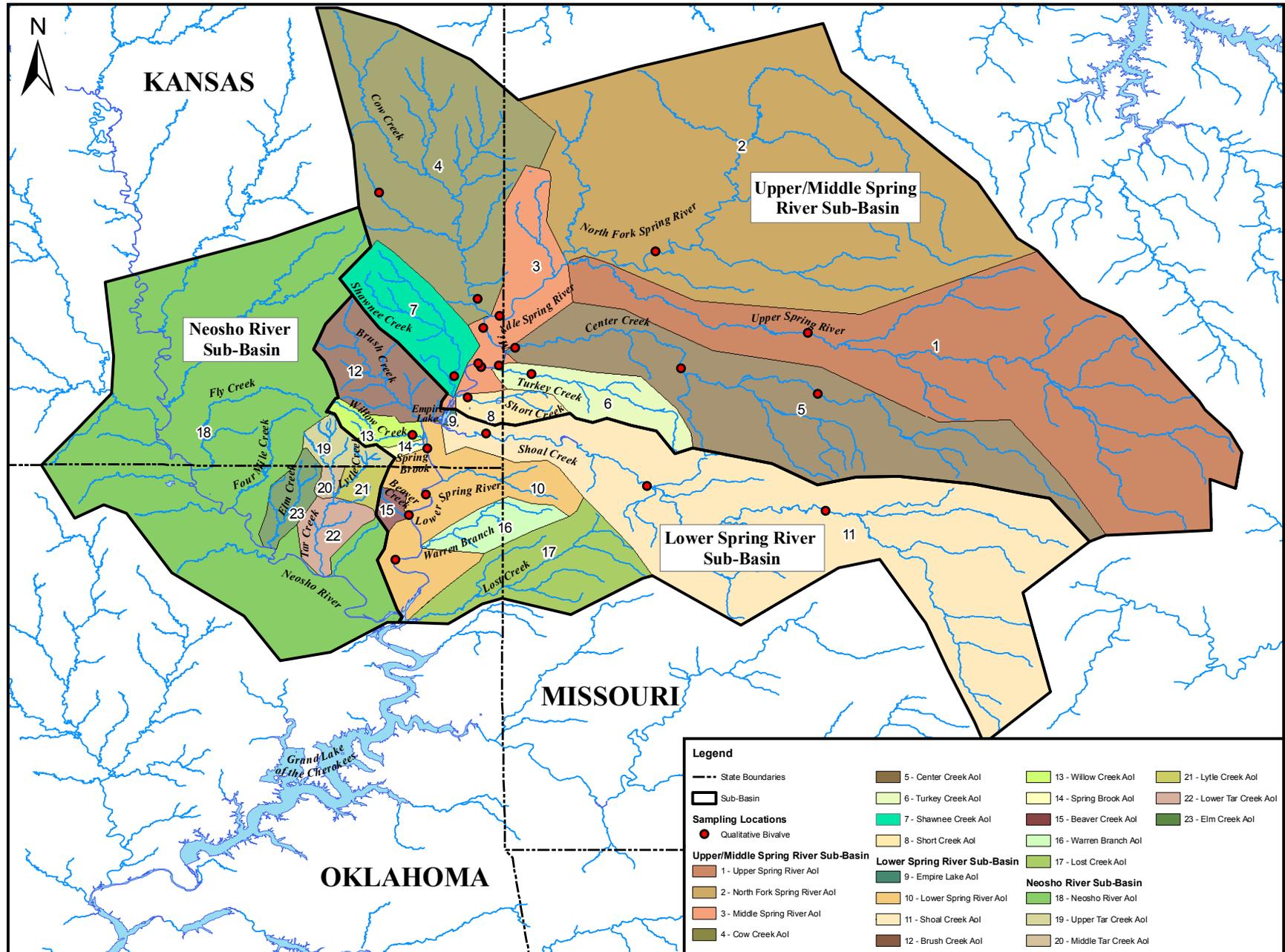


Figure 22. Map of Study Area, showing locations with sediments that were toxic and not toxic to the midge, *Chironomus dilutus* (Endpoint Measured: Survival).

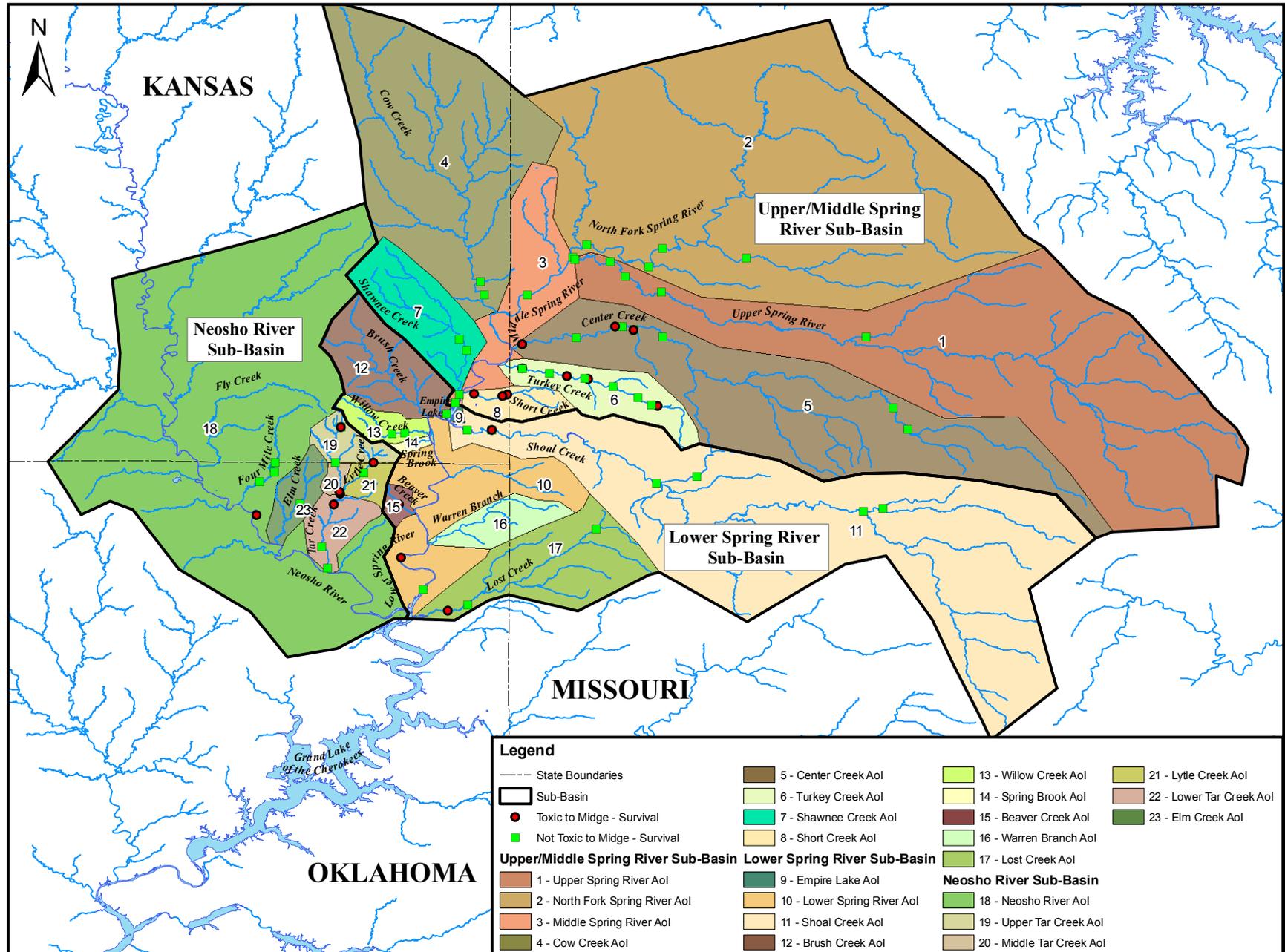


Figure 23. Map of Study Area, showing locations with sediments that were toxic and not toxic to the midge, *Chironomus dilutus* (Endpoint Measured: Biomass).

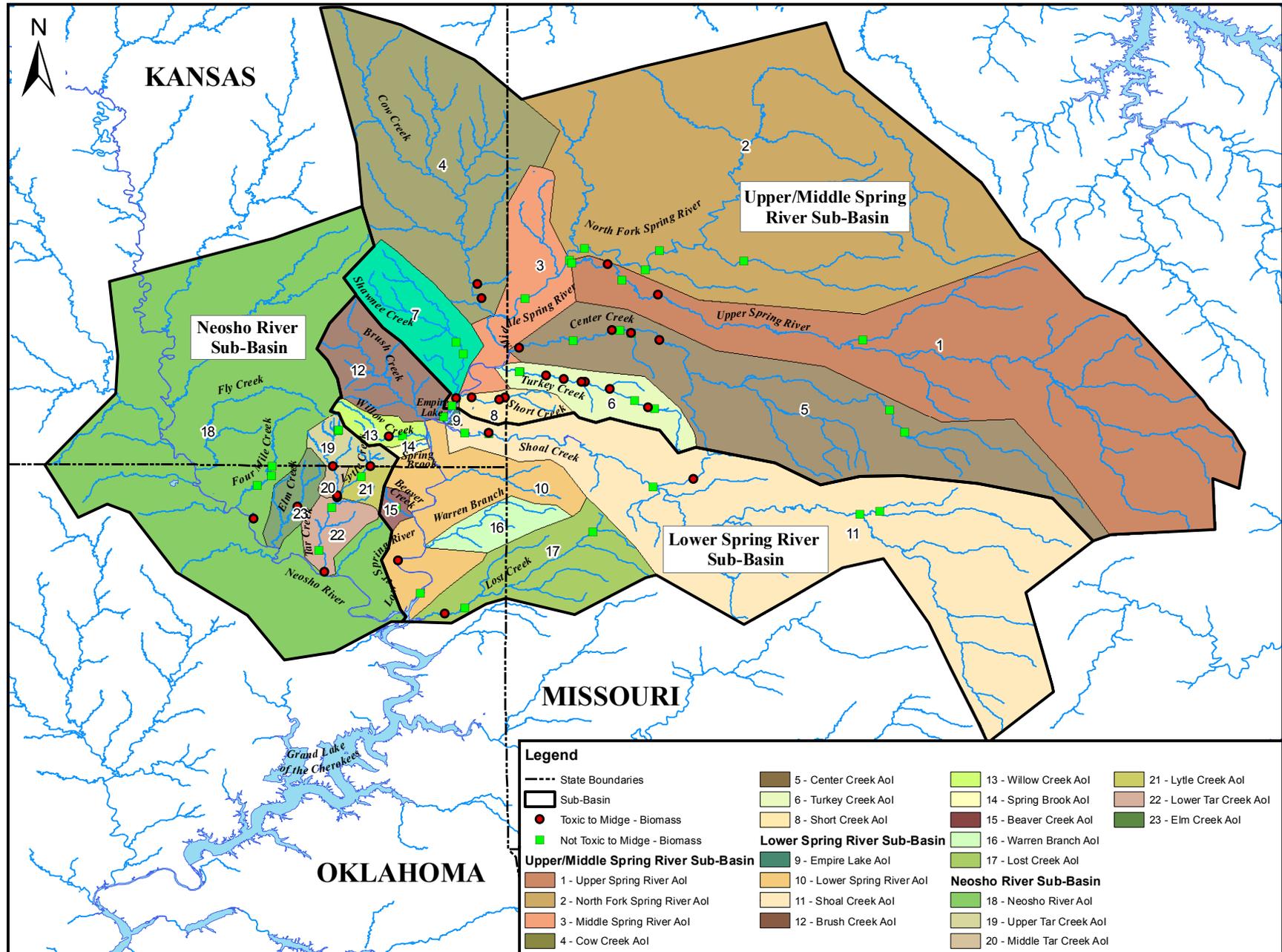


Figure 24. Map of Study Area, showing locations with sediments that were toxic and not toxic to the amphipod, *Hyaella azteca* (Endpoint Measured: Survival).

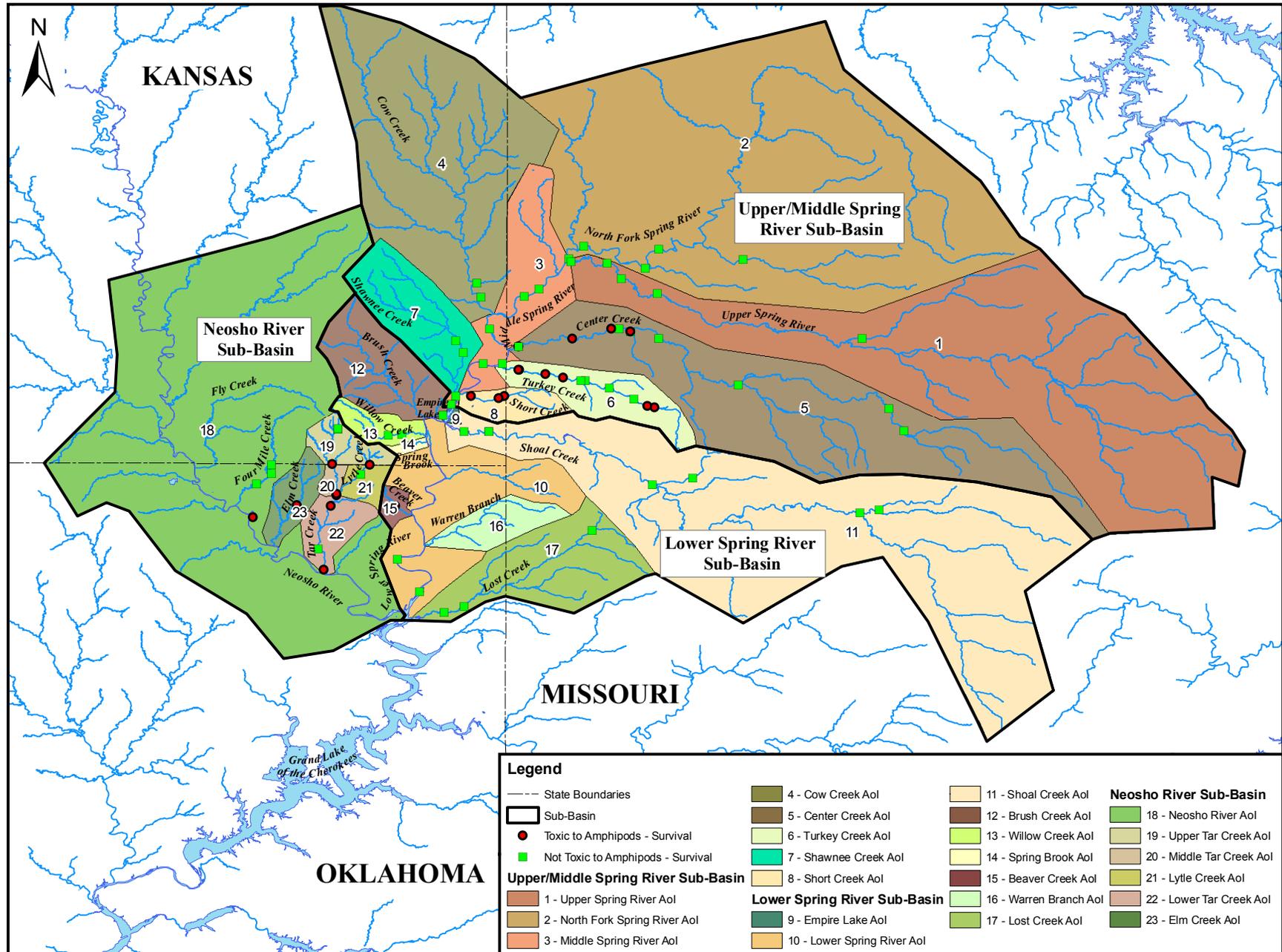


Figure 25. Map of Study Area, showing locations with sediments that were toxic and not toxic to the amphipod, *Hyaella azteca* (Endpoint Measured: Biomass).

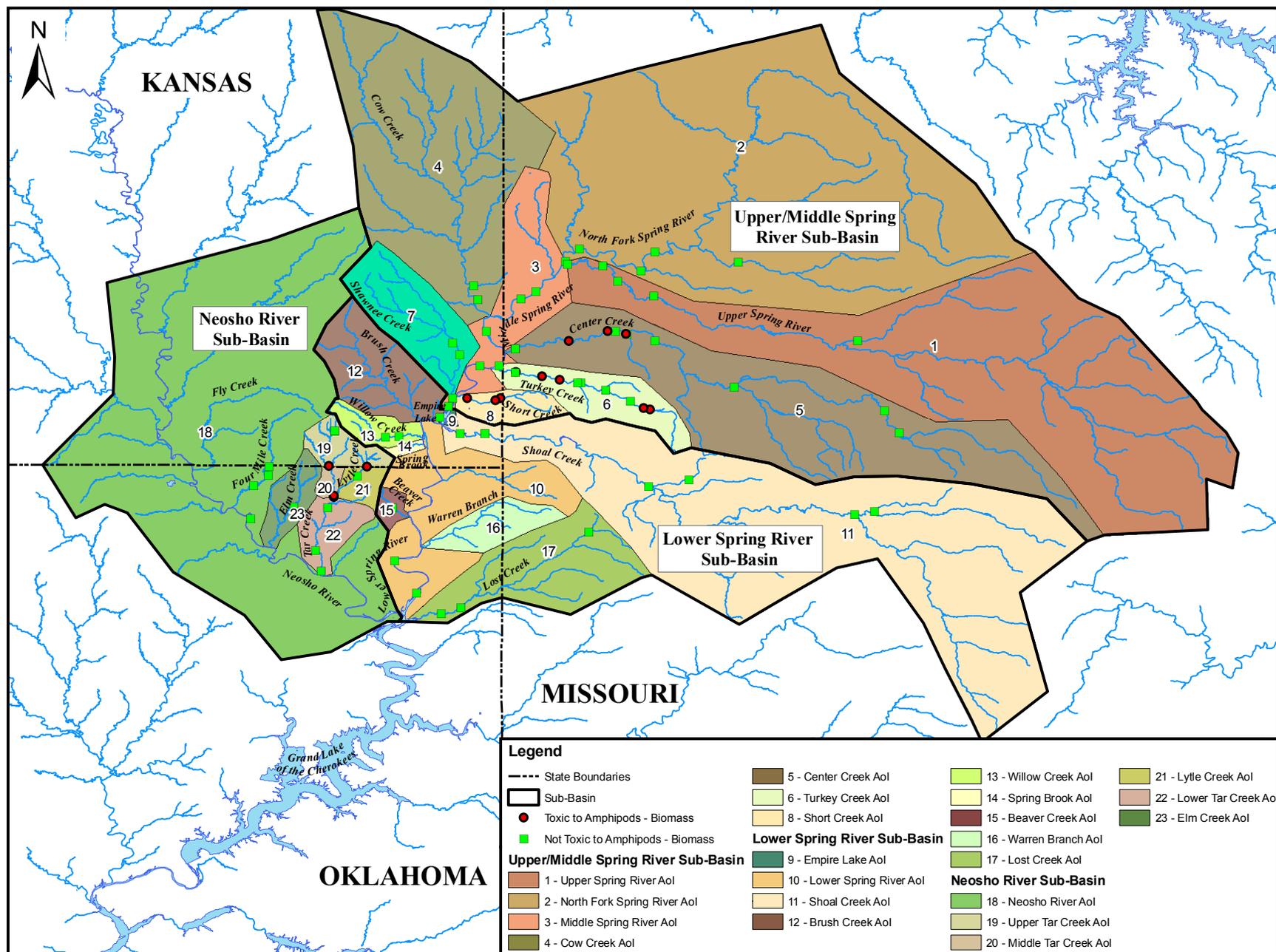


Figure 26. Map of Study Area, showing locations with sediments that were toxic and not toxic to freshwater mussels, *Lampsilis siliquoidea* (Endpoint Measured: Survival).

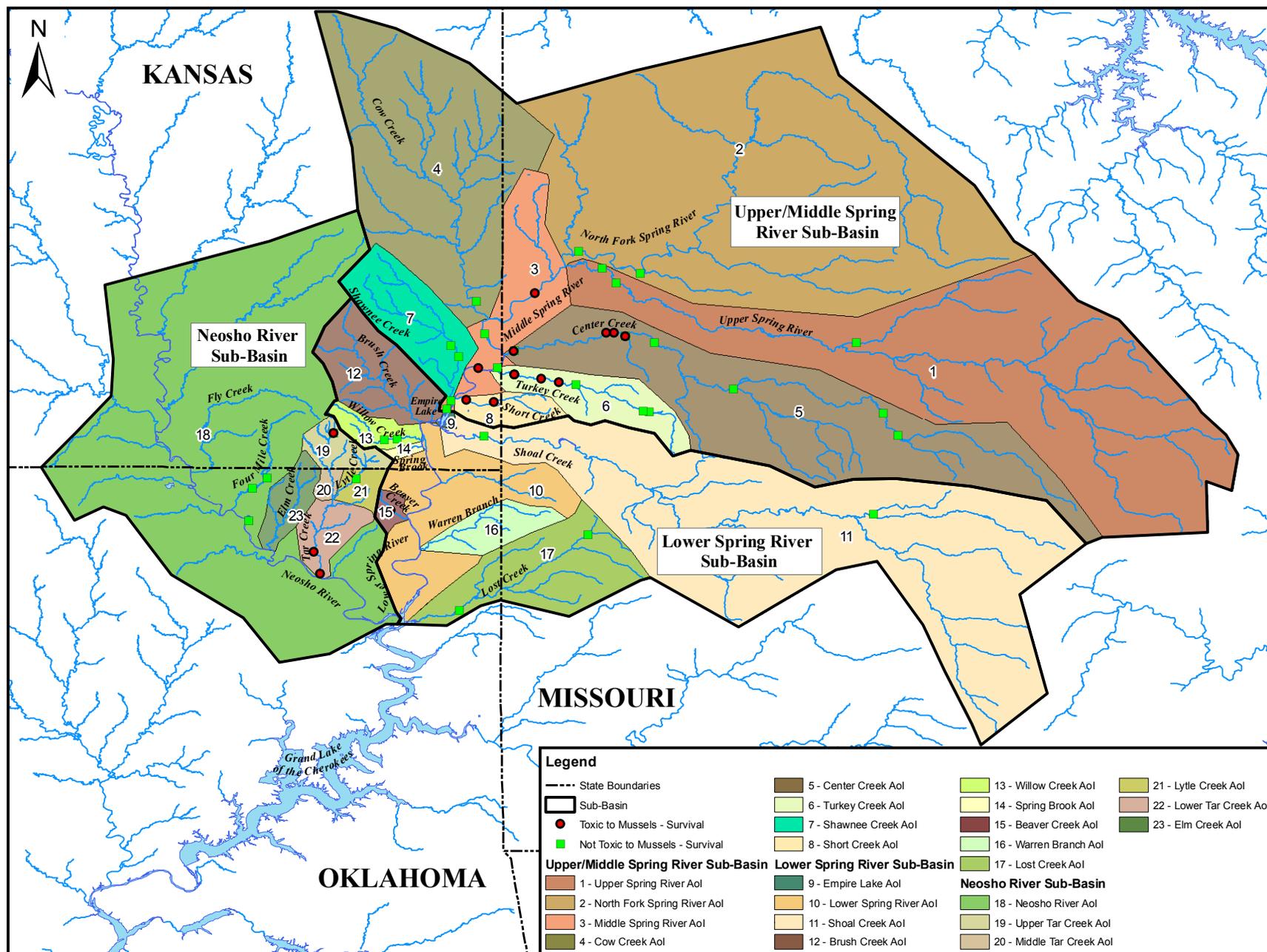
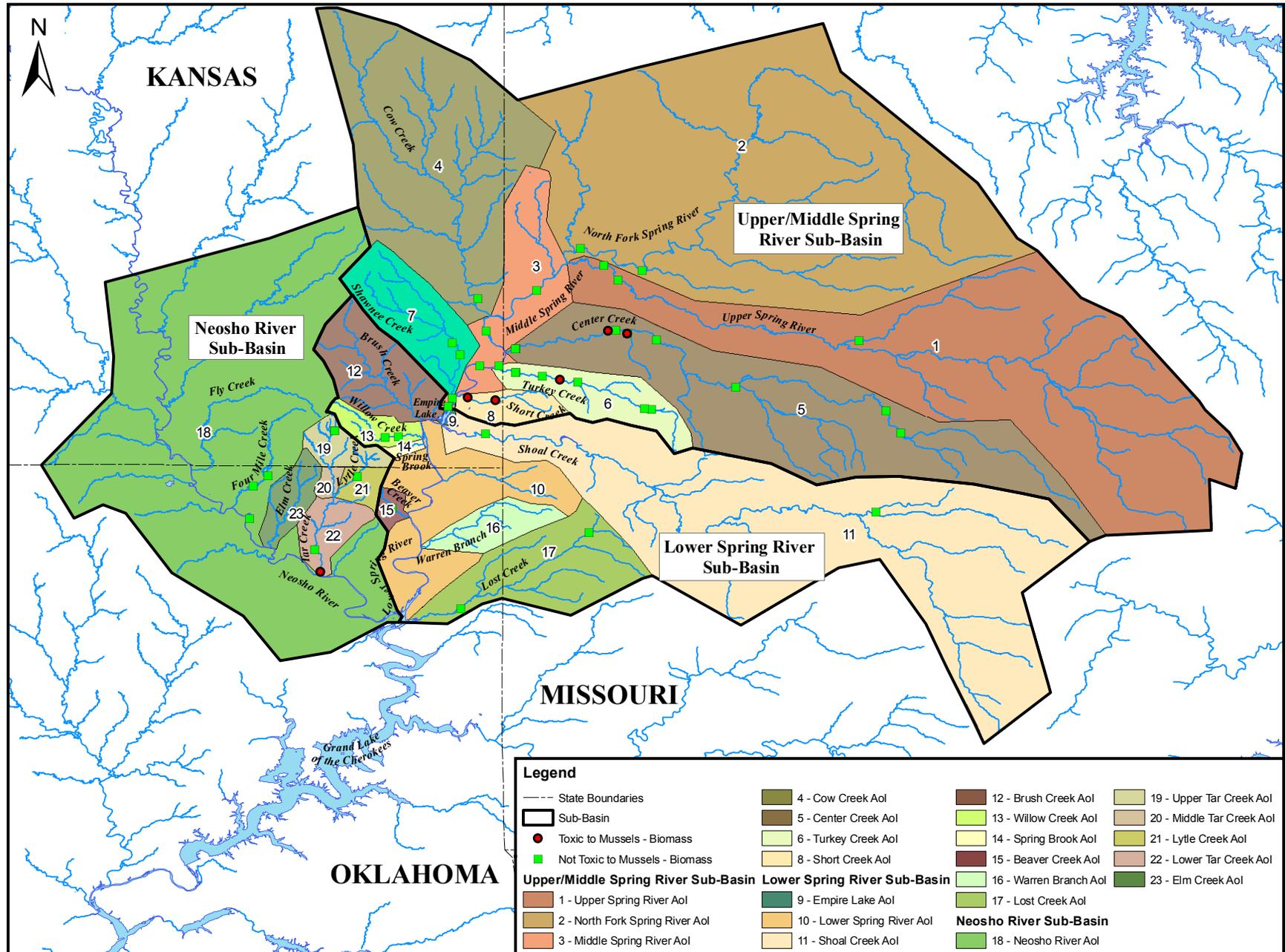


Figure 27. Map of Study Area, showing locations with sediments that were toxic and not toxic to freshwater mussels, *Lampsilis siliquoidea* (Endpoint Measured: Biomass).



0 5 10 20 30 40 50 Kilometers

Figure 28. Map of Study Area, showing locations where exposure to sediment poses low, moderate, or high risk to benthic invertebrates, based on toxicity to the amphipod, *Hyaella azteca* (Endpoint Measured: Survival).

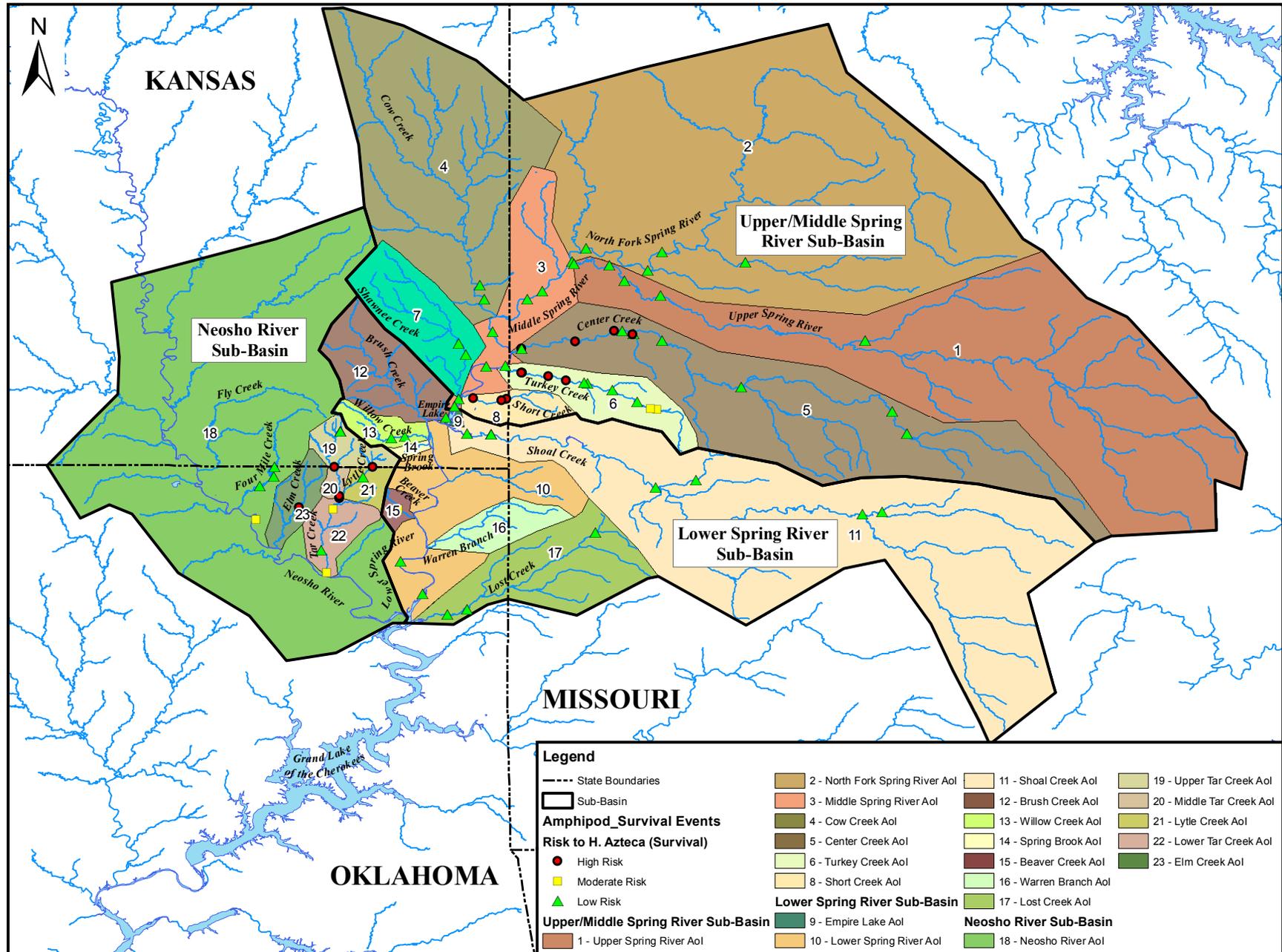


Figure 29. Map of Study Area, showing locations where exposure to sediment poses low, moderate, or high risk to benthic invertebrates, based on toxicity to the amphipod, *Hyaella azteca* (Endpoint Measured: Biomass).

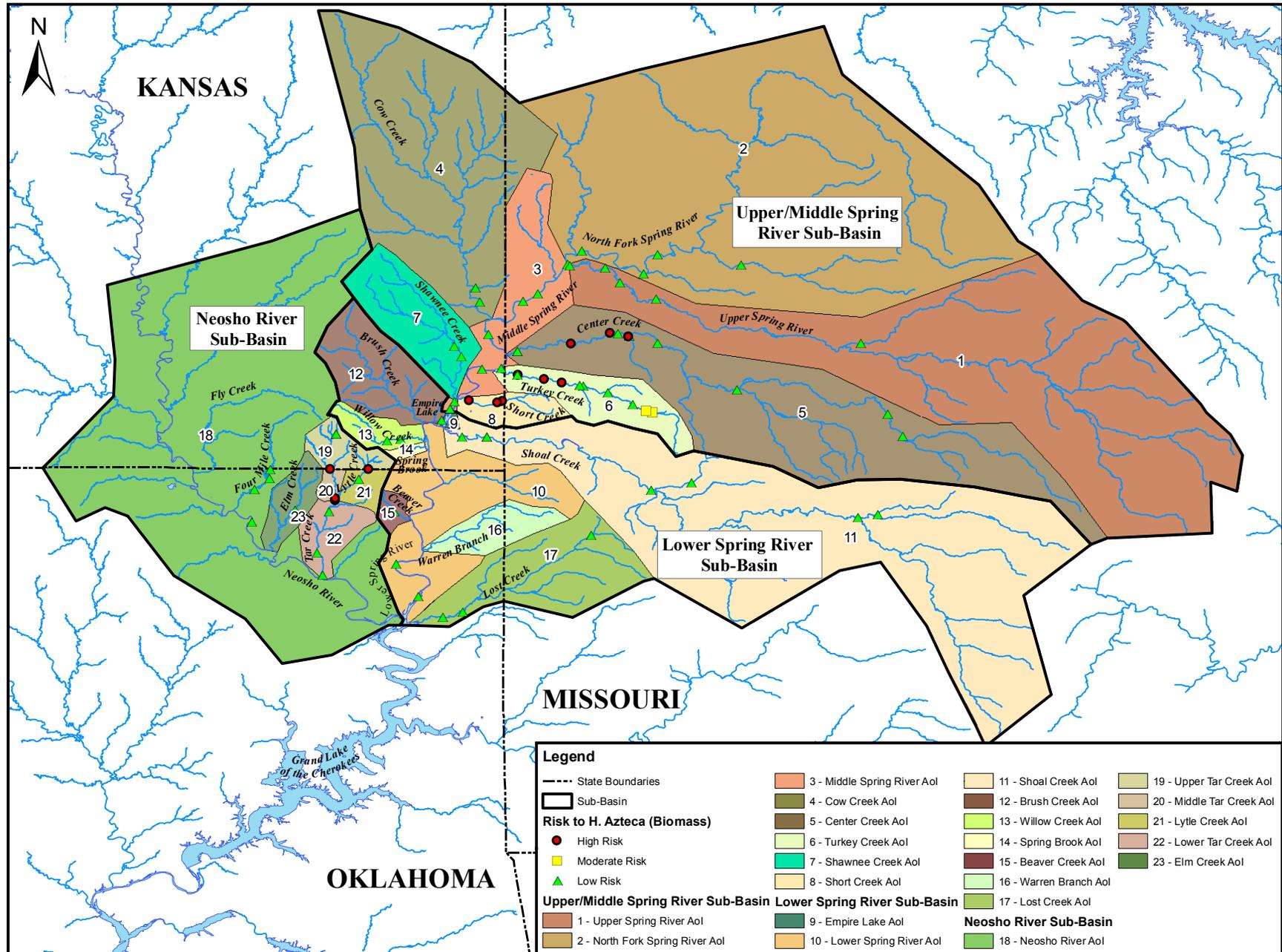


Figure 30. Map of Study Area, showing locations where exposure to sediment poses low, moderate, or high risk to benthic invertebrates, based on toxicity to the midge, *Chironomus dilutus* (Endpoint Measured: Survival).

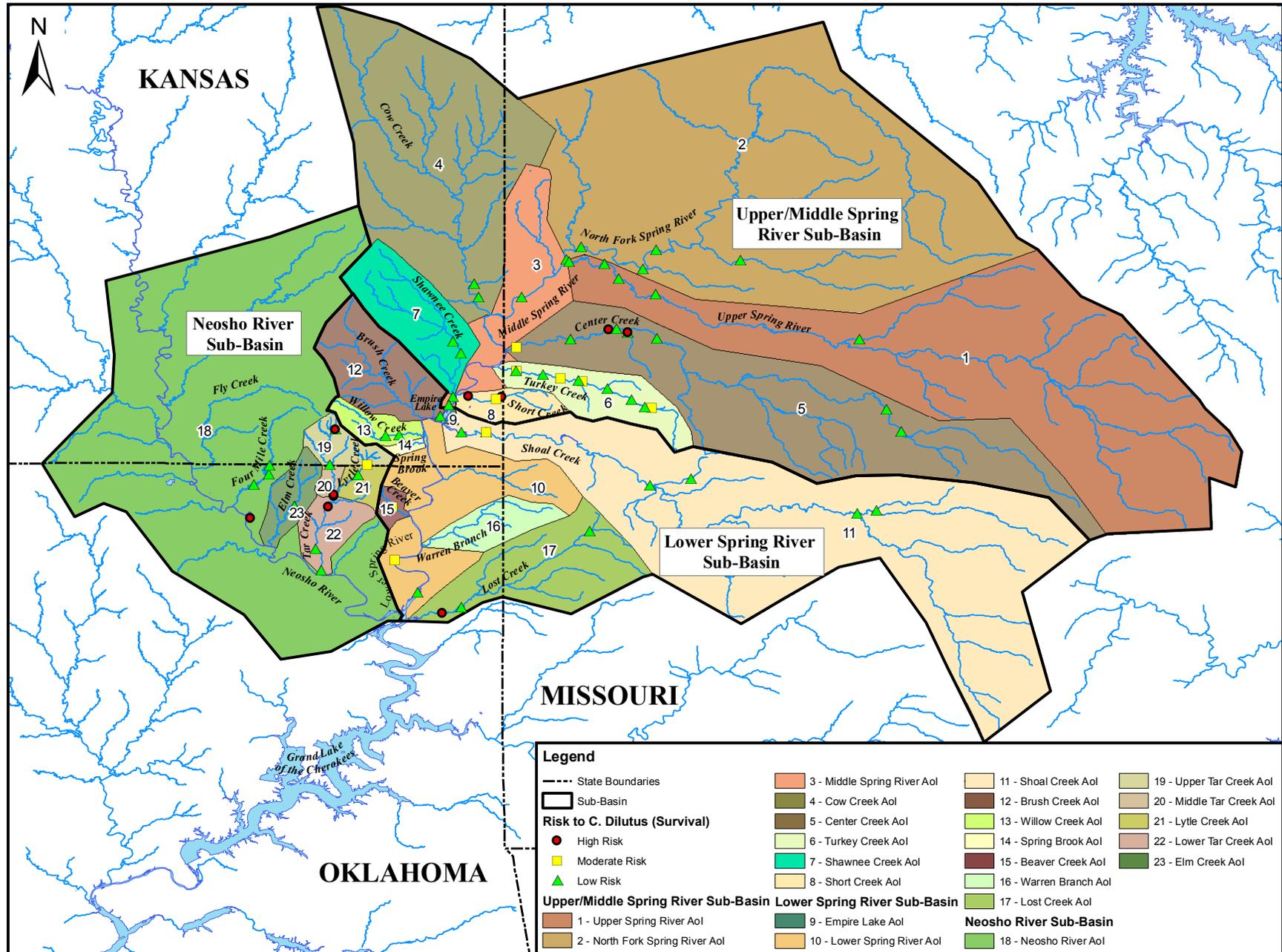


Figure 31. Map of Study Area, showing locations where exposure to sediment poses low, moderate, or high risk to benthic invertebrates, based on toxicity to the midge, *Chironomus dilutus* (Endpoint Measured: Biomass).

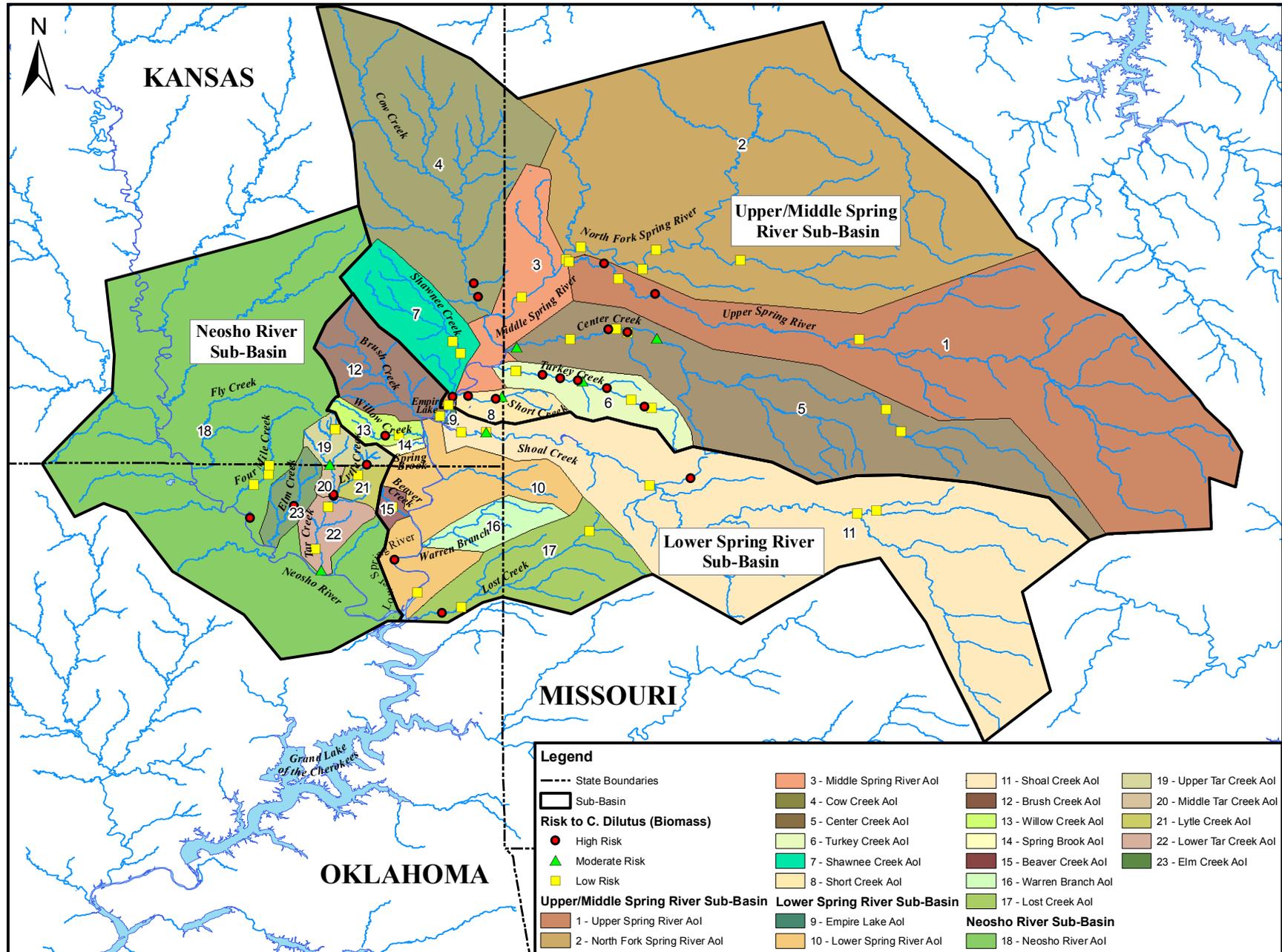


Figure 32. Map of Study Area, showing locations where exposure to sediment poses low, moderate, or high risk to benthic invertebrates, based on toxicity to the mussel, *Lampsilis siliquoides* (Endpoint Measured: Survival).

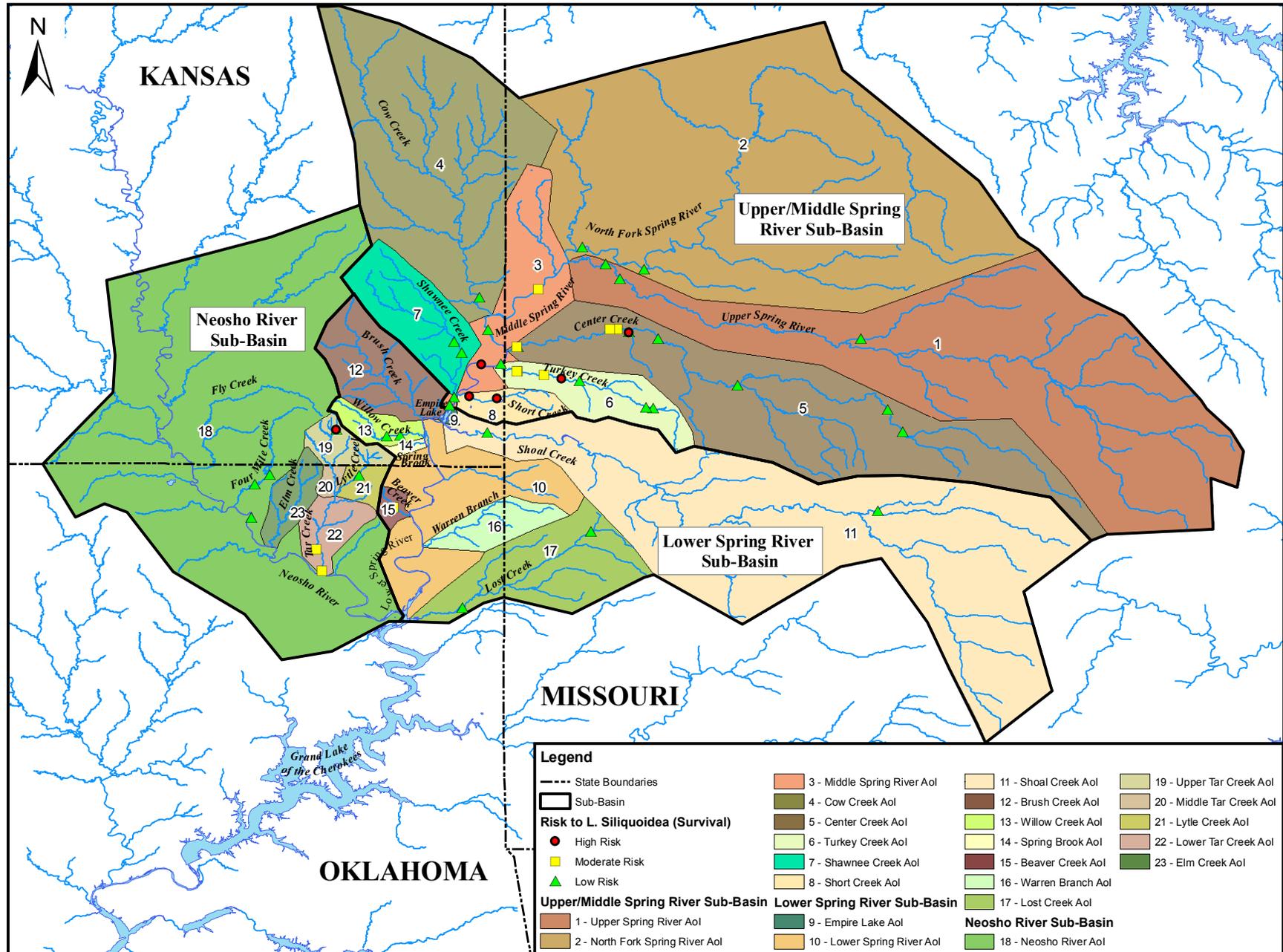


Figure 33. Map of Study Area, showing locations where exposure to sediment poses low, moderate, or high risk to benthic invertebrates, based on toxicity to the mussel, *Lampsilis siliquoidea* (Endpoint Measured: Biomass).

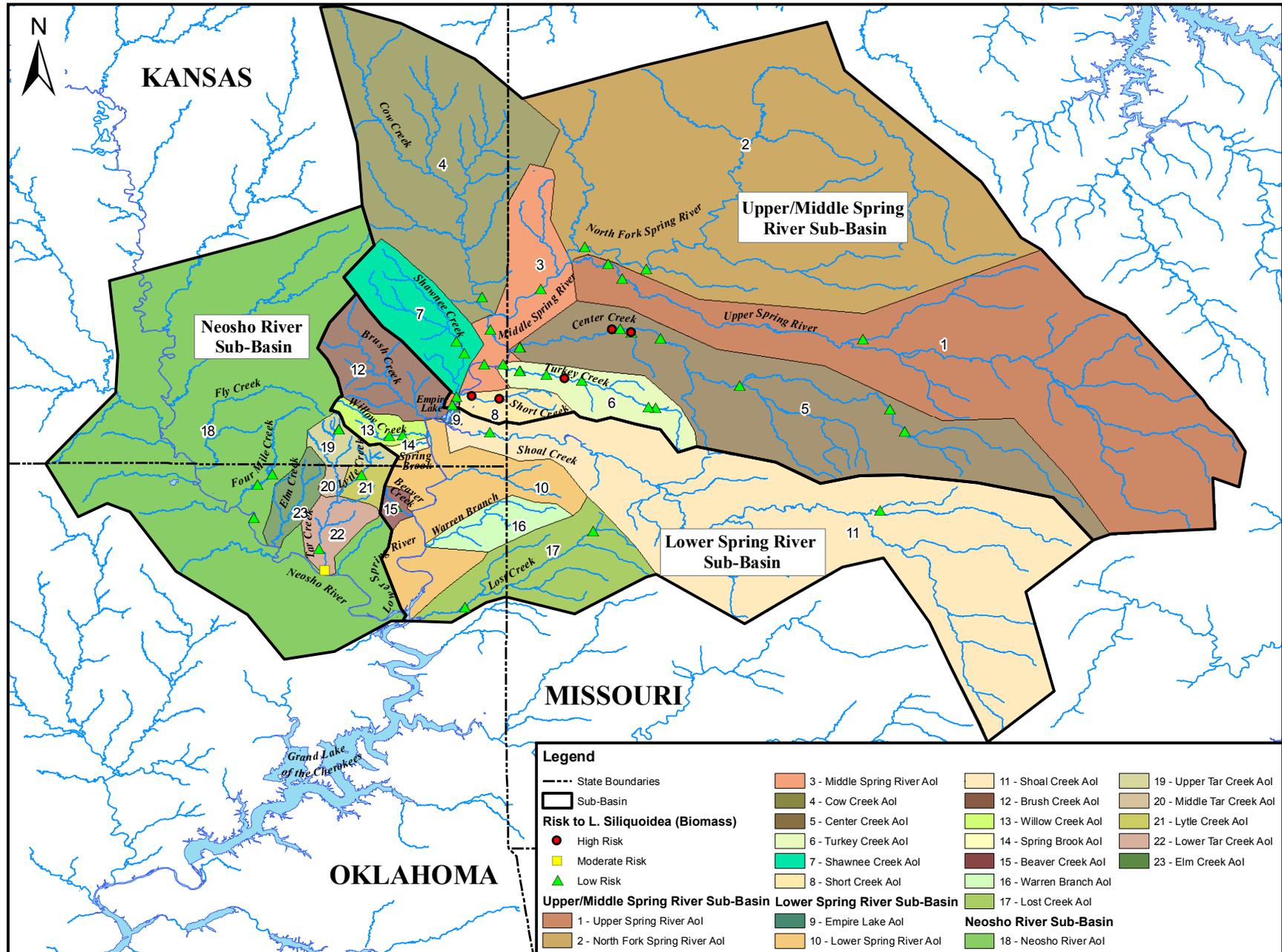


Figure 34. Map of Study Area, showing locations with sediments that are toxic or not toxic to the mussel, *Lampsilis siliquoidea* (Endpoints Measured: Survival or Biomass).

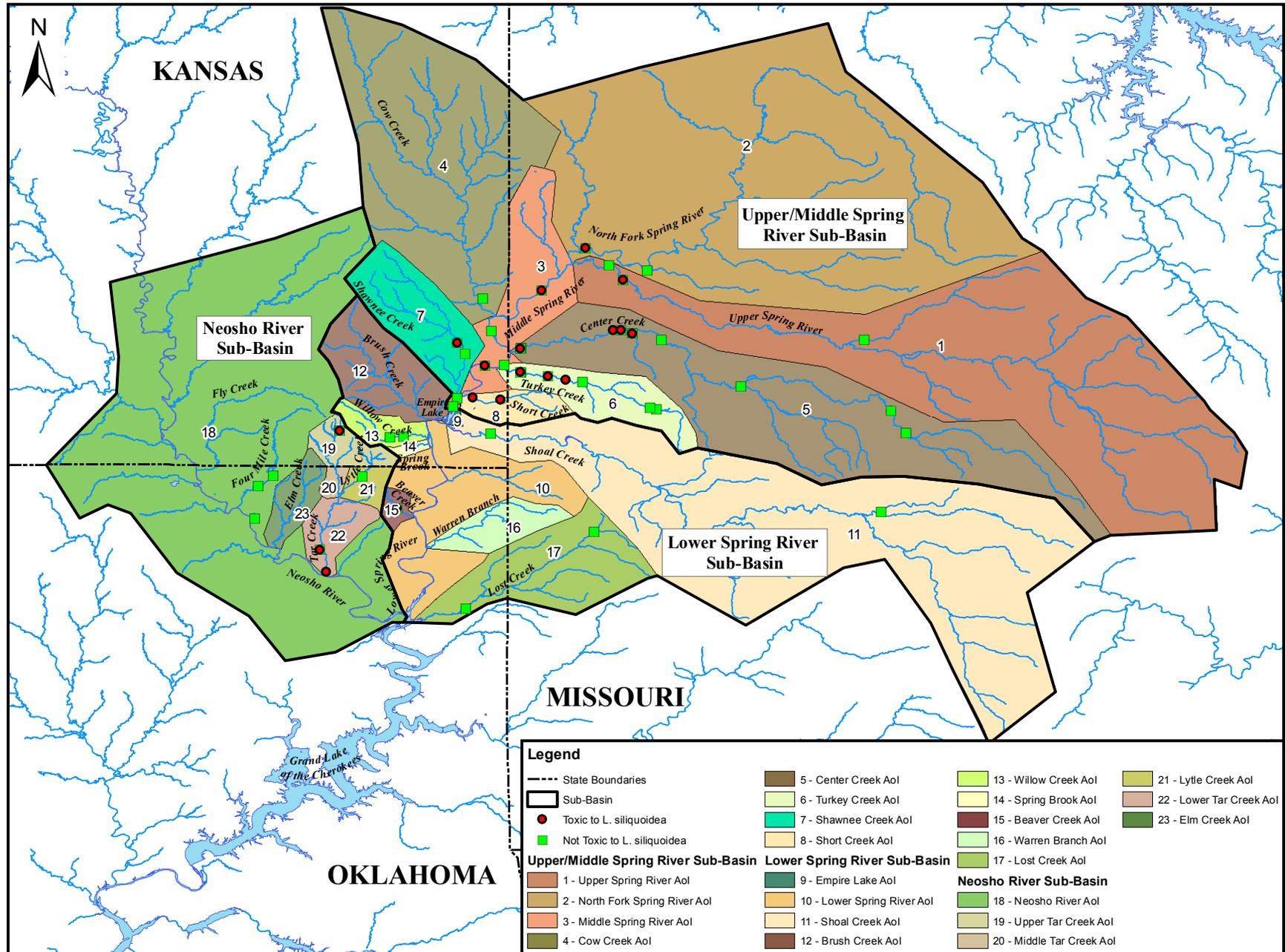


Figure 35. Map of the Upper Spring River AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

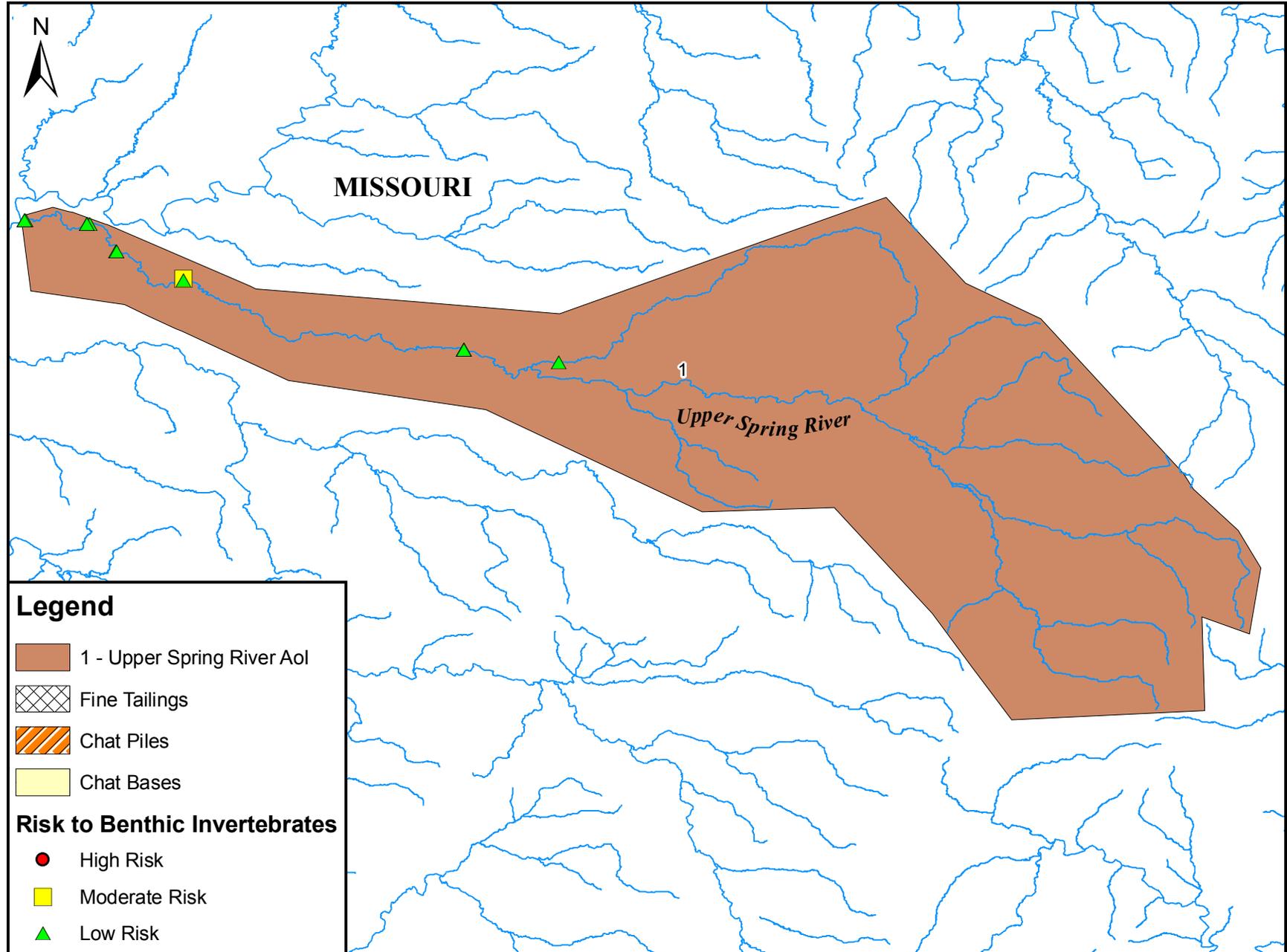
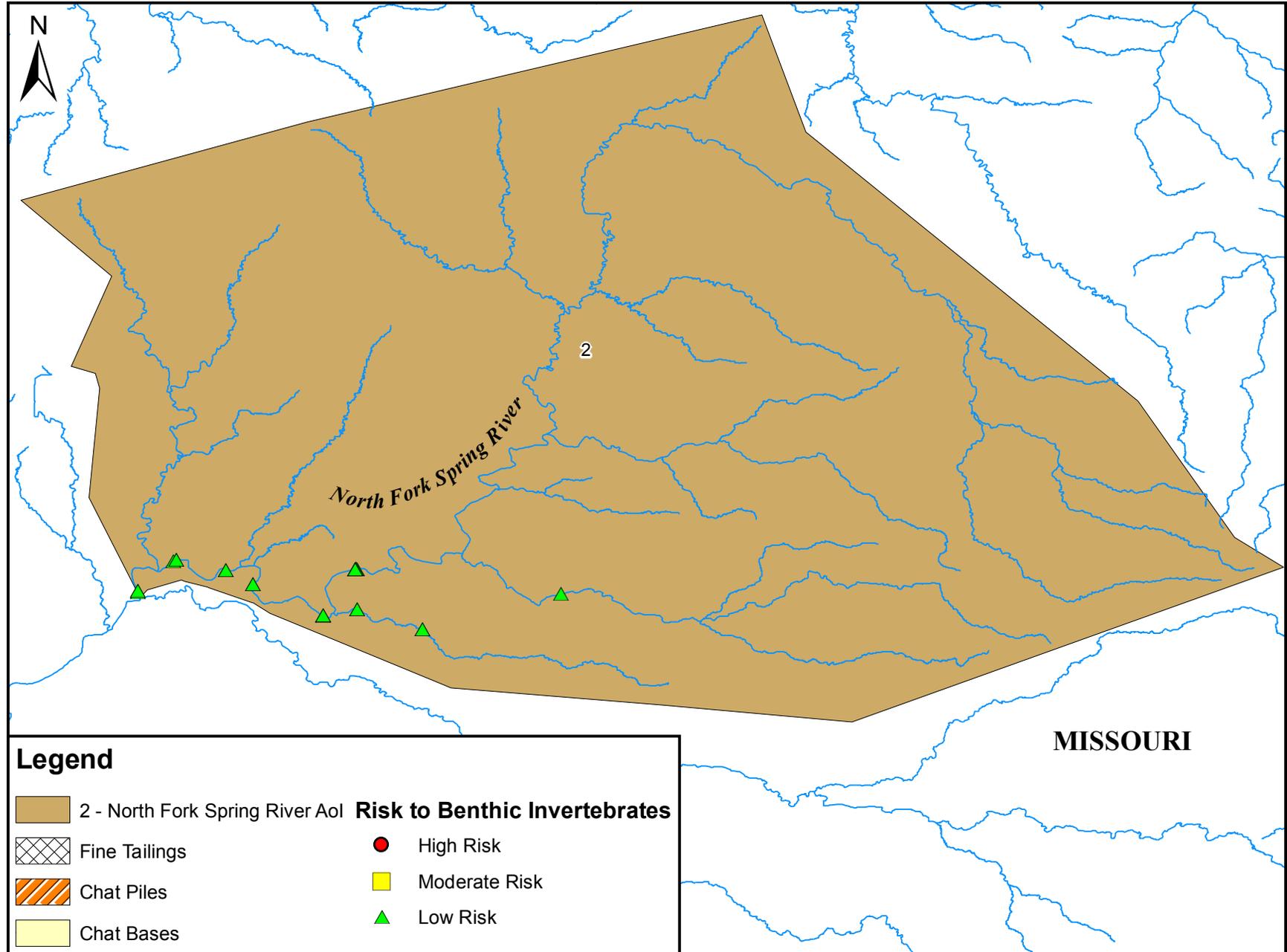


Figure 36. Map of the North Fork Spring River AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.



0 2.5 5 10 15 20 Kilometers

Figure 37. Map of the Middle Spring River AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

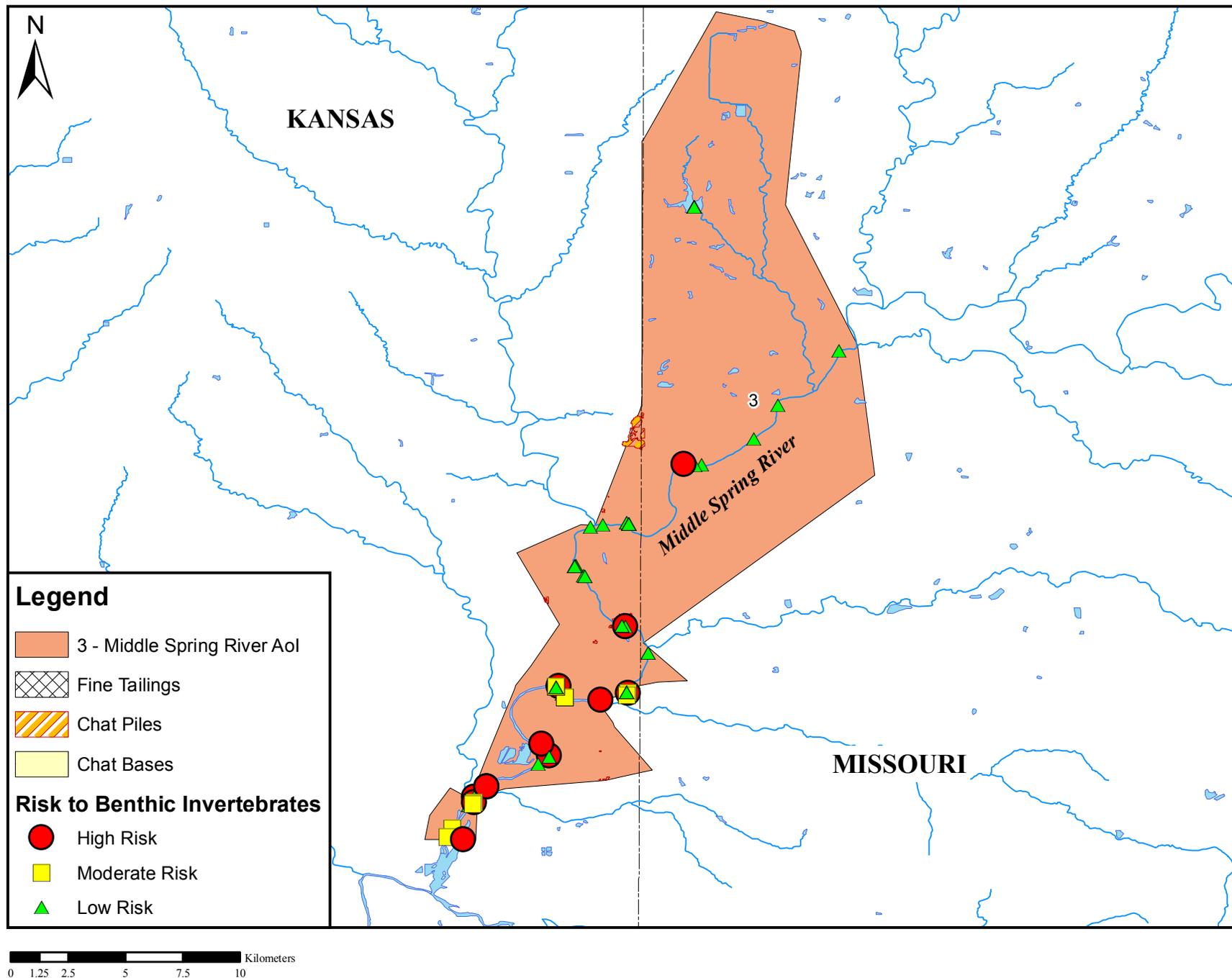


Figure 38. Map of the Cow Creek AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

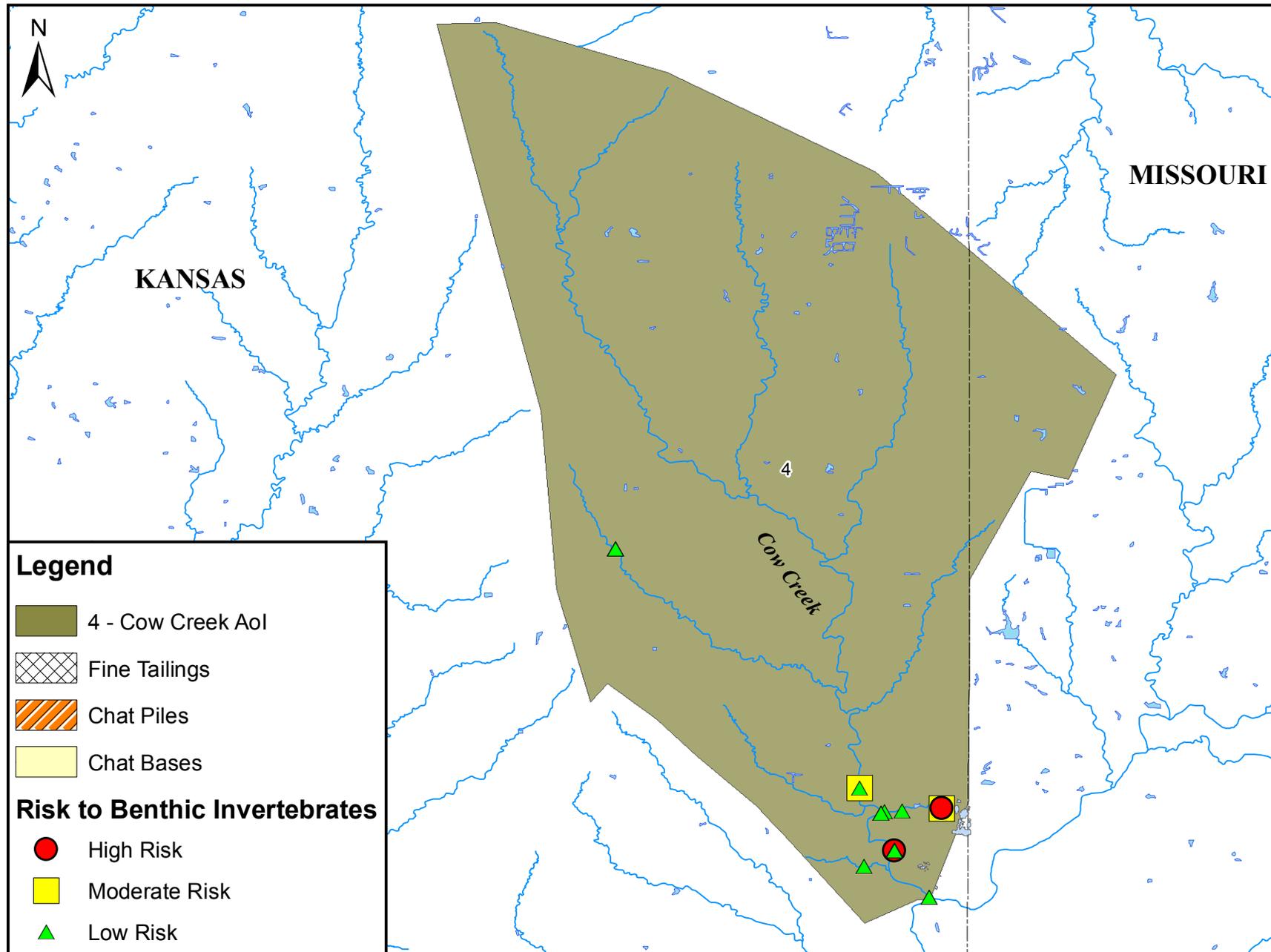


Figure 39. Map of the Center Creek AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

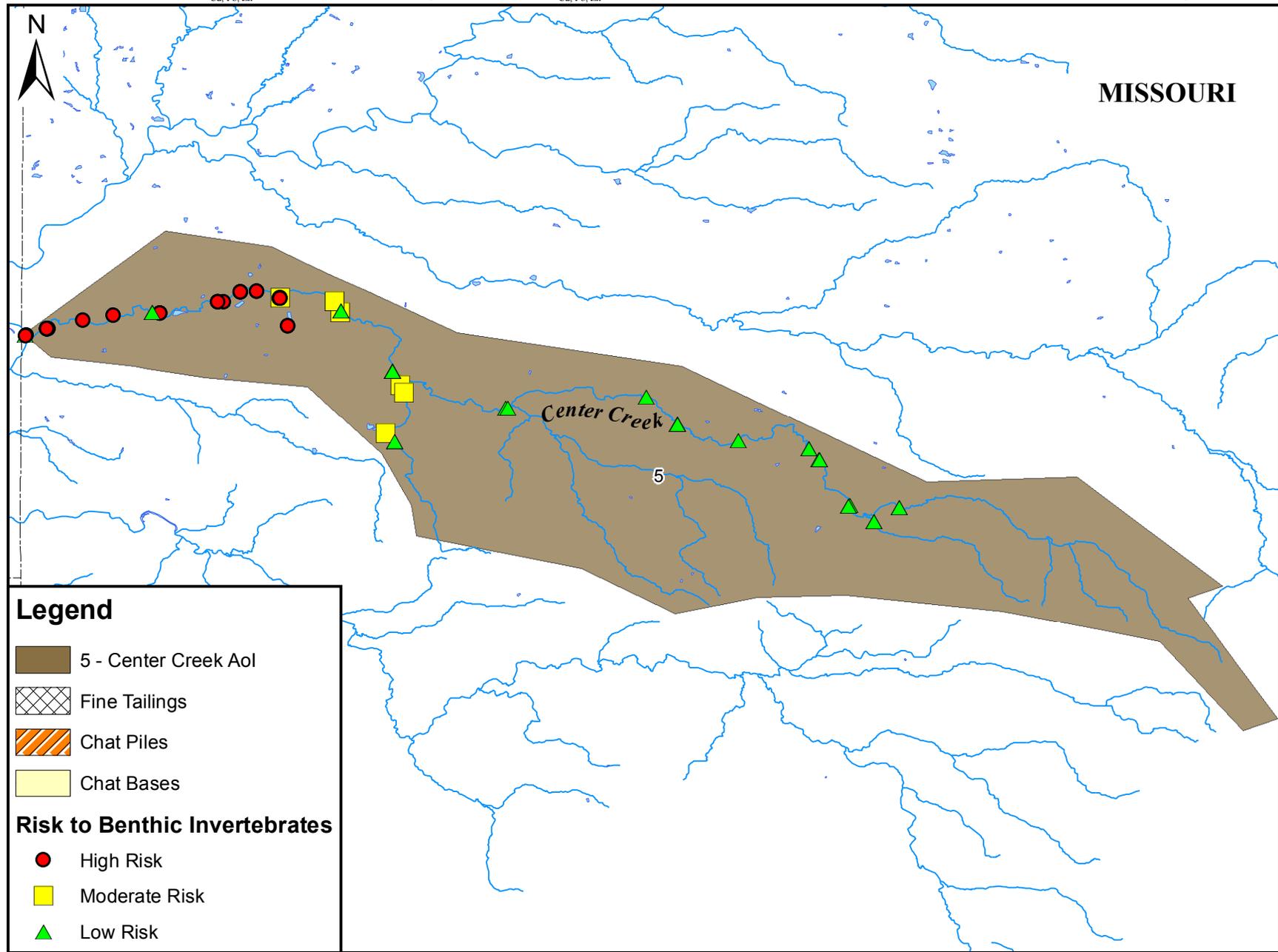


Figure 40. Map of the Turkey Creek AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

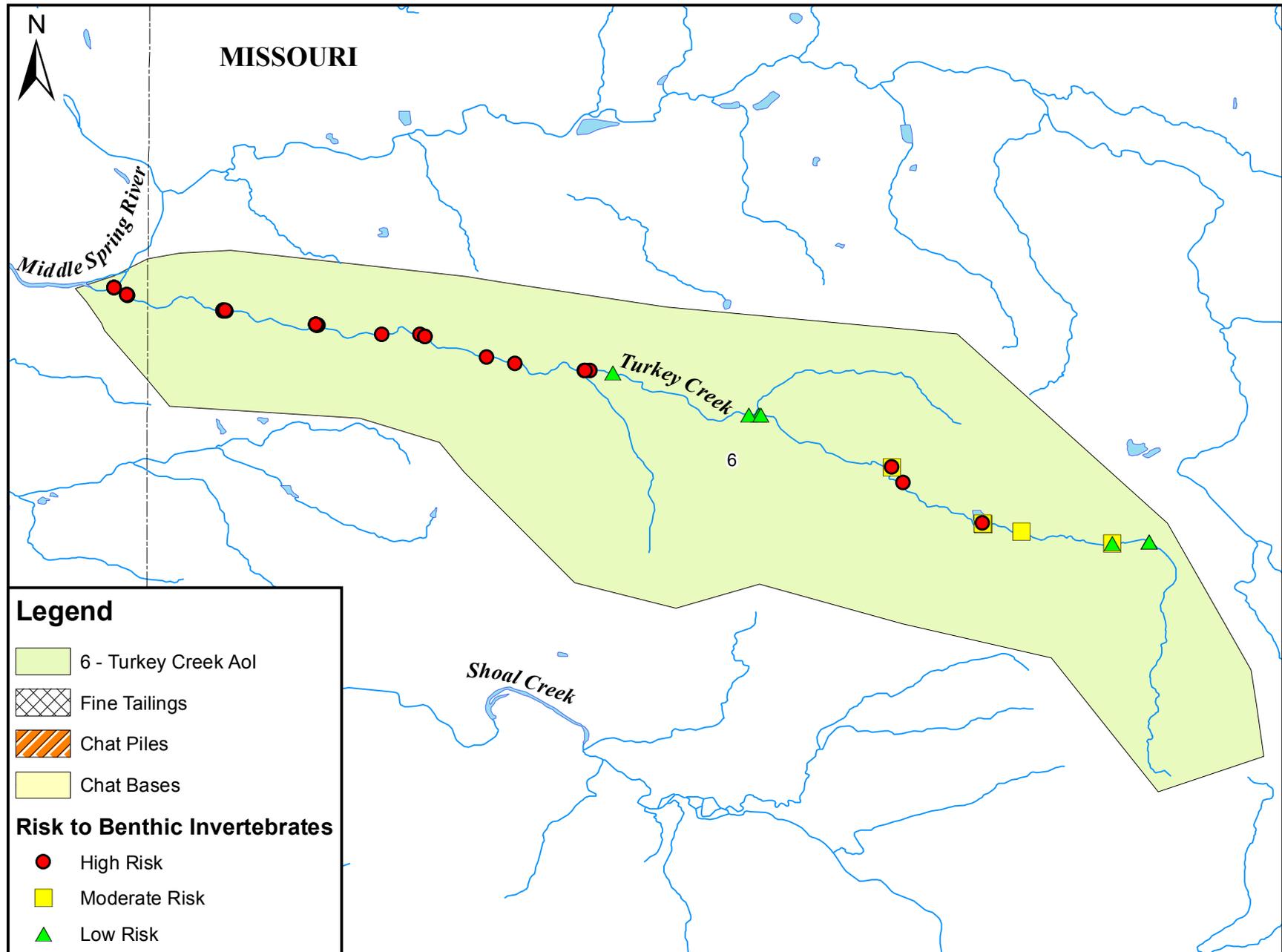


Figure 41. Map of the Shawnee Creek Aol, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

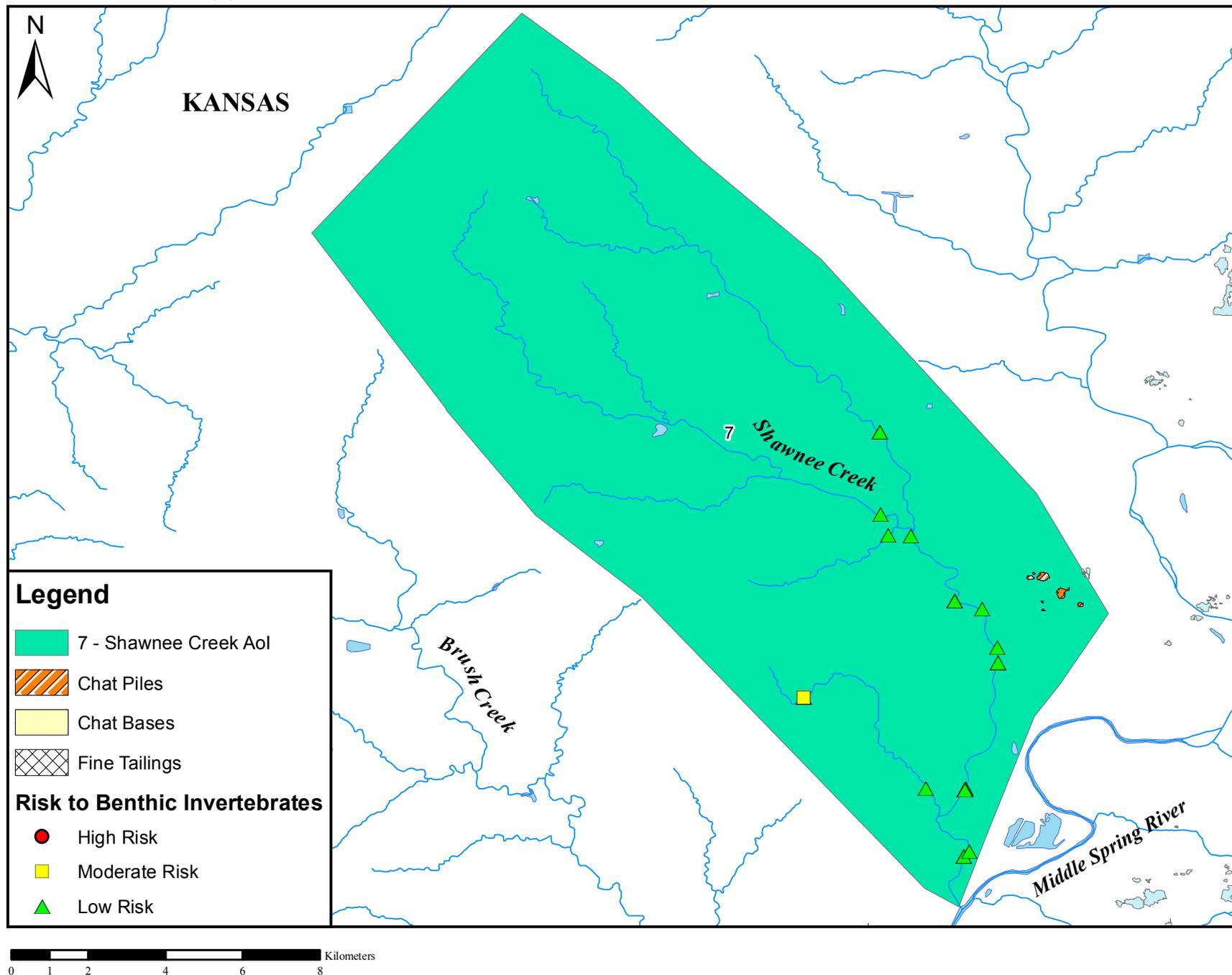


Figure 42. Map of the Short Creek AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

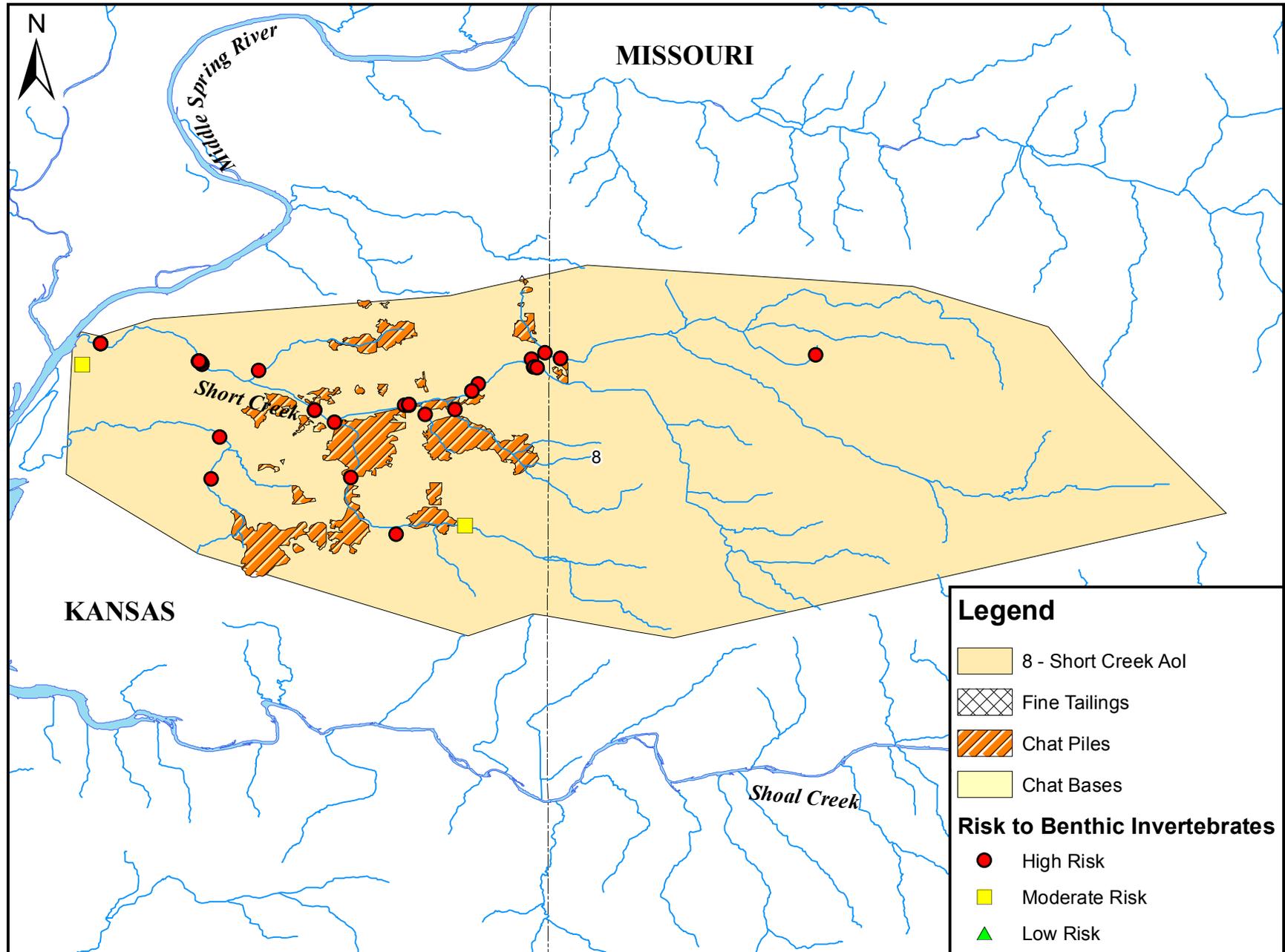


Figure 43. Map of Study Area, showing locations where exposure to pore water poses low ($\sum \text{PW-TU}_{\text{Zn}} < 0.581$), moderate ($\sum \text{PW-TU}_{\text{Zn}} 0.581 - 0.867$), or high ($\sum \text{PW-TU}_{\text{Zn}} > 0.867$) risks to the benthic community in the Tri-State Mining District.

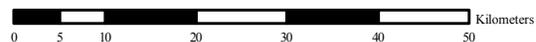
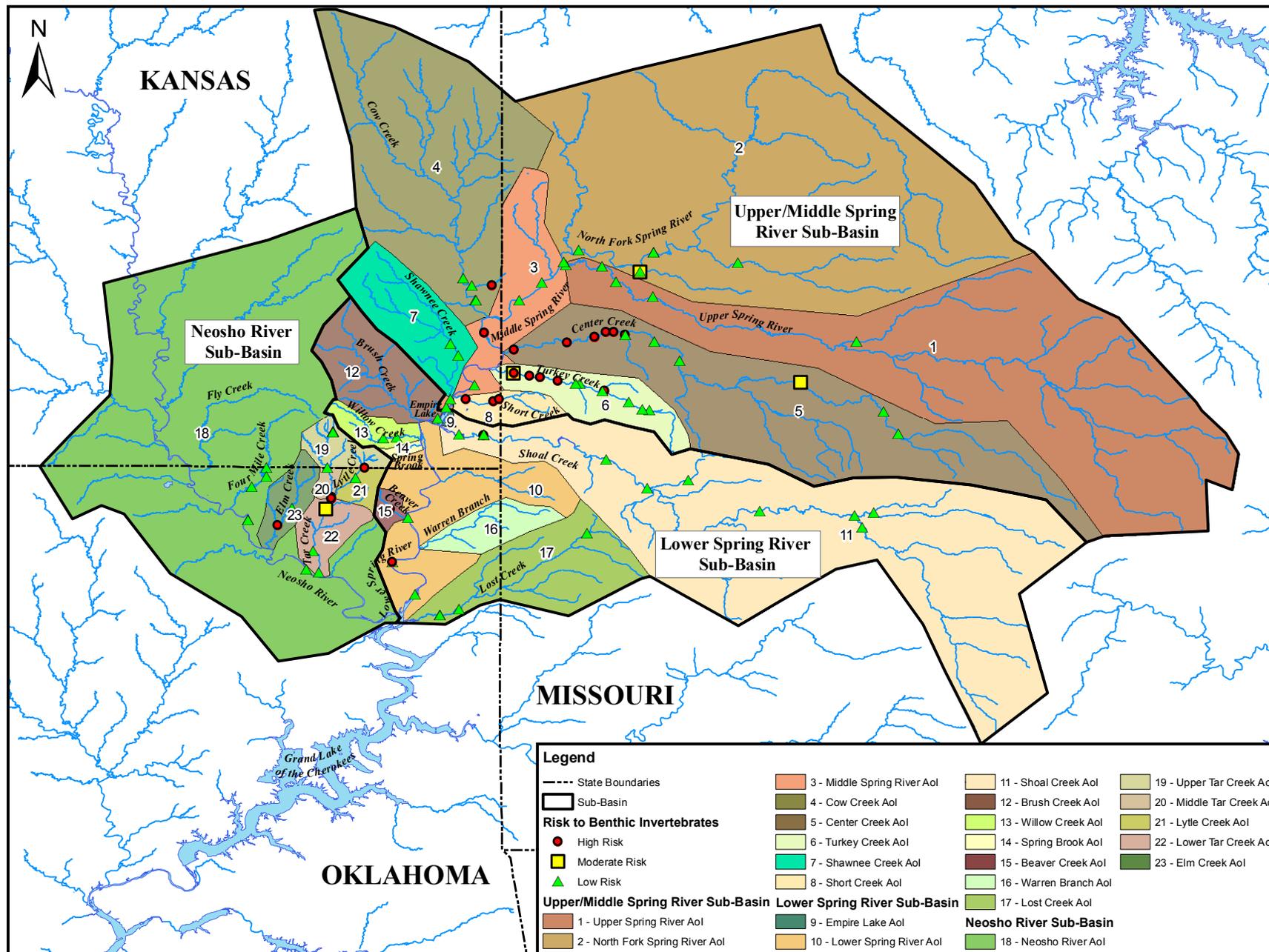


Figure 44. Map of Study Area, showing locations with sediments that are toxic or not toxic to the midge, *Chironomus dilutus* (Endpoints Measured: Survival or Biomass).

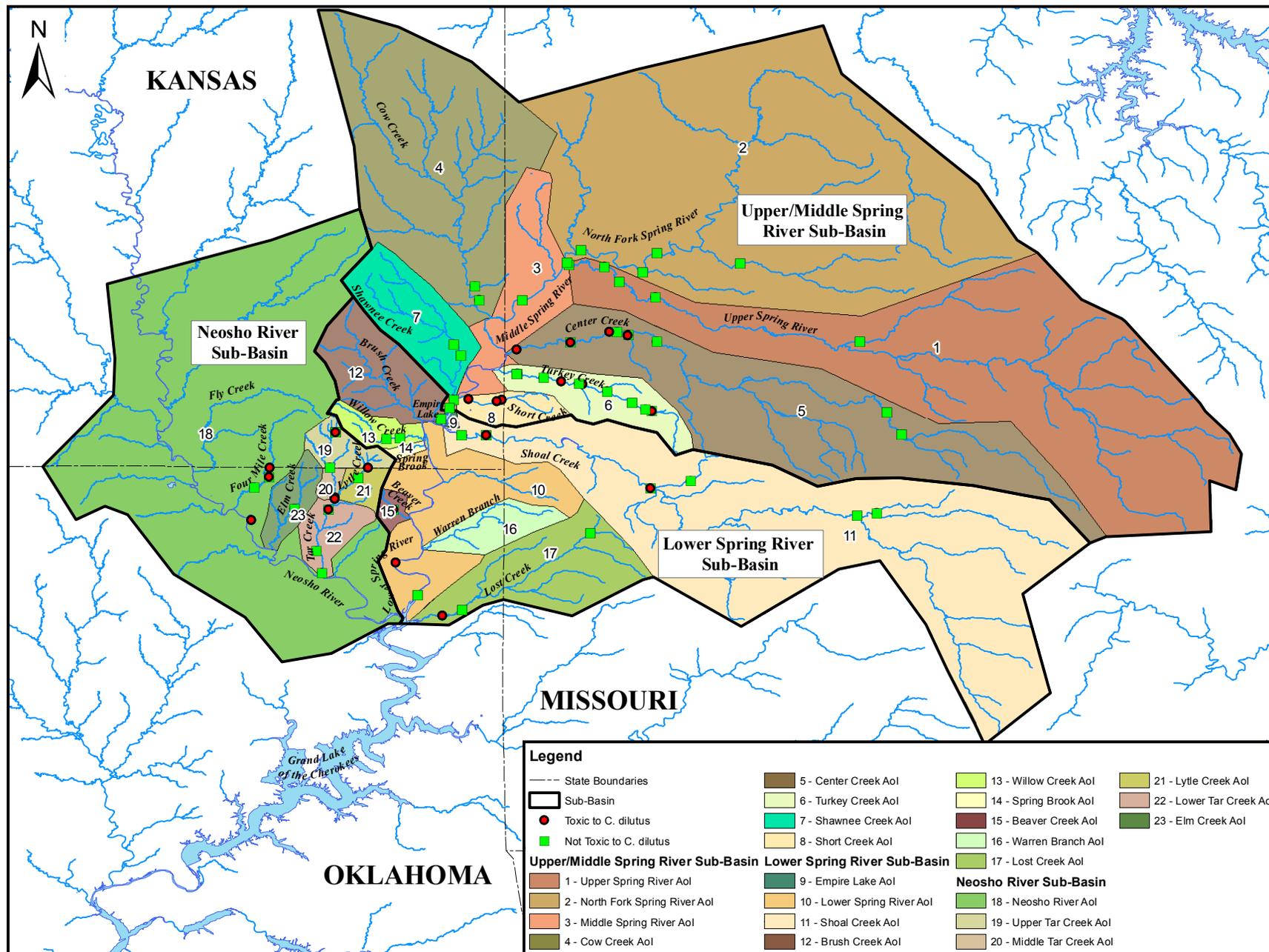


Figure 46. Map of the Empire Lake AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

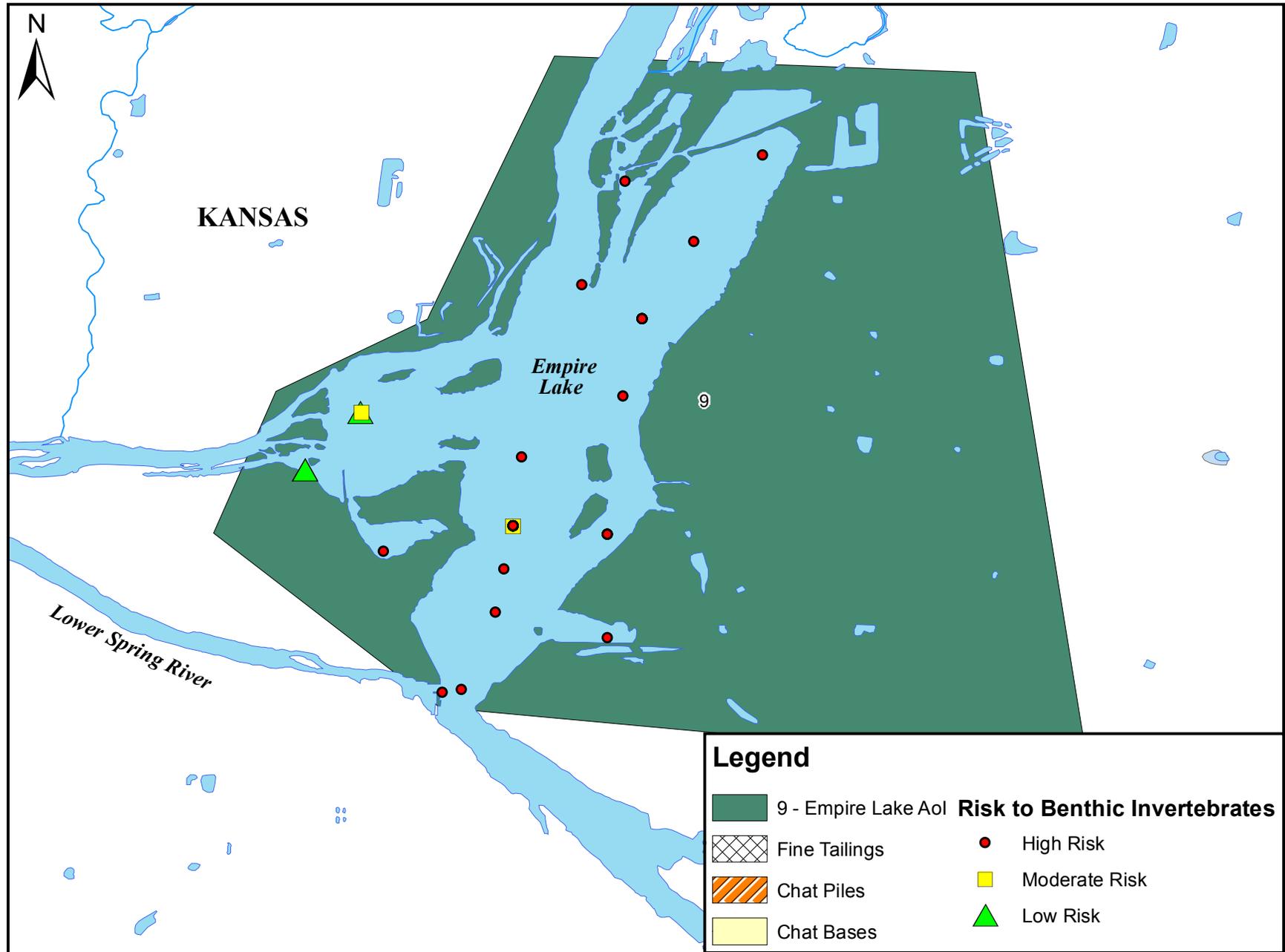


Figure 47. Map of the Lower Spring River AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

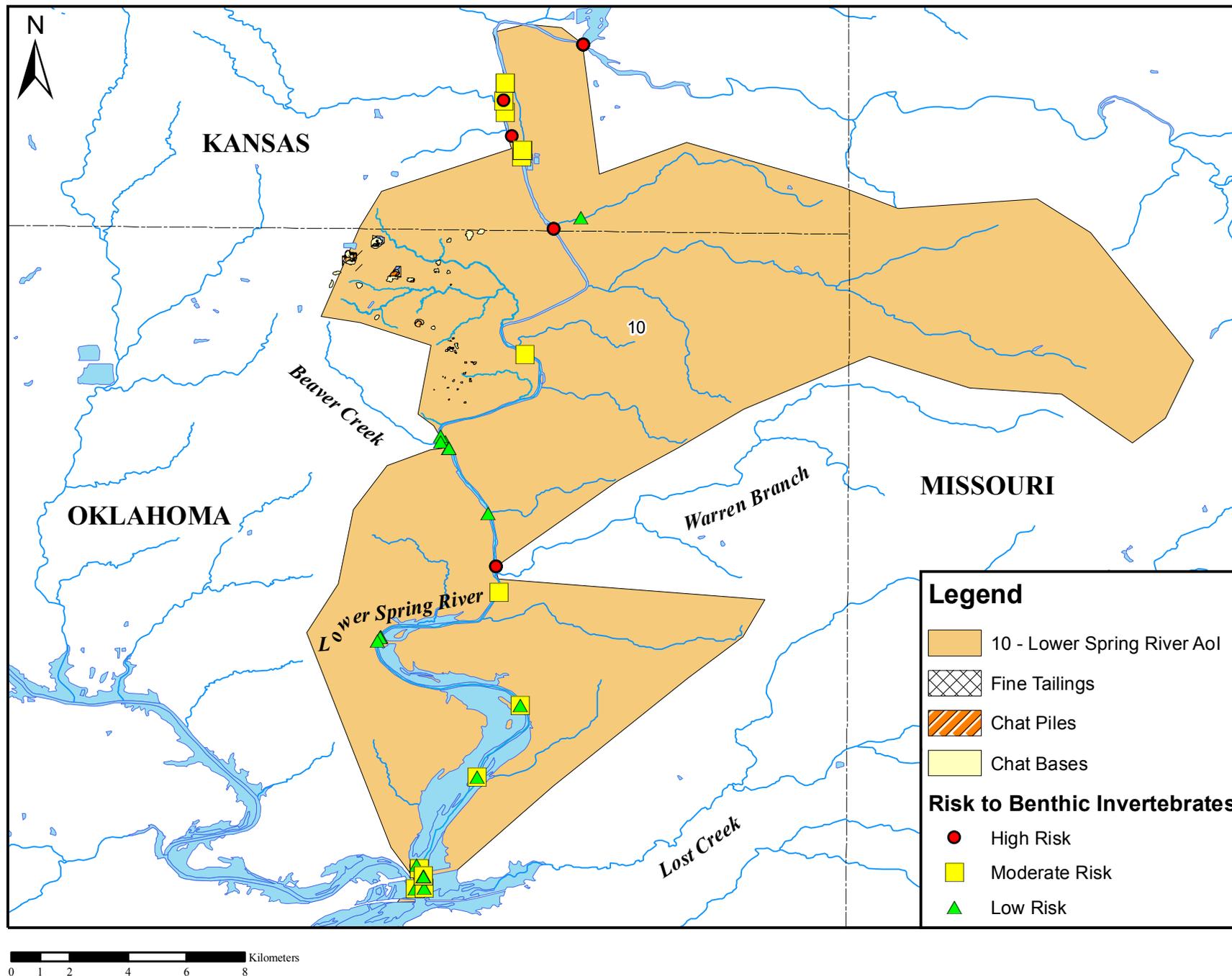
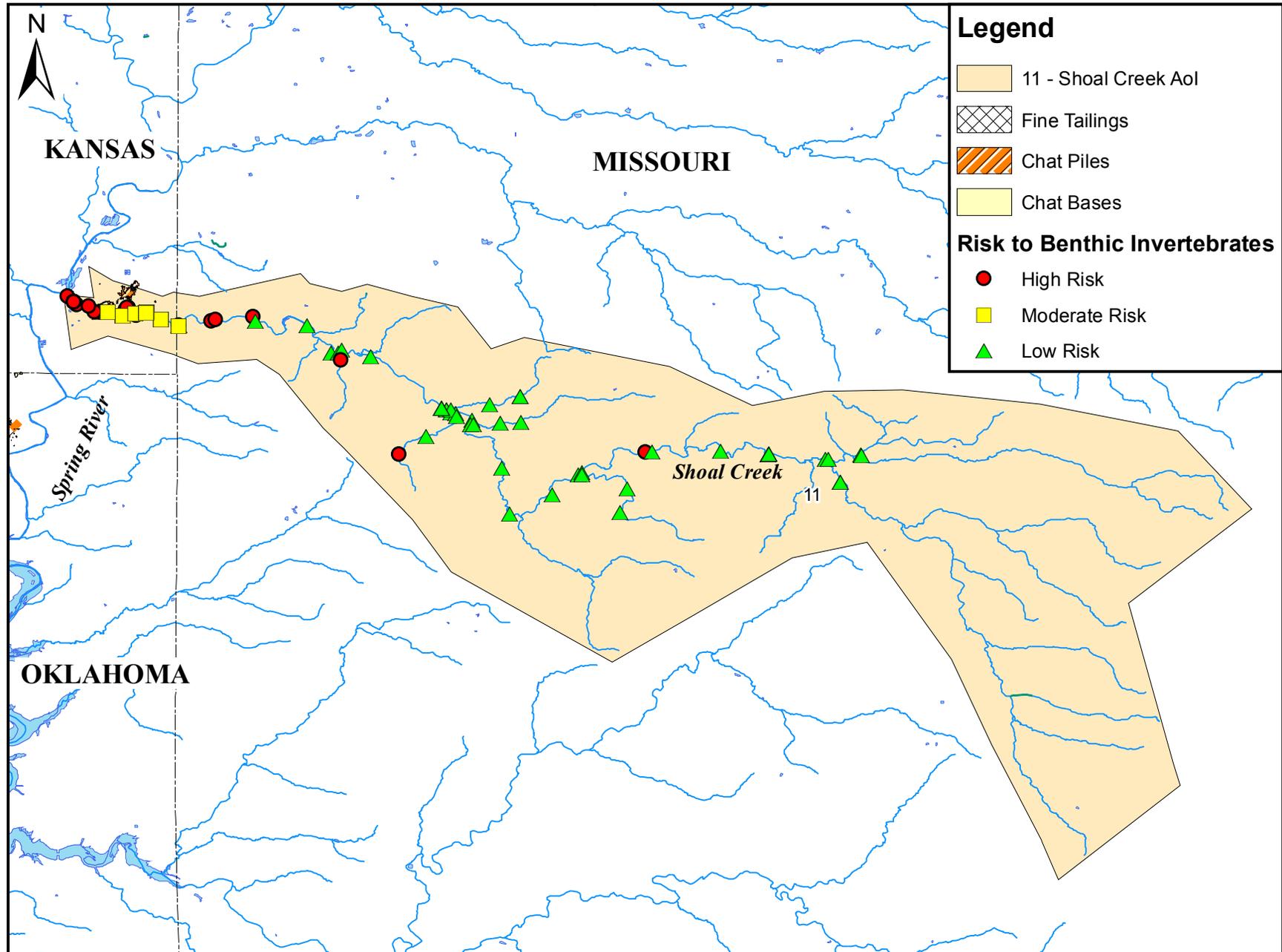


Figure 48. Map of the Shoal Creek AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.



0 2.5 5 10 15 20 Kilometers

Figure 49. Map of the Brush Creek AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

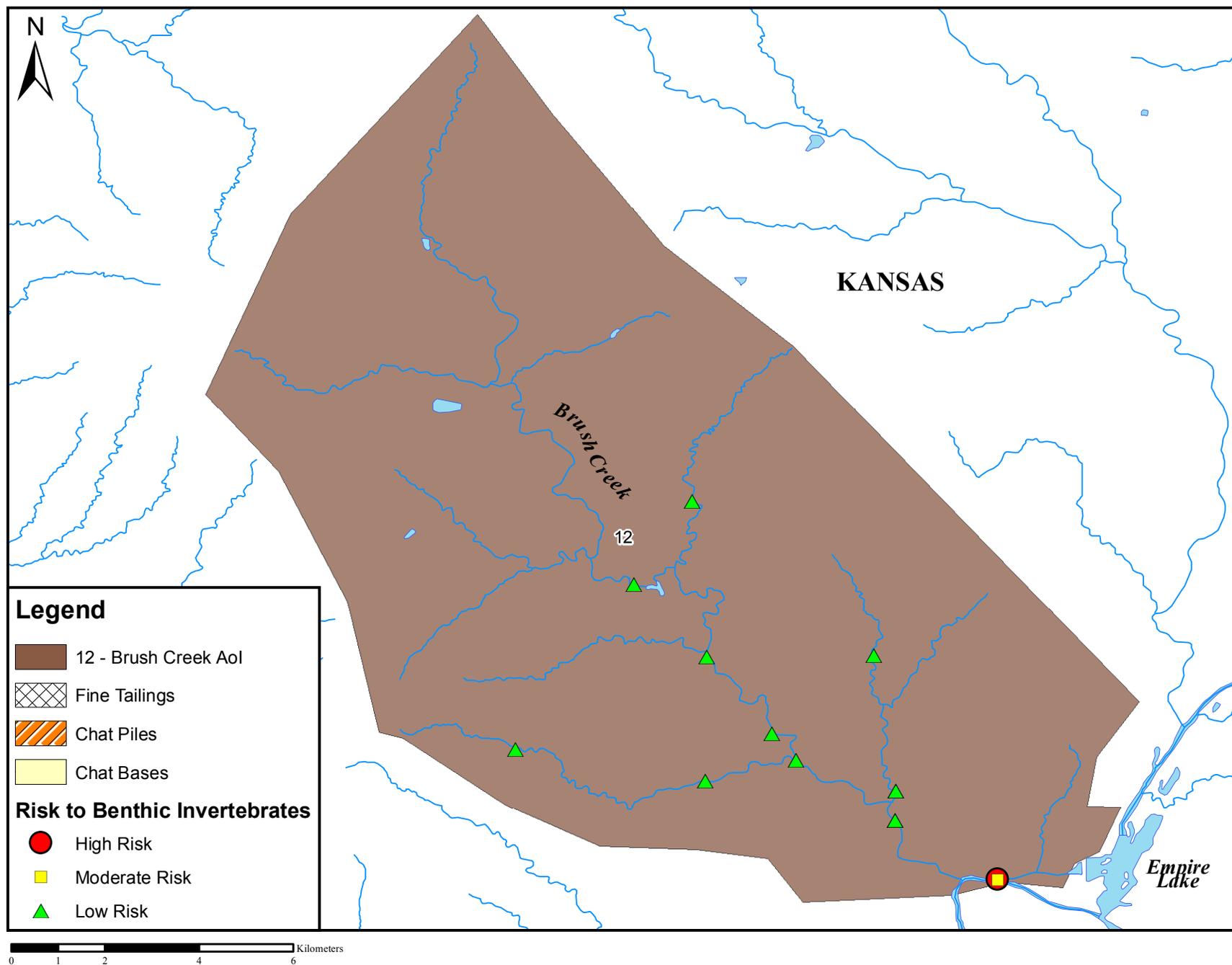


Figure 50. Map of the Willow Creek AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

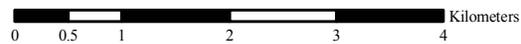
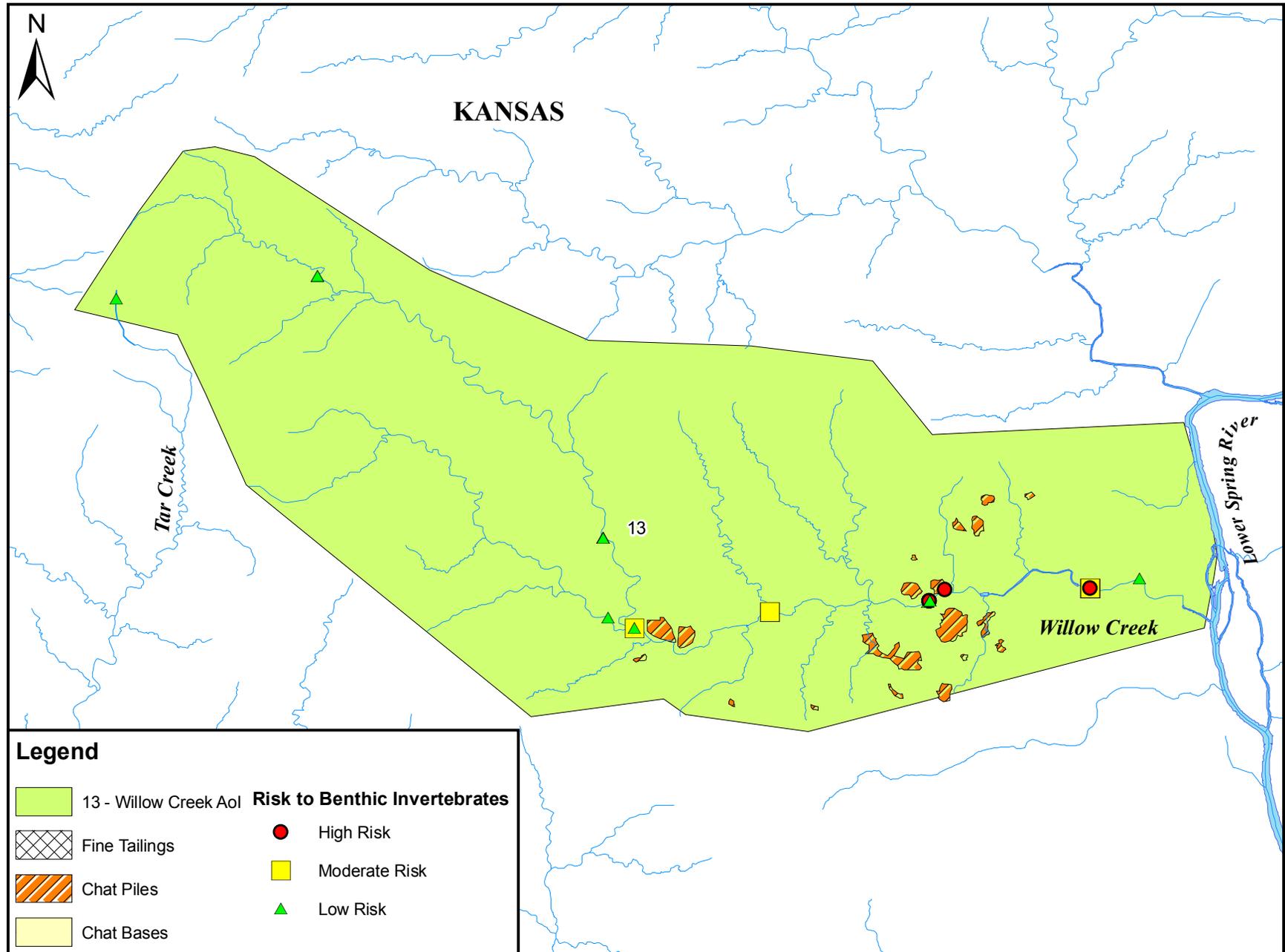


Figure 51. Map of the Spring Brook AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

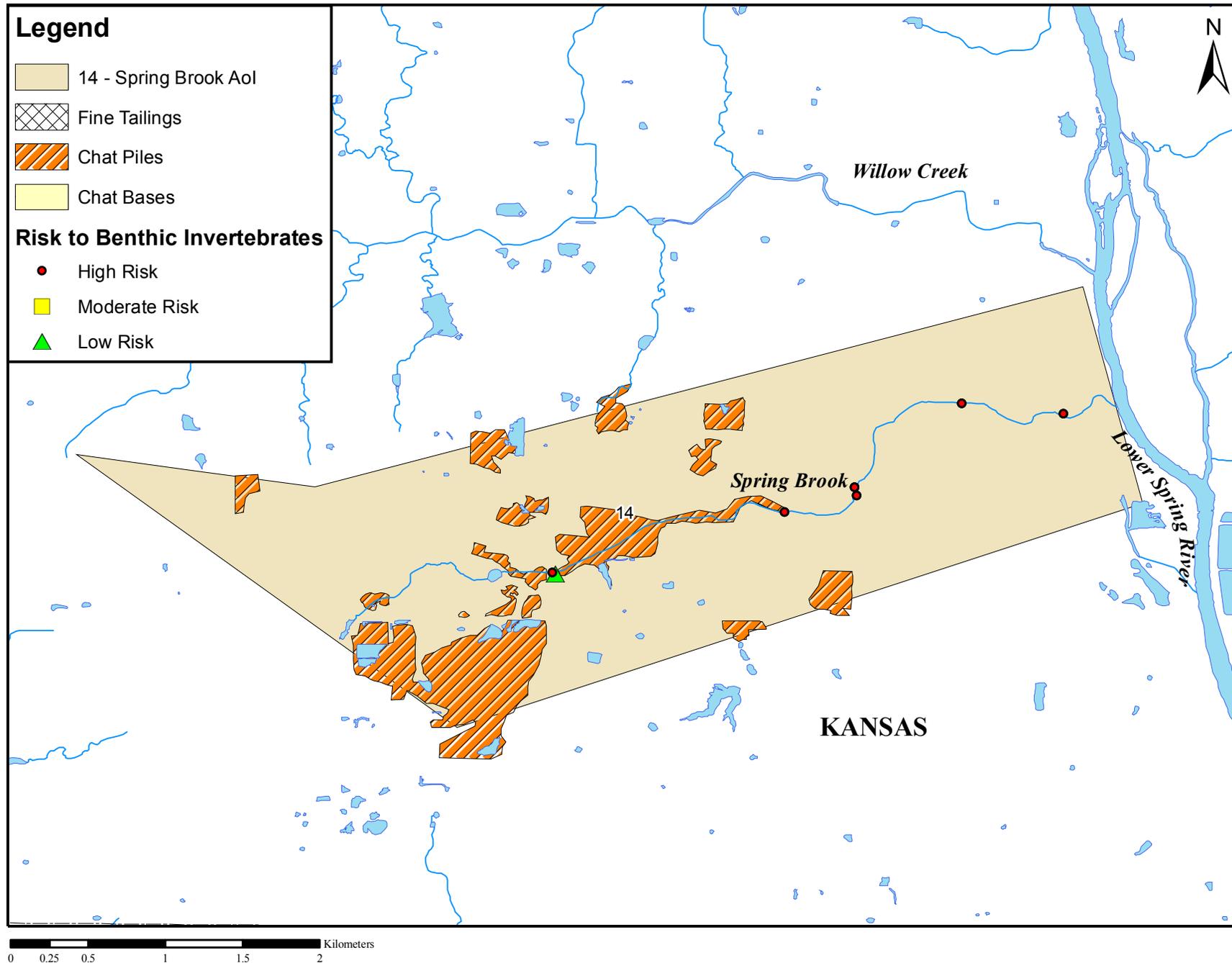


Figure 52. Map of the Beaver Creek AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

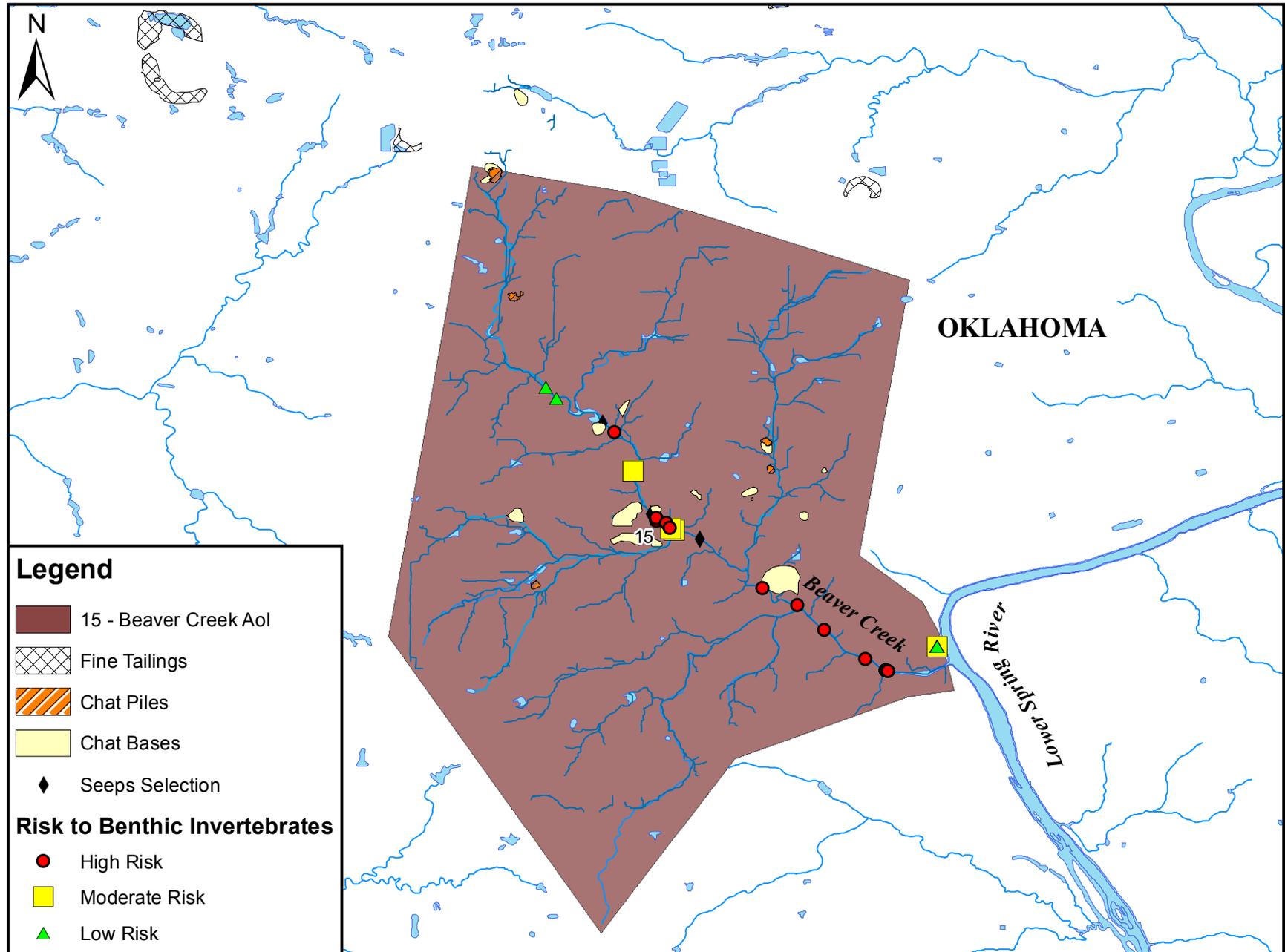


Figure 53. Map of the Warren Branch Aol, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

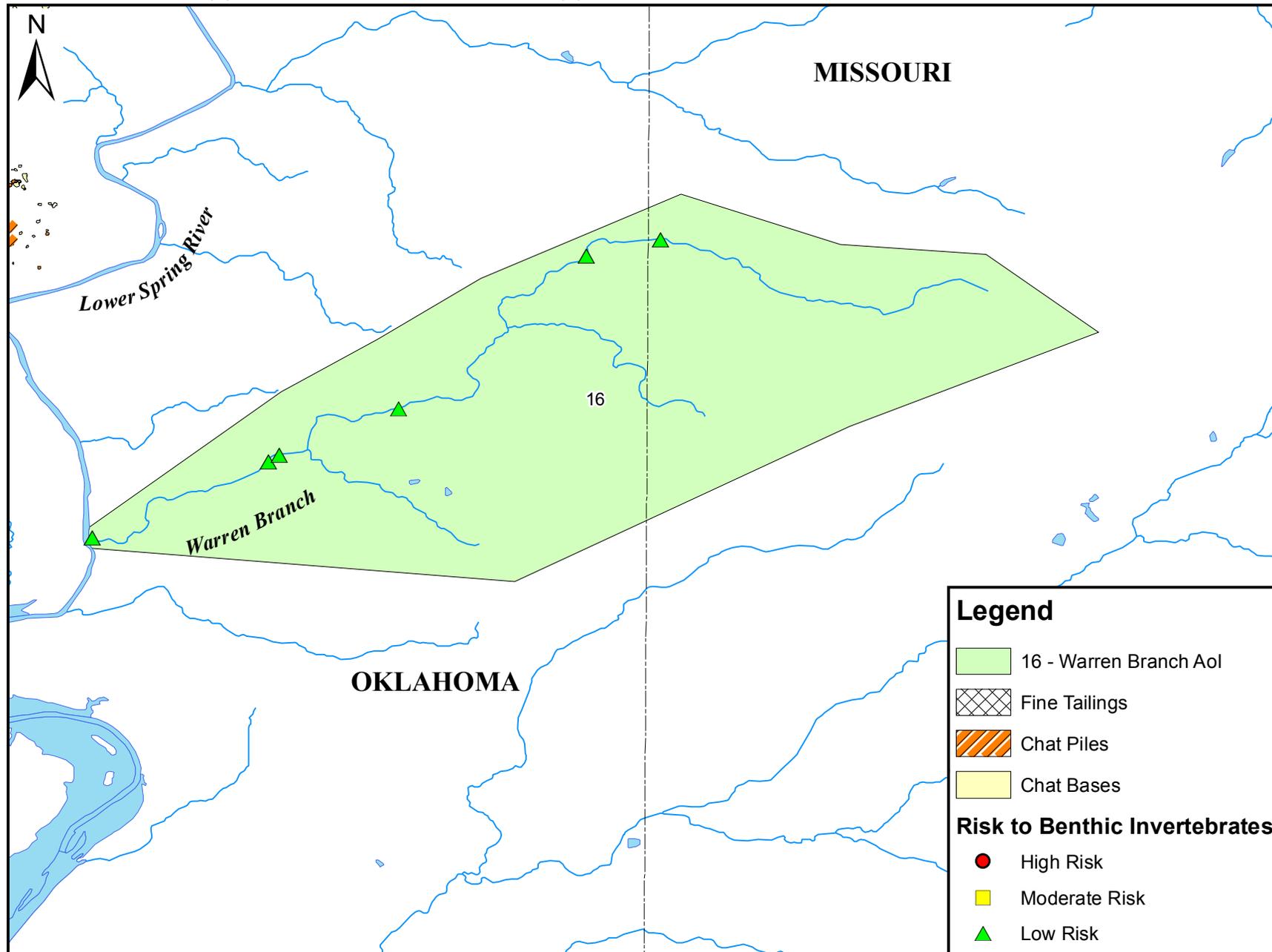


Figure 54. Map of the Lost Creek AoI, showing locations where exposure to sediment poses low ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} < 6.47$), moderate ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} 6.47 - 10.04$), or high ($\sum \text{PEC-Q}_{\text{Cd, Pb, Zn}} > 10.04$) risks to the benthic community in the Tri-State Mining District.

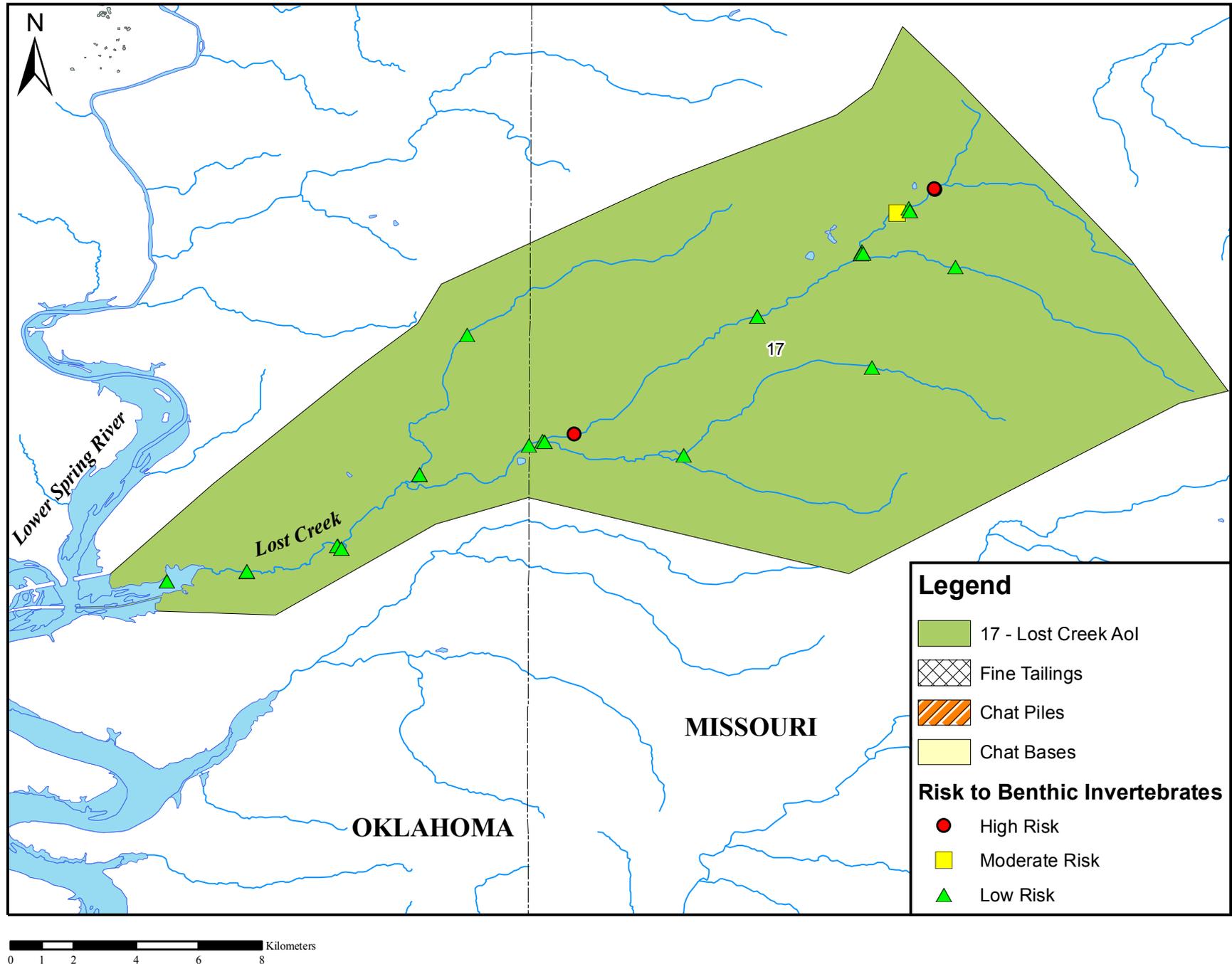


Figure 55. Map of Study Area, showing locations with sediments that are toxic or not toxic to the amphipod, *Hyaella azteca* (Endpoints Measured: Survival or Biomass).

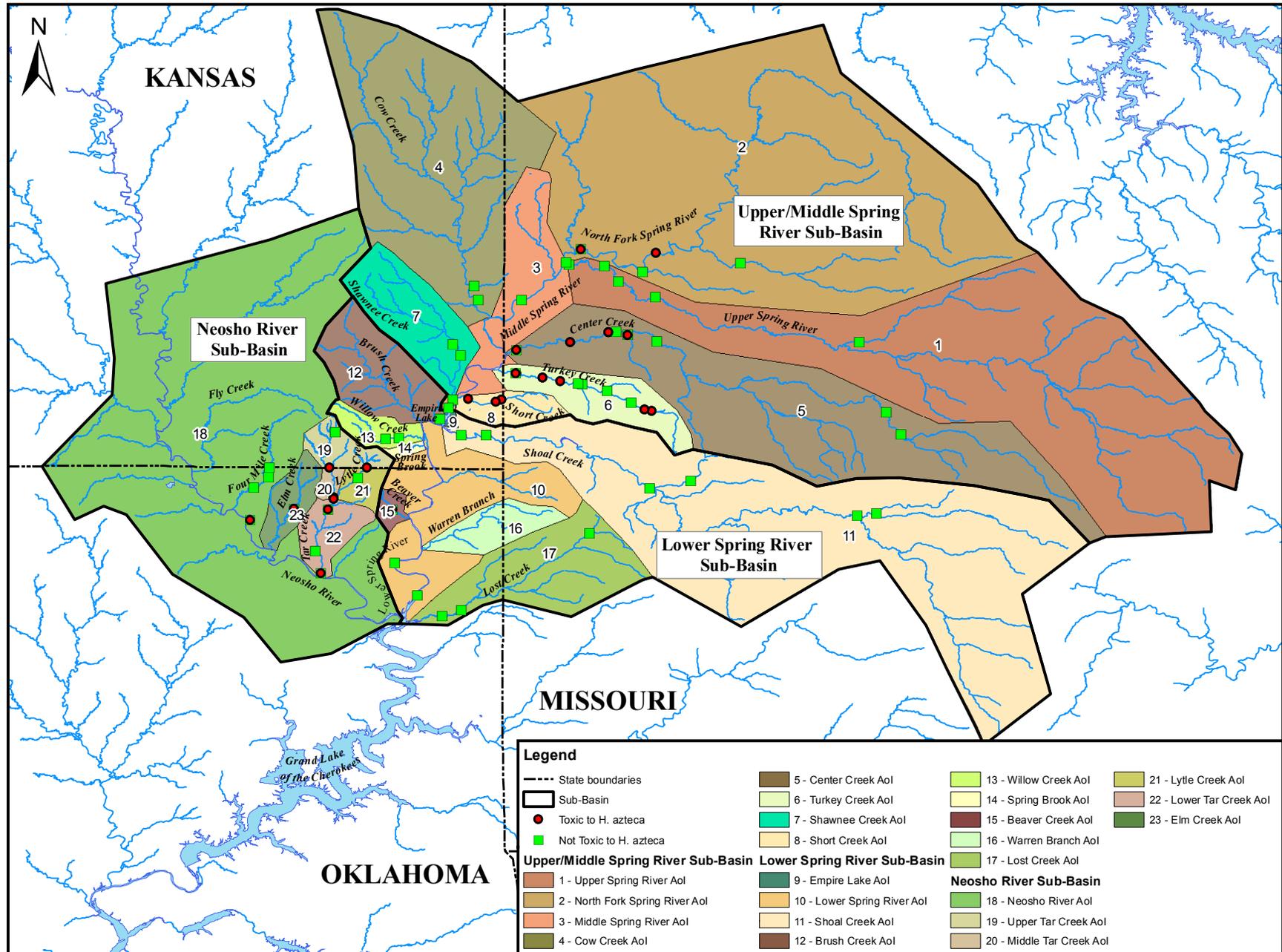


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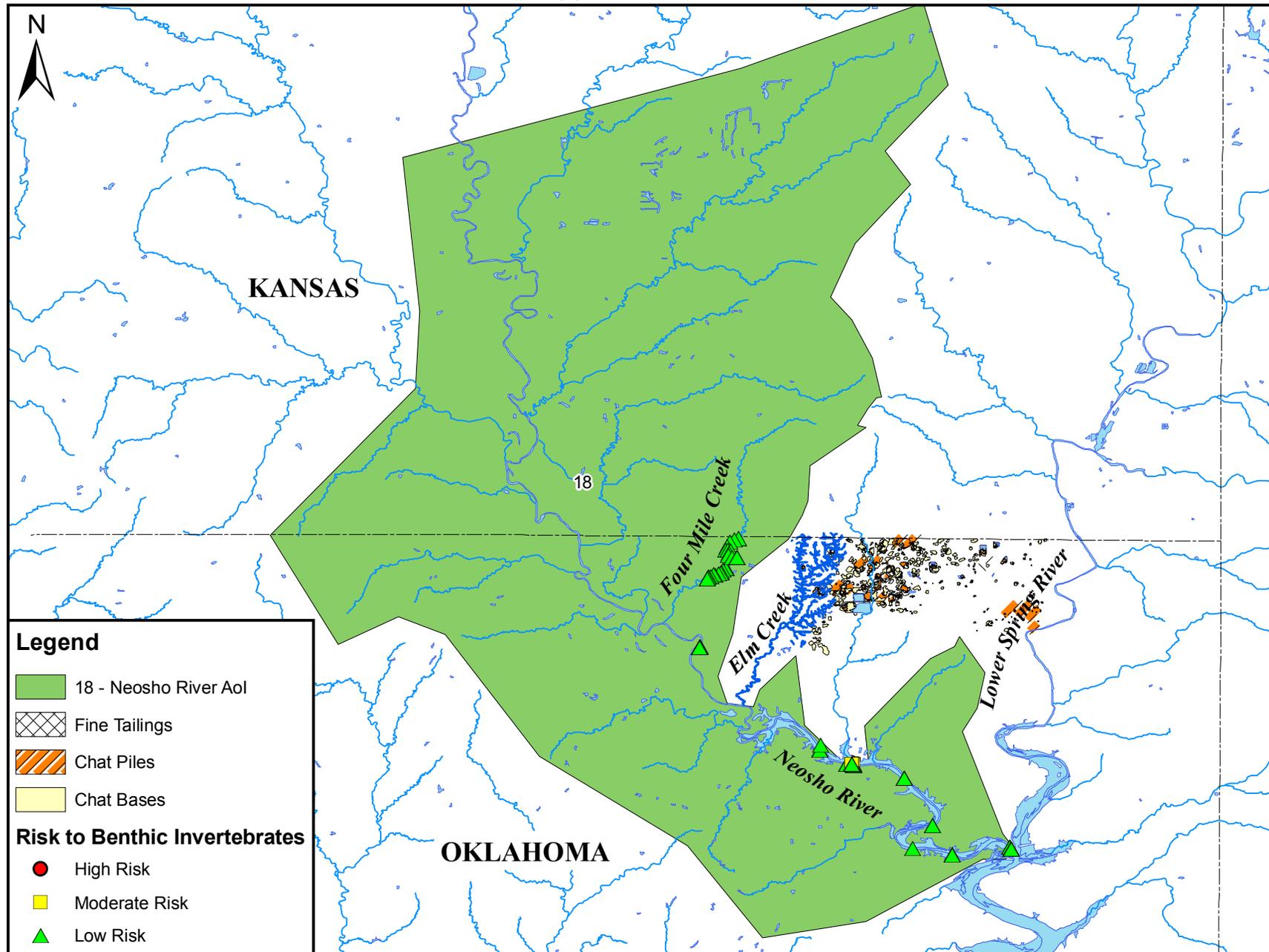
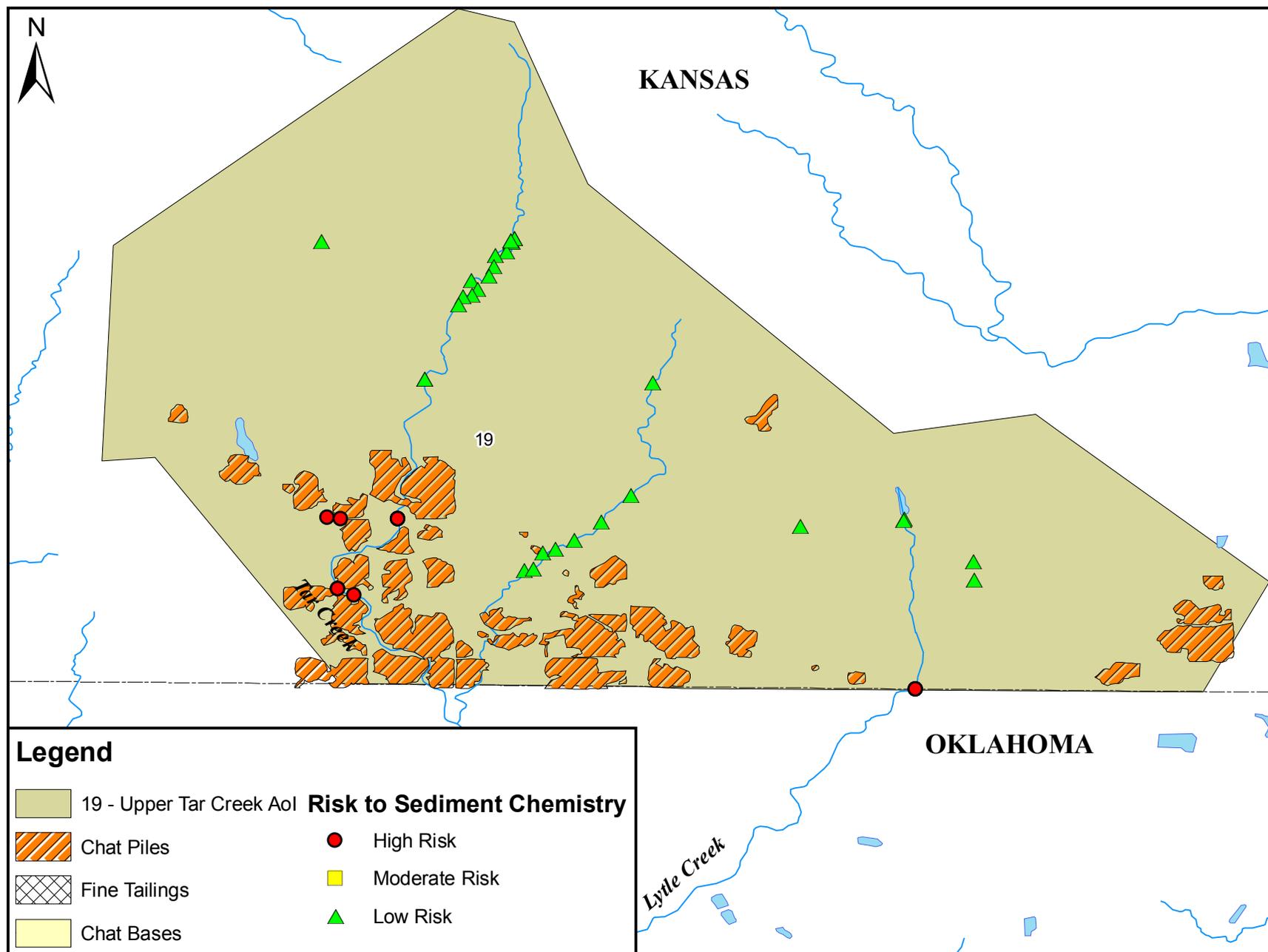


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0 0.375 0.75 1.5 2.25 3 Kilometers

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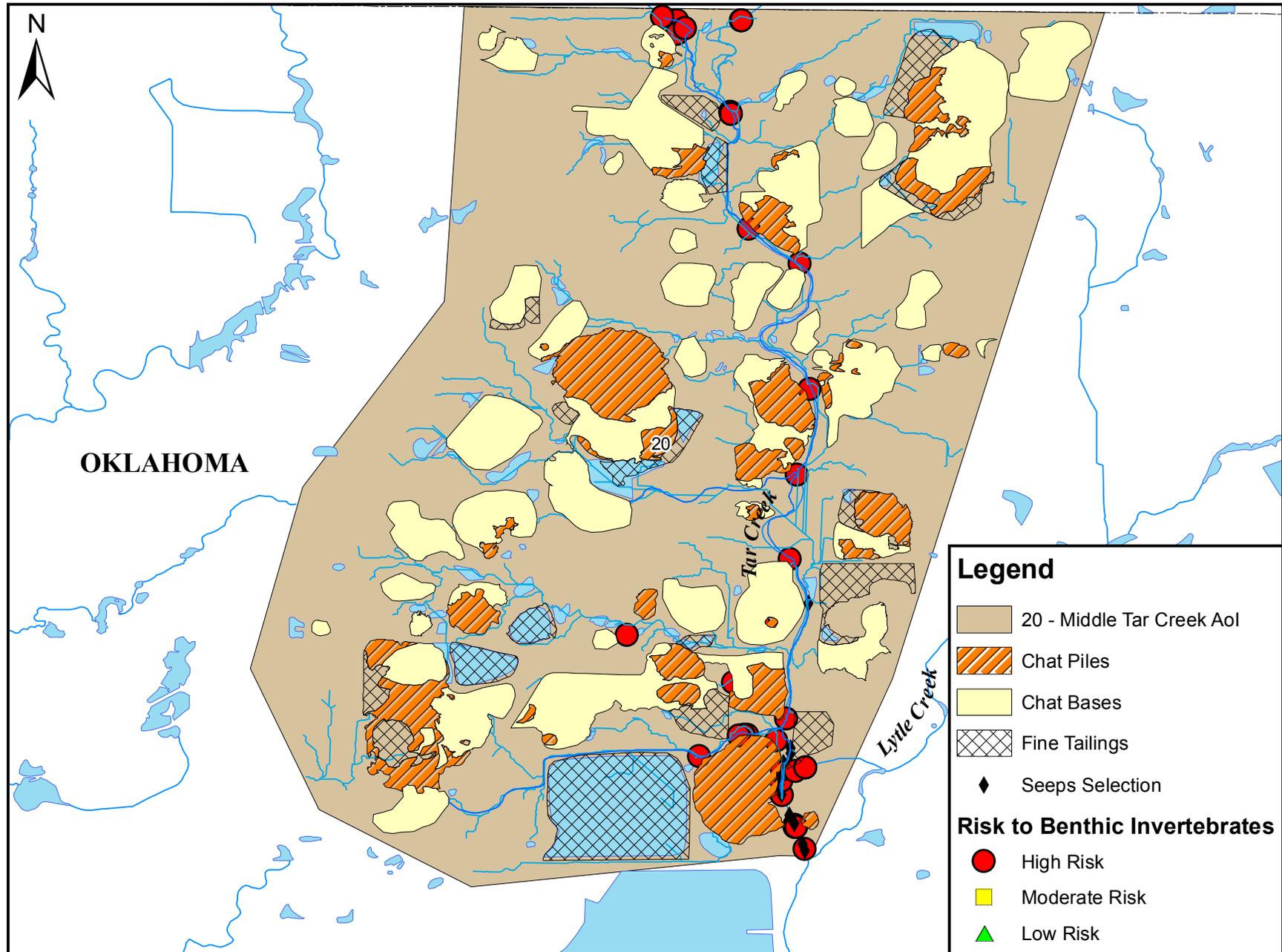


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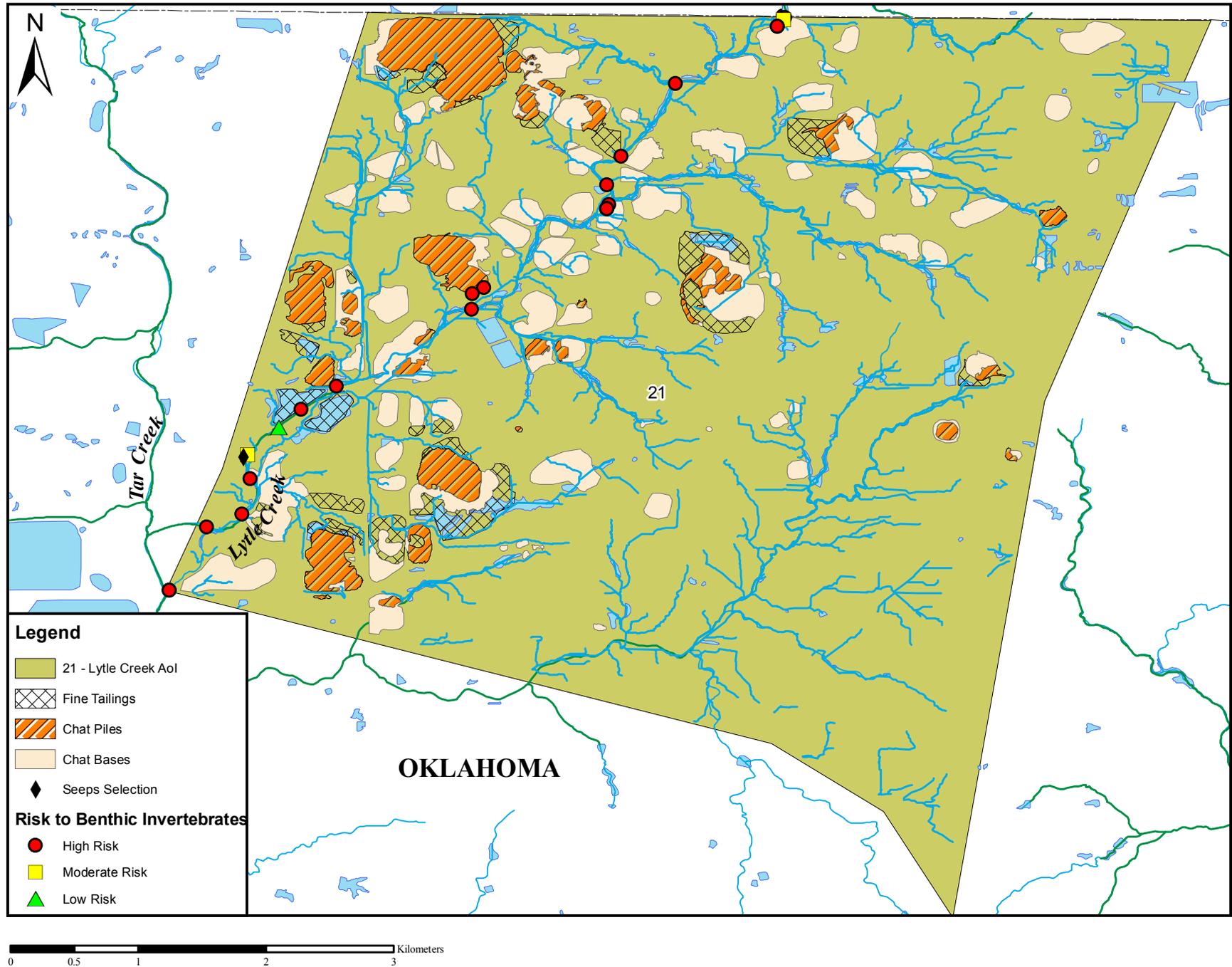


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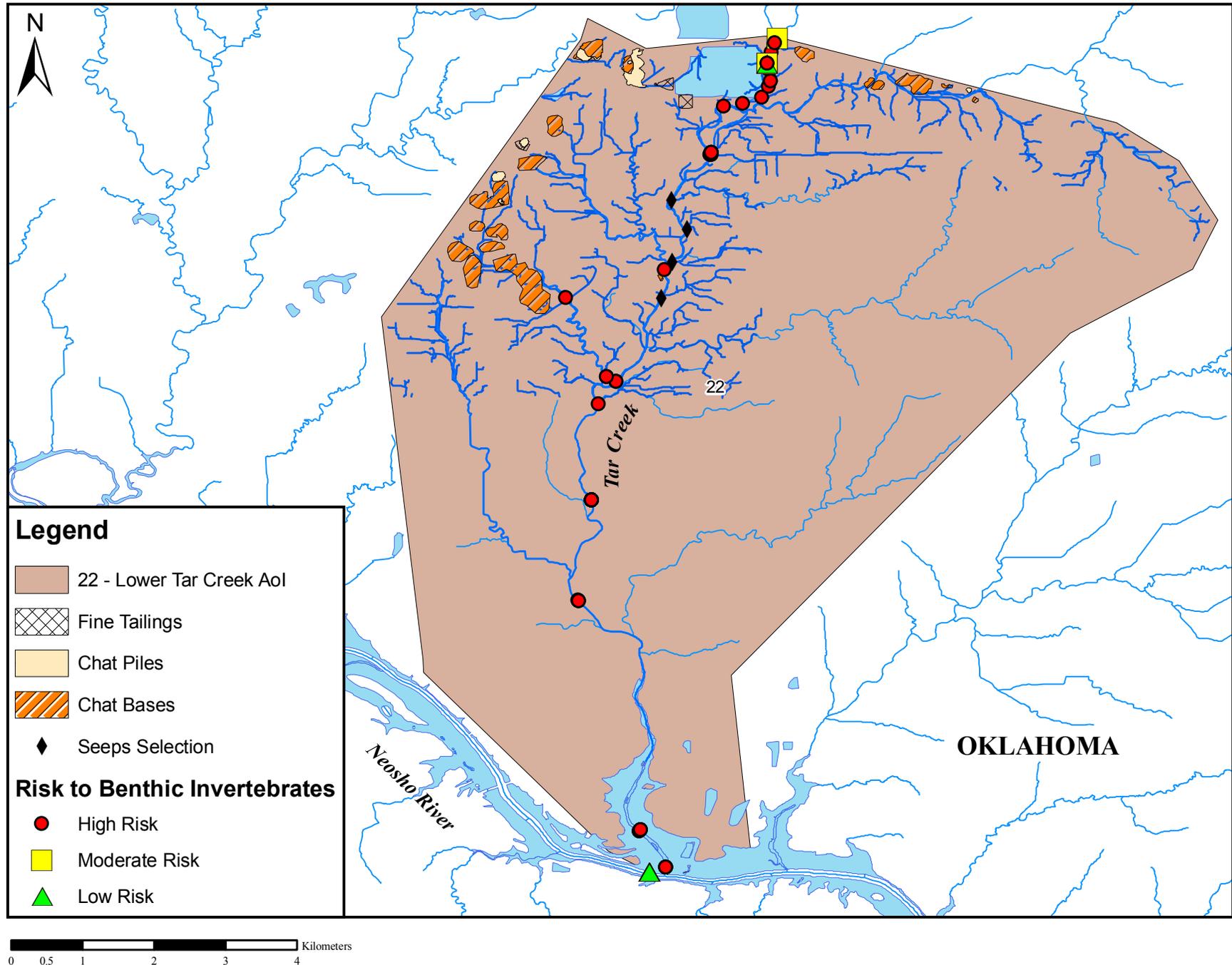


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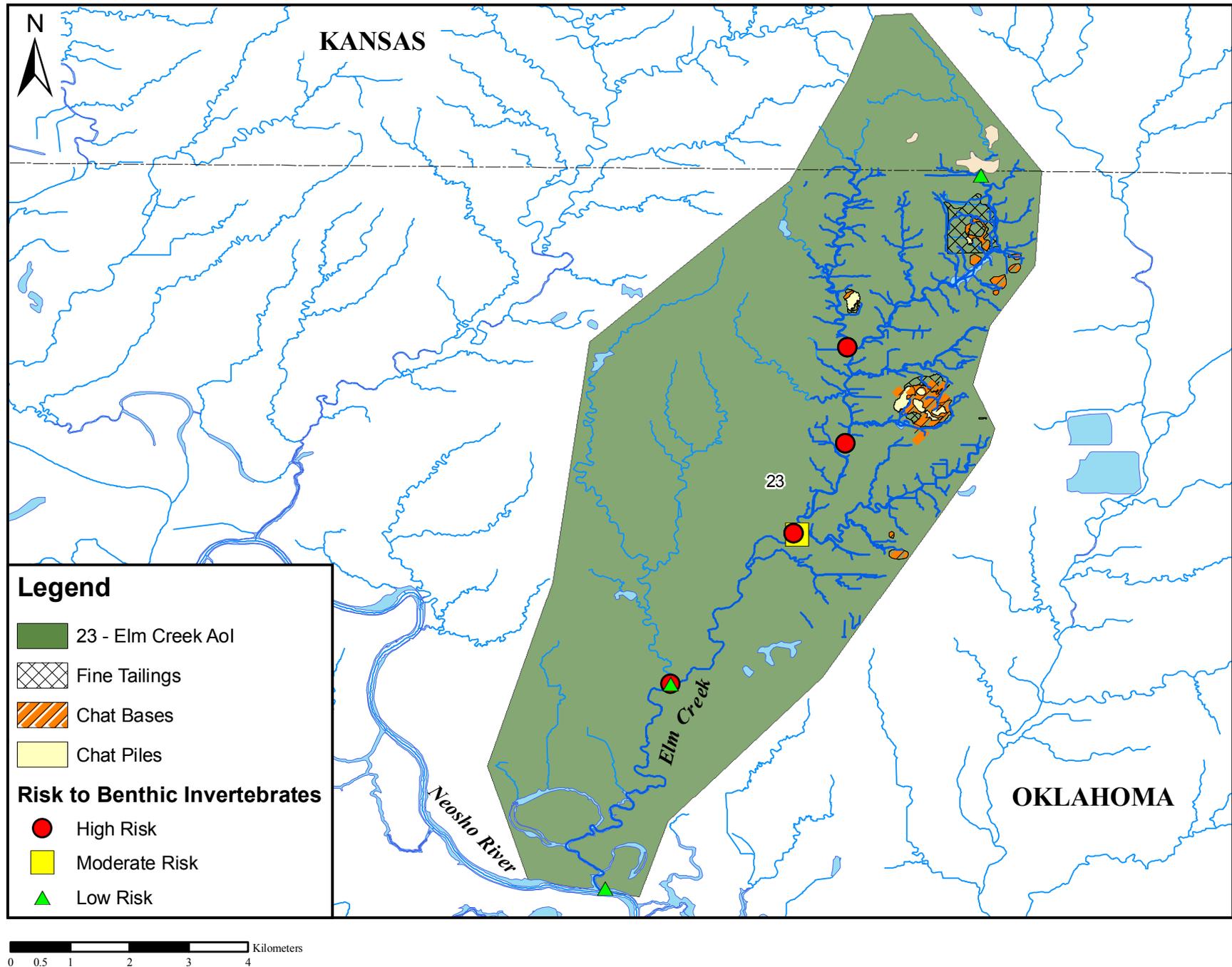
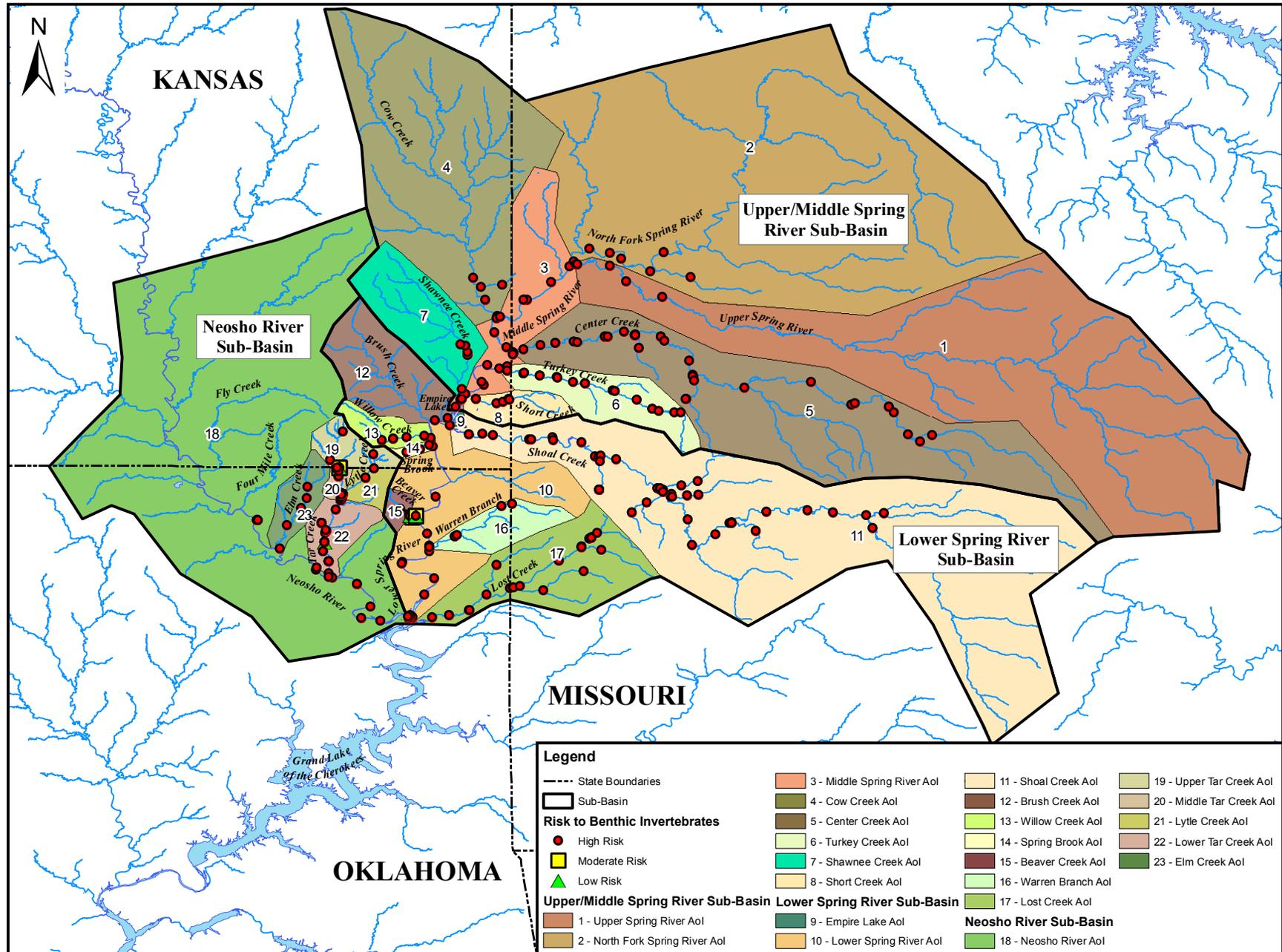


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0 5 10 20 30 40 50 Kilometers

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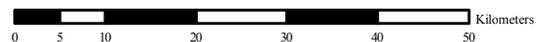
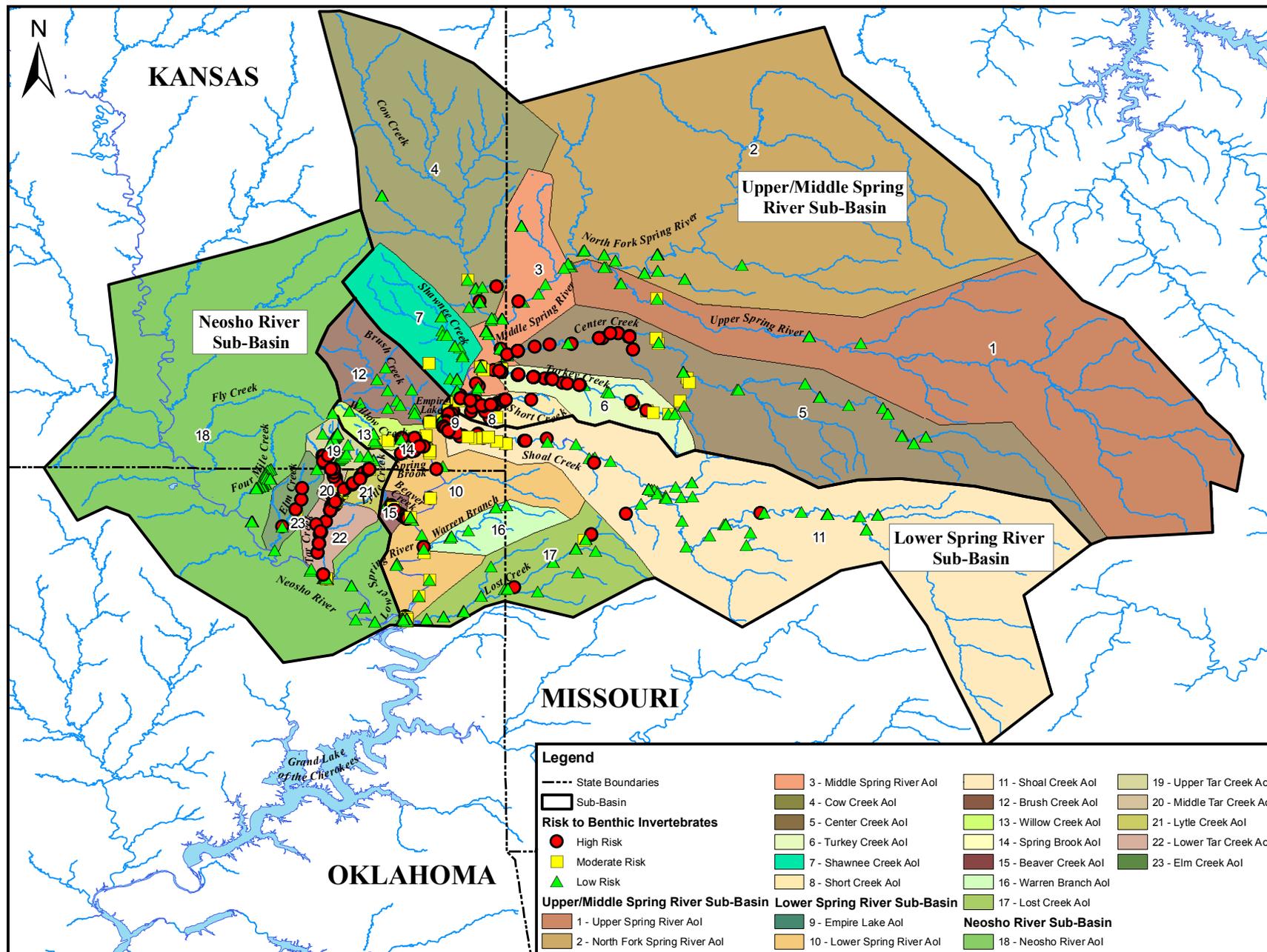


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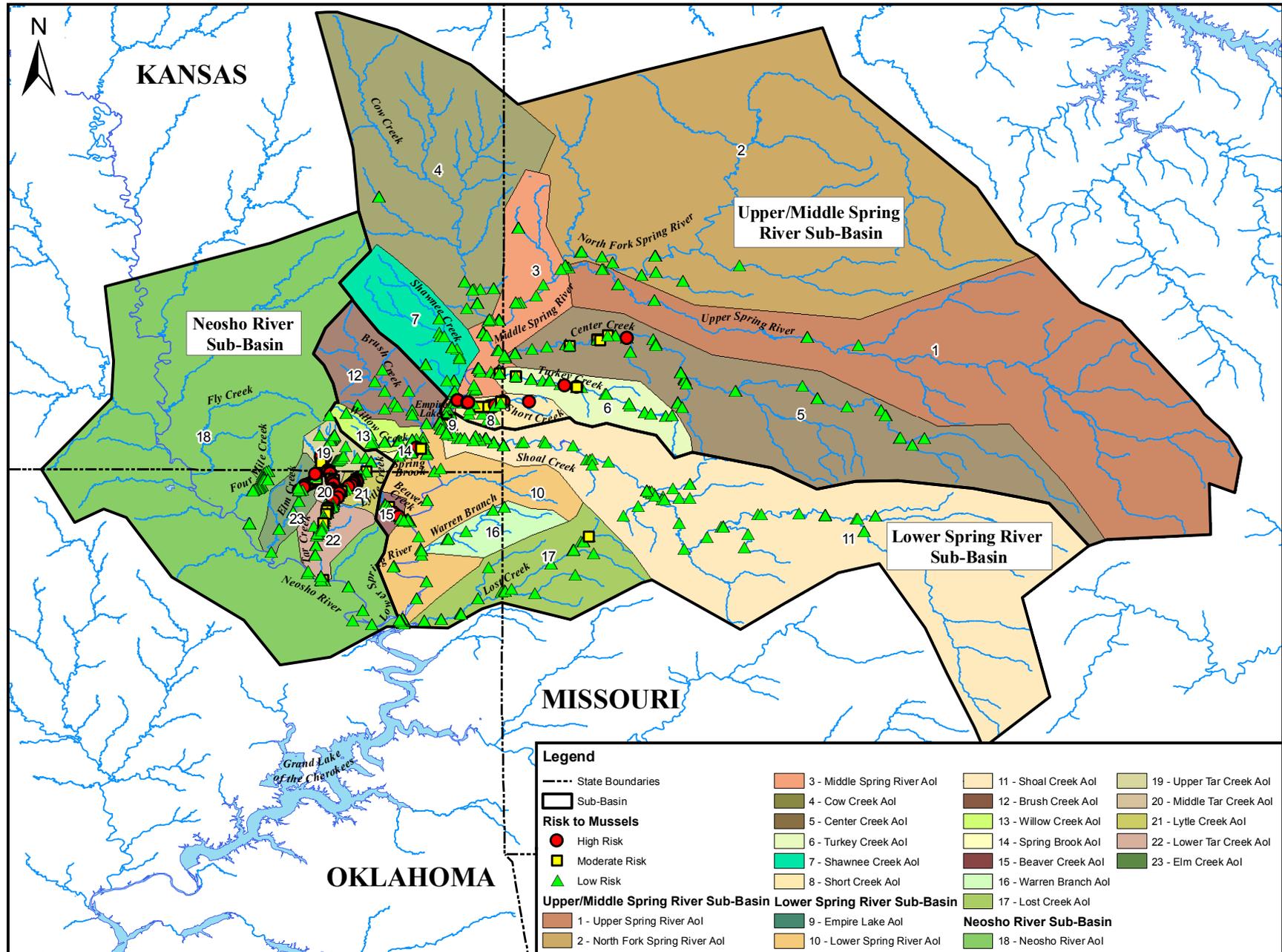


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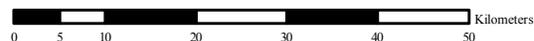
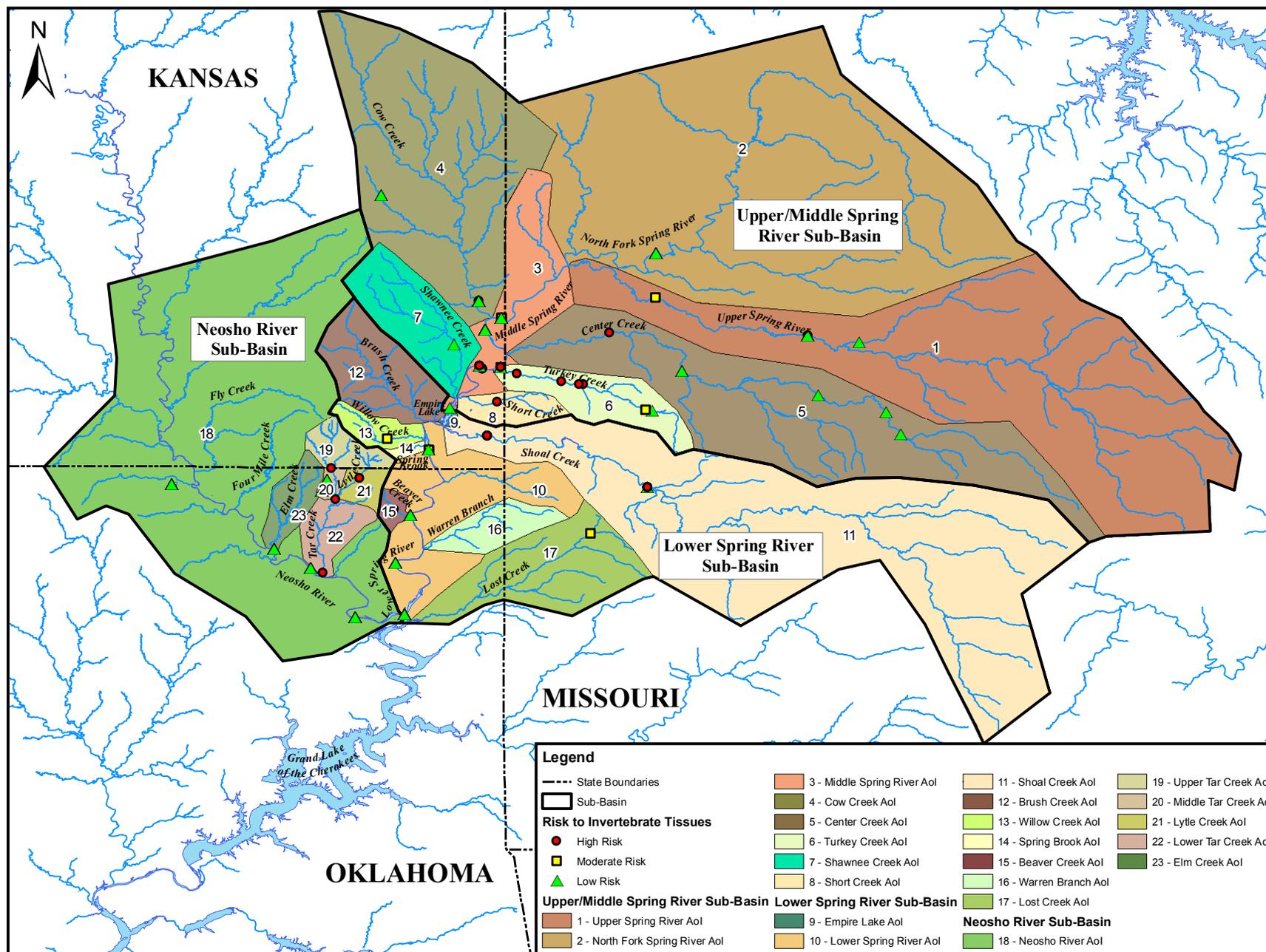
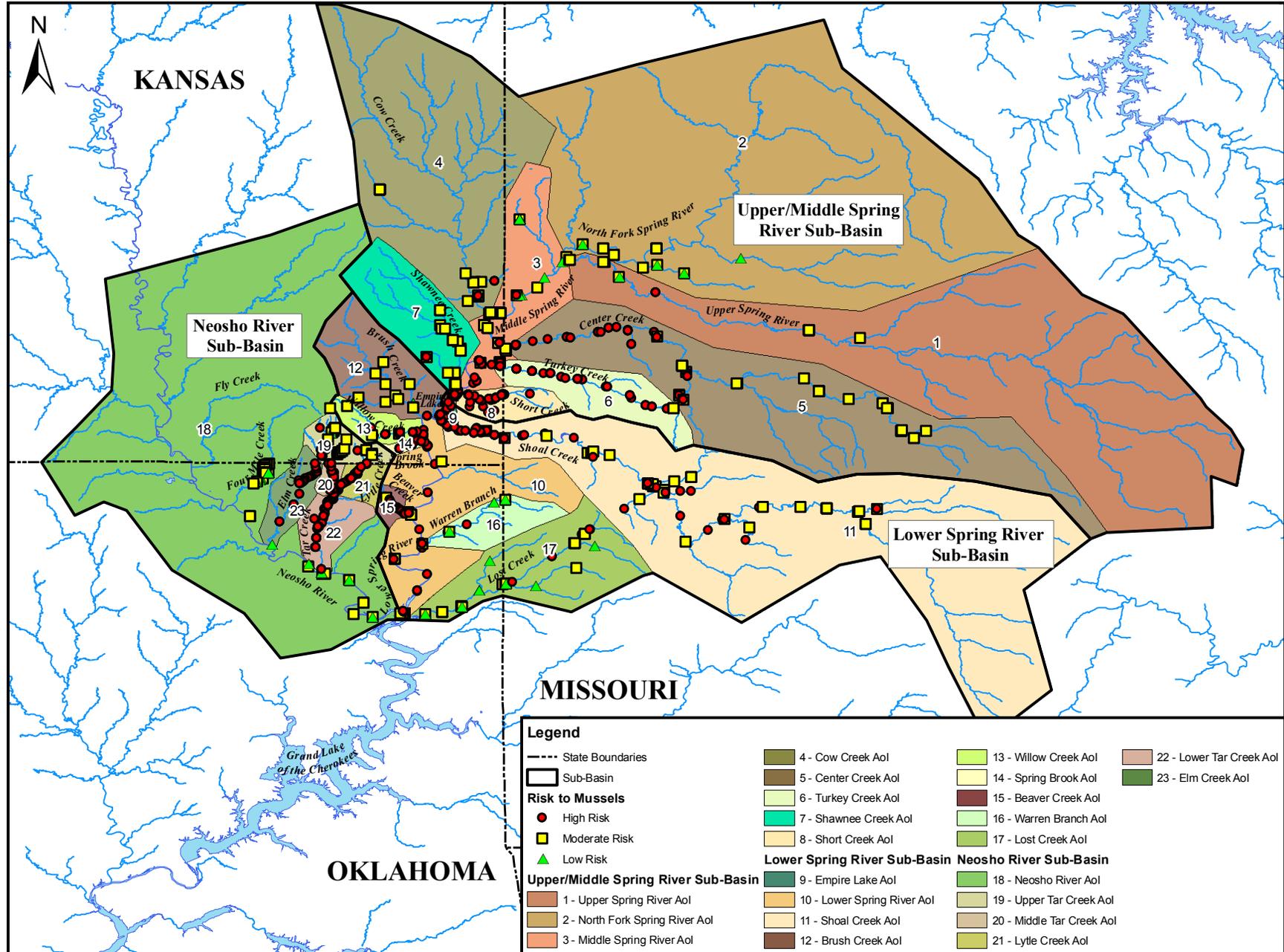


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Appendix 1
DERA PF

Problem Formulation for the Detailed Ecological Risk Assessment (DERA) of Aquatic Habitats in the Tri-State Mining District in Missouri, Kansas, and Oklahoma

Version 3.0 (Drafted April, 2007; Revised August, 2009)

Prepared for:

John Meyer
U.S. Environmental Protection Agency
1445 Ross Avenue
Dallas, Texas 75231

Mark Doolan and Dave Drake
U.S. Environmental Protection Agency
901 North 5th Street
Kansas City, Kansas 66101

Prepared – April, 2007 (Revised August, 2009) – by:

D.D. MacDonald¹, D.E. Smorong¹, C.G. Ingersoll², J.J. Jackson¹, Y.K. Muirhead¹, and S. Irving³

¹**MacDonald Environmental Sciences Ltd.**
#24 - 4800 Island Highway North
Nanaimo, British Columbia V9T 1W6

²**United States Geological Survey**
4200 New Haven Road
Columbia, Missouri 65201

³**CH2M Hill**
Suite 10 - 12377 Merit Drive
Dallas, Texas 75251



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¹MacDonald Environmental Sciences Ltd.
#24 - 4800 Island Highway North
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²United States Geological Survey
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³CH2M Hill
Suite 10 - 12377 Merit Drive
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List of Acronyms

%	=	percent
AHH	=	aryl hydrocarbon hydroxylase
AE	=	assessment endpoints
AoI	=	Area of Interest
AQUIRE	=	Aquatic Toxicity Information Retrieval System
As	=	arsenic
ASTM	=	American Society for Testing and Materials
ATSDR	=	Agency for Toxic Substances and Disease Registry
AVS	=	acid volatile sulfide
B	=	Boron
BCF	=	bioconcentration factor
BEHP	=	bis(2-ethylhexyl)phthalate
BERA	=	baseline ecological risk assessment
BI	=	bioavailability index
BOD	=	biological oxygen demand
BSAF	=	biota-sediment bioaccumulation factor
BTEX	=	benzene, toluene, ethyl benzene, and xylene
BW	=	body weight
C	=	Celsius
Cd	=	cadmium
CAS	=	Chemical Abstracts Service
CCC	=	criterion continuous concentration
CCME	=	Canadian Council of Ministers of the Environment
CCREM	=	Canadian Council of Resource and Environment Ministers
CERCLIS	=	Comprehensive Environmental Response, Compensation, and Liability Information System
CERCLA	=	Comprehensive Environmental Response, Compensation, and Liability Act of 1980, 42 U.S.S. 9601 <u>et seq.</u>
CLP	=	Contract Laboratory Program
cm	=	centimeter
CMA	=	Chemical Manufacturer's Association
CMC	=	criteria maximum concentration
COPC	=	chemical of potential concern
Cr	=	chromium
Cr(III)	=	trivalent chromium
Cr(IV)	=	hexavalent chromium
CSM	=	conceptual site model
Cu	=	copper
DCE	=	1,2-dichloroethane
DEHP	=	di(2-ethylhexyl)phthalate; synonym of BEHP
DELT	=	deformities, fin erosion, lesions, and tumors
DERA	=	detailed ecological risk assessment
DL	=	detection limit

DNA	=	deoxyribonucleic acid
DO	=	dissolved oxygen
DQO	=	data quality objectives
DW	=	dry weight
EC ₅₀	=	median effect concentration
EDTA	=	ethylenediaminetetraacetic acid
Eh	=	oxidation/reduction potential
EPC	=	exposure point concentration
EPT	=	Ephemeroptera, Plecoptera, Tricoptera
ERA	=	ecological risk assessment
EROD	=	ethoxyresorufin <i>O</i> -deethylase
ESB-TUs	=	equilibrium partitioning sediment benchmark toxic units model
FDA	=	Food and Drug Administration
foc	=	fraction organic carbon
FS	=	feasibility study
g/L	=	grams per liter
g/m ³	=	grams per cubic meter
g/mole	=	grams per mole
g/kg	=	grams per kilogram
H ₂ S	=	hydrogen sulfide
Hg	=	mercury
HMW-PAHs	=	high molecular weight polycyclic aromatic hydrocarbons
HI	=	hazard index
HQ	=	hazard quotient
HR	=	high risk
HSDB	=	hazardous substance databank
HSP	=	health and safety plan
IARC	=	International Agency for Research on Cancer
IPCS	=	International Program on Chemical Safety
IRIS	=	Integrated Risk Information System
ITEF	=	international toxicity equivalency factor
kg	=	kilogram
K _{oc}	=	organic carbon-partition coefficient
K _{ow}	=	octanol/water-partition coefficient
KS	=	Kansas
LC ₅₀	=	median lethal concentration
LCL	=	lower confidence limit
LD ₅₀	=	median lethal dose
Li	=	Lithium
LMW-PAHs	=	low molecular weight polycyclic aromatic hydrocarbons
LNHP	=	Louisiana Natural Heritage Program
LOAEL	=	lowest observed adverse effect level
LOEC	=	lowest observed effect concentration
LR	=	low risk
ME	=	measurement endpoints

MESL	=	MacDonald Environmental Sciences Ltd.
mg	=	milligram
mg/kg	=	milligrams per kilogram
mg/L	=	milligrams per liter
mg/m ³	=	milligrams per cubic meter
mm	=	millimeter
MFO	=	mixed function oxidase
MO	=	Missouri
mPa	=	millipascals (standard international unit for pressure)
MS	=	matrix spike
MSD	=	matrix spike duplicate
NAS	=	National Academy of Sciences
ng	=	nanogram
NG	=	no guideline
NH ₃	=	un-ionized ammonia
NH ₄ ⁺	=	ionized ammonia
Ni	=	nickel
NIOSH	=	National Institute for Occupational Safety and Health
NOAA	=	National Oceanic and Atmospheric Administration
NOAEL	=	no observed adverse effect level
NOEL	=	no observed effect level
NPDES	=	National Pollutant Discharge and Elimination System
NPL	=	National Priorities List
NRC	=	National Research Council
NRCC	=	National Research Council of Canada
NTP	=	National Toxicology Program
OC	=	organic carbon
OH ⁻	=	hydroxide
OK	=	Oklahoma
P	=	phosphorus
Pa	=	pascals (standard international unit for pressure)
PAH	=	polycyclic aromatic hydrocarbon
Pb	=	lead
PCB	=	polychlorinated biphenyl
PCS	=	Permit Compliance System
PEC	=	probable effect concentration
PEC-Q	=	probable effect concentration quotient
PEL	=	probable effect level
ppb	=	parts per billion
ppm	=	parts per million
QA/QC	=	quality assurance/quality control
QAPP	=	quality assurance project plan
QMP	=	quality monitoring program
QP	=	quality procedure
RCRA	=	Resource Conservation and Recovery Act

RI	=	remedial investigation
RNA	=	ribonucleic acid
ROI	=	receptors of interest
RQ	=	risk questions
RTECS	=	Registry of Toxic Effects of Chemical Substances
SAP	=	sampling and analysis plan
SD	=	standard deviation
Se	=	Selenium
SEM	=	simultaneously extracted metal
SMDP	=	scientific management decision point
SO ₄ ⁻	=	sulfate
SPF	=	specific pathogen free
SRI	=	Stanford Research Institute
SQG	=	sediment quality guideline
SSTTs	=	site-specific sediment toxicity thresholds
STORET	=	Storage and Retrieval System for water quality data
SVOCs	=	semi-volatile organic compounds
TAL	=	target analyte list
TCE	=	trichloroethane
TEC	=	threshold effect levels
TEF	=	toxic equivalency factor
TEL	=	threshold effect concentration
TEQ	=	toxic equivalents
TM	=	total metals
TOC	=	total organic carbon
TRI	=	Toxic Release Inventory
TSMD	=	Tri-State Mining District
TSS	=	total suspended solids
TU	=	toxic units
UCL	=	upper confidence limit
USDA	=	United States Department of Agriculture
USEPA	=	United States Environmental Protection Agency
USFWS	=	United States Fish and Wildlife Service
µg/kg	=	micrograms per kilogram
µg/L	=	micrograms per liter
µmol/g	=	micromoles per gram
VOCs	=	volatile organic compounds
WHO	=	World Health Organization
WQC	=	water quality criteria
WQG	=	water quality guideline
WW	=	wet weight
Zn	=	zinc

Glossary of Terms

Acute toxicity threshold – The concentration of a substance above which adverse effects are likely to be observed in short-term toxicity tests.

Acute toxicity – The immediate or short-term response of an organism to a chemical substance. Lethality is the response that is most commonly measured in acute toxicity tests.

Adverse effects – Any injury (i.e., loss of chemical or physical quality or viability) to any ecological or ecosystem component, up to and including at the regional level, over both long and short terms.

Ambient – Of or relating to the immediate surroundings.

Aquatic organisms – The species that utilize habitats within aquatic ecosystems (e.g., aquatic plants, invertebrates, fish, amphibians and reptiles).

Aquatic-dependent species – Species that are dependent on aquatic organisms and/or aquatic habitats for survival.

Aquatic-dependent wildlife – Wildlife species that are dependent on aquatic organisms and/or wildlife habitats for survival, including fish, amphibians, reptiles, birds, and mammals (e.g., egrets, herons, kingfishers, osprey, racoons, mink, otter).

Aquatic ecosystem – All the living and nonliving material interacting within an aquatic system (e.g., pond, lake, river, ocean).

Aquatic invertebrates – Animals without backbones that utilize habitats in freshwater, estuaries, or marine systems.

Benchmarks – Guidelines that are intended to define the concentration of a contaminant that is associated with a high or a low probability of observing harmful biological effects or unacceptable levels of bioaccumulation.

Benthic invertebrate community – The assemblage of sediment-dwelling organisms that are found within an aquatic ecosystem.

Bioaccumulation – The net accumulation of a substance by an organism as a result of uptake from all environmental sources.

Bioaccumulative substances – The chemicals that tend to accumulate in the tissues of aquatic and terrestrial organisms.

Bioavailability – Degree to which a chemical can be absorbed by and/or interact with an organism.

Bioconcentration – The accumulation of a chemical in the tissues of an organism as a result of direct exposure to the surrounding medium (i.e., it does not include food web transfer).

Biological half-life – The time required for one-half of the total amount of a particular substance in a biological system to be consumed or broken down by biological processes.

Biomagnification – The accumulation of a chemical in the tissues of an organism as a result of food web transfer.

Brood – The young animals produced during one reproductive cycle.

Calanoid (copepods) – Small crustaceans, 1-5 mm in length, commonly found as part of the free-living zooplankton in freshwater lakes and ponds.

Catabolism – The phase of metabolism which consists in breaking down of complex substances into simpler substances.

Chelating agent – An organic chemical that can bond with a metal and remove it from a solution.

Chronic toxicity – The response of an organism to long-term exposure to a chemical substance. Among others, the responses that are typically measured in chronic toxicity tests include lethality, decreased growth, and impaired reproduction.

Chronic toxicity threshold – The concentration of a substance above which adverse effects on sediment-dwelling organisms are likely to occur in longer-term toxicity tests.

Colloids – Very small, finely divided solids (that do not dissolve) that remain dispersed in a liquid for a long time due to their small size and electrical charge.

Confluence – The location where two waterways meet.

Congener – A member of a group of chemicals with similar chemical structures (e.g., PCDDs generally refers to a group of 75 congeners that consist of two benzene rings connected to each other by two oxygen bridges).

Chemicals of potential concern – The substances that occur in environmental media at levels that pose a potential risk to ecological receptors or human health.

Contaminated sediment – Sediment that contains chemical substances at concentrations that could harm sediment-dwelling organisms, wildlife, or human health.

Degradation – A breakdown of a molecule into smaller molecules or atoms.

Demethylated – Removal of a methyl group from a chemical compound.

Diagenesis – The sum of the physical and chemical changes that take place in sediments after its initial deposition (before they become consolidated into rocks, excluding all metamorphic changes).

Dimorphic – Existing in two forms (e.g., male and female individuals in animals).

Endpoint – A measured response of a receptor to a stressor. An endpoint can be measured in a toxicity test or a field survey.

Estivate – To pass the summer or dry season in a dormant condition.

Fumarolic – Describes a vent in or near a volcano from which hot gases, especially steam are emitted.

Gavage – Forced feeding by means of a tube inserted into the stomach through the mouth.

Genotoxic – Describes the toxic effects of a substance which damages DNA.

Half-life – The length of time required to reduce the concentration of a substance by 50% in a particular medium.

Halogenated aliphatic compound – A chemical compound with a halogen atom (F, Cl, Br, I) associated with an alkane chain.

Hepatomegaly – A condition in which the liver is enlarged beyond its normal size.

Hepatotoxic – Refers to anything which poisons the liver.

Hibernate – To pass the winter in a dormant condition, in which metabolism is slowed down.

Homeostasis – The maintenance of metabolic equilibrium within an animal.

Hyperplasia – An abnormal multiplication or increase in the number of normal cells in a tissue.

Hypertrophy – Enlargement of an organ resulting from an increase in the size of the cells.

Lethal dose – The amount of a chemical necessary to cause death.

Littoral (vegetation) – Pertaining to or along the shore.

Mast – The fruit of forest trees.

Microsomal – Describing the membrane-bound vesicles that result from the fragmentation of the endoplasmic reticulum.

Miscible – Capable of being mixed.

Morphometry (bone) – The quantitative study of the geometry of bone shapes.

Necrosis – Necrosis is the death of plant or animal cells or tissue.

Neoplastic – Refers to abnormal new growth.

Neotenic (salamander) – The retention of juvenile characteristics in the adult individual.

Nephrotoxic – Refers to anything that poisons the kidney.

Order of magnitude – A single exponential value of the number ten.

Organogenesis – The basic mechanisms by which organs and tissues are formed and maintained in an animal or plant.

Osmoregulation – The control of the levels of water and mineral salts in the blood

Partition coefficient – A variable that is used to describe a chemical's lipophilic or hydrophobic properties.

Petechial (hemorrhages) – A minute discolored spot on the surface of the skin or mucous membrane, caused by an underlying ruptured blood vessel.

Photolysis – Chemical decomposition caused by light or other electromagnetic radiation.

Porphyria – A hereditary disease of body metabolism that is caused by a change in the amount of porphyrins (nitrogen-containing substances) found in the blood.

Pyrolysis – Decomposition of a chemical by extreme heat.

Ranid (frog) – The family of true frogs of the order Anura.

Receiving water – A river, ocean, stream or other watercourse into which wastewater or treated effluent is discharged.

Receptor – A plant or animal that may be exposed to a stressor.

Sediment – Particulate material that usually lies below water.

Sediment-associated contaminants – Contaminants that are present in sediments, including whole sediments or pore water.

Sediment-dwelling organisms – The organisms that live in, on, or near bottom sediments, including both epibenthic and infaunal species.

Seminiferous tubules – The glandular part of testicles that contain the sperm producing cells.

Sorption – The process by which one substance takes up or holds another; adsorption or absorption.

Stressor – Physical, chemical, or biological entities that can induce adverse effects on ecological receptors or human health.

Sublethal dose – The amount, or dosage, of a toxin necessary to cause adverse effects, not including death.

Teratogenic – Causing birth defects.

Terrestrial habitats – Habitats associated with the land, as opposed to the sea or air.

Tissue – A group of cells, along with the associated intercellular substances, which perform the same function within a multicellular organism.

Trophic level – A portion of the food web at which groups of animals have similar feeding strategies.

Volatilization – To change or cause to change from a solid or liquid to a vapor.

Wet deposition – The transfer of an element from the atmosphere to land or water through rain or snow.

Chapter 1 Introduction

1.0 Background

This document was prepared to support the design and implementation of a detailed ecological risk assessment (DERA) of the Tri-State Mining District (TSMD) in Missouri, Kansas, and Oklahoma (Figure 1). More specifically, this document defines the questions that need to be addressed during the DERA, a process that is termed problem formulation. This chapter of the problem formulation document provides an overview of the ecological risk assessment (ERA) process, describes the purpose of the report, and includes a description of the organization of the report. It is important to note that the scope of the DERA is limited to evaluating potential risks to benthic invertebrates associated with exposure to chemicals of potential concern (COPCs) in the TSMD. As such, risks to aquatic-dependent wildlife and terrestrial receptors are not addressed in the problem formulation document.

1.1 Remedial Investigation and Feasibility Study (RI/FS)

In response to concerns regarding environmental contamination, a DERA is being conducted in the TSMD. This DERA will be conducted in general accordance with the Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessment (USEPA 1997). The United States Environmental Protection Agency (USEPA) guidance document describes an ERA framework (Figure 2) and an eight-step process for conducting an ERA (Figure 3), including:

- Step 1: Screening-Level Preliminary Problem Formulation and Ecological Effects Evaluation;
- Step 2: Screening-Level Preliminary Exposure Estimate and Risk Calculation Scientific Management Decision Point (SMDP);
- Step 3: Baseline Risk Assessment Problem Formulation SMDP;
- Step 4: Study Design and Data Quality Objectives SMDP;
- Step 5: Field Verification of Sampling Design SMDP;
- Step 6: Site Investigation and Analysis of Exposure and Effects SMDP;
- Step 7: Risk Characterization; and,
- Step 8: Risk Management SMDP.

The DERA of the TSMD is being conducted using this stepwise approach. The objectives of this DERA are:

- To estimate the risks posed to selected ecological receptors (i.e., benthic invertebrates) by environmental contamination of aquatic habitats in the four NPL sites that comprise the TSMD; and,
- To provide the information needed by risk managers to make decisions regarding the need for remedial actions, including source control measures and the establishment of clean-up goals for the site.

A DERA is being conducted for the TSMD because the results of the sampling that has been conducted to date indicate that total metal concentrations in surface water and sediment exceed conservative toxicity thresholds (i.e., threshold effect concentrations; TECs; MacDonald *et al.* 2000) throughout much of the study area. Because the TECs were considered to overestimate toxicity, MacDonald *et al.* (2009) developed site-specific toxicity thresholds for individual COPCs and selected COPC mixtures. This site-specific calibration of the generic sediment quality guidelines was intended to provide more reliable tools for evaluating risks to ecological receptors in

the study area, thereby reducing uncertainty in the results of the assessment. While the DERA will provide risk managers with relevant information for risk management priorities in the study area, it is not intended to represent a baseline ERA (BERA) or supplant the BERAs that have been conducted previously at the site.

1.2 Purpose of this Report

As indicated previously, the DERA of the TSMD is being conducted by USEPA, with the support of the Natural Resources Trustees. While the work that has been completed to date provides relevant information on environmental conditions in the vicinity of the study area, there is a need to further define the scope and goals of the DERA. The process of defining the questions that will be addressed during the DERA is termed problem formulation. Problem formulation is a systematic planning process that identifies the factors to be addressed in a DERA and consists of five major activities (USEPA 1997), including:

- Identification of contaminant sources in the study area and development of the preliminary list of COPCs at the site;
- Characterization of the potential ecological effects of the COPCs at the sites;
- Compilation of the information on the fate and transport of COPCs, on potential exposure pathways, and on the receptors potentially at risk;
- Selection of assessment and measurement endpoints; and,
- Development of a conceptual model with testable hypotheses (or risk questions) that the site investigation will address.

At the conclusion of the problem formulation, there is a scientific/management decision point, which consists of agreement on four items: the assessment endpoints, the exposure pathways, the risk questions, and the conceptual model that integrates these components (USEPA 1997).

This document was prepared to define the issues that need to be addressed during the DERA of the TSMD and, in so doing, to establish the goals, scope, and focus of the assessment. The preliminary problem formulation document is intended to inform the study design (as defined in the various sampling and analysis plans) and data quality objectives process by establishing the measurement endpoints that will be used in the DERA. More specifically, the information developed during the problem formulation process is intended to provide a basis for evaluating the applicability of the risk questions/testable hypotheses, exposure pathway models, and measurement endpoints that have been proposed for the DERA. The problem formulation process is also intended to define how the information collected during the site investigation will be used to characterize exposures, ecological effects, and ecological risks, including associated uncertainties.

This preliminary problem formulation document was developed, in part, using the results of an ERA workshop that was conducted in Joplin, MO during January 18 and 19, 2007. This workshop was attended by the tribal, state, and federal NRTs, as well as personnel representing USEPA Region 6 and Region 7. Accordingly, the preliminary problem formulation document reflects the input of a broad range of individuals with specialized risk assessment and hazard assessment expertise, and intimate knowledge of the study area. The document was updated in August, 2009 to reflect the current goals and objectives of the project.

1.3 Organization of this Report

This report is organized into a number of sections to facilitate access to the information associated with the problem formulation for the DERA of the TSMD, including:

- Introduction (Chapter 1);
- Geographic Scope of Study Area (Chapter 2);
- Identification of Chemicals of Potential Concern and Areas of Interest in the TSMD (Chapter 3);
- Environmental Fate and Ecological Effects of Chemicals of Potential Concern (Chapter 4);
- Identification of Key Exposure Pathways in the TSMD (Chapter 5);
- Identification of Receptors Potentially at Risk in the TSMD (Chapter 6);
- Overview of Conceptual Site Model (Chapter 7);
- Selection of Assessment and Measurement Endpoints for Evaluating Risks to Ecological Receptors in the TSMD (Chapter 8);
- Risk Analysis Plan and Uncertainty Analysis (Chapter 9);
- References (Chapter 10).

Appendix 2 provides additional information on the environmental fate and effects of many of the COPCs identified in this document. Finally, a glossary of terms and a list of acronyms are provided to define the various scientific terms that are used throughout this document.

Chapter 2 Geographic Scope of the Study Area

2.0 Introduction

The TSMD is comprised of a total of four NPL sites in Missouri, Kansas, and Oklahoma, including the Jasper County Site, MO, Newton County Site, MO, Cherokee County Site, KS, and the Ottawa Country Site, OK (Figure 1). Although there are a variety of land use activities within the Spring River and Neosho River watersheds, environmental concerns in the area have focused primarily on releases of metals from historic mining activities. Ores baring lead, zinc, and other base metals were mined, milled, and smelted in the TSMD between 1850 and 1970. During this period, metals may have been released from a vast number of mining, milling, and smelting operations in the study area. The total mass of metals released from these operations is uncertain, however.

In response to public concerns, a DERA is being conducted to assess risks to selected ecological receptors and to evaluate remedial options for addressing environmental contamination in the TSMD. Although the TSMD consists of four NPL sites, there are a number of similarities among the sites. Importantly, historic land use activities were similar throughout the four sites, with mining and smelting occurring throughout the TSMD. There are also numerous similarities in terms of the physical, chemical, and biological characteristics of the areas. For this reason, USEPA has decided to conduct a screening level assessment of risks to aquatic organisms that spans the entire TSMD. In this way, the results of the DERA will provide a consistent basis for identifying priorities for further investigation within each of the individual NPL sites.

2.1 Considerations for Determining the Geographic Scope of the Study Area

For the purposes of assessing risks to ecological receptors, it is necessary to define the scope of the study area. According to Suter *et al.* (2000), the spatial extent of a site can be established based on one or more of the following criteria:

- The areas in which wastes have been deposited;
- The areas believed to be contaminated;
- The area owned or controlled by the responsible party;
- The extent of transport processes; and,
- Buffer zones.

In keeping with the site-wide approach to the DERA, it may be beneficial to identify a number of areas of interest (i.e., spatial units) within the study area. The decision about how to divide the site into spatial units must be based on two considerations: the location of the contaminants and the dynamics of the site (i.e., both hydrological and biological; Suter *et al.* 2000). Therefore, detailed biological surveys and habitat evaluations are often conducted to facilitate the identification of ecologically-relevant areas of interest and reaches within each area of interest. Reference areas are also commonly identified to support evaluations of risks to ecological receptors.

2.2 Geographic Scope of the Study Area

The geographic scope of the TSMD is defined as the in-channel, riparian, and floodplain areas from the headwaters of the Spring River to Grand Lake and from the headwaters of Tar Creek to the confluence with the Neosho River and downstream

to Grand Lake. However, that definition of the study area does not provide a basis for evaluating spatial patterns in contamination or associated risks to aquatic receptors. For this reason, the study area was initially divided into eight areas of interest (AoIs). These preliminary AoIs provided an effective basis for designating the Phase II Sampling Program for the TSMD. Subsequently, the study area was divided into a total of 23 AoIs to support evaluation of the spatial extent of risks to ecological receptors.

Because mining activities have been conducted throughout the study area, it is difficult to identify reference areas within the TSMD. For this reason, reference samples (rather than reference areas) were identified on an *a posteriori* basis, using the criteria described in Appendix 4. These reference samples were used to help identify conditions that have been relatively unaffected by mining activities.

Chapter 3 Identification of Chemicals of Potential Concern and Areas of Interest in the Tri-State Mining District

3.0 Introduction

The DERA that will be conducted as part of the overall RI/FS is intended to evaluate the risks posed to selected aquatic receptors (i.e., benthic invertebrates) associated with exposure to environmental contamination within the TSMD. In addition, the DERA is intended to provide risk managers with some of the information required to make timely decisions regarding the need for remedial actions (e.g., early action). The problem formulation process provides a basis for systematically planning the various elements of the DERA and communicating this strategy to all stakeholders.

This chapter is intended to provide key background information needed to support the problem formulation for the DERA. More specifically, this chapter provides information on the sources and releases of environmental contaminants in the TSMD. Additionally, this chapter describes the process that was used to identify the COPCs in the study area.

3.1 Sources and Releases of Environmental Contaminants

There are a number of natural and anthropogenic sources of toxic and bioaccumulative substances in the TSMD. Natural sources of such substances include weathering and erosion of terrestrial soils, bacterial decomposition of vegetation and animal matter, and long-range transport of substances originating from forest fires or

other natural combustion sources. Recently (January 18 and 19, 2007), a workshop was convened in Joplin, MO to support planning of an ecological risk assessment of the TSMD. As part of the workshop, participants were asked to identify anthropogenic sources of COPCs within the Spring River and Neosho River watersheds. Workshop participants indicated that there were a number of sources of COPCs to aquatic ecosystems within the TSMD, including:

- NPDES permitted outfalls (Table 1; it was suggested that the conditions of the permits, violations, and spills be reviewed to identify the COPCs from each facility);
- Agricultural runoff (including cattle operations, chicken farms, and turkey farms; land application of manure can be source of arsenic to the environment. In addition, application of fertilizers, pesticides, and herbicides can result in releases of COPCs to receiving water systems);
- Urban stormwater runoff;
- Runoff from chat piles;
- Releases from mill ponds (including tailings ponds, slime ponds, and tailings impoundments);
- Runoff and discharges from chat washing facilities (which result in the production of fines, which may be routed to floatation ponds; in some cases, floatation ponds exist under chat piles and represent sources of COPCs during and following rain events);
- Relocation of chat for other uses (chat has been used in the construction of roads, driveways, railroad beds, foundations for houses; sewer lines; Use of chat during sewer line construction represents a problem because metals can infiltrate into the sewer lines and result in transport of metals to sewage treatment plants);

- Groundwater discharges and seeps [this type of source includes chat piles (which contain perched groundwater, which seeps out over time), groundwater seeps (which can occur as a diffuse source along the streams and rivers, and groundwater upwelling into streambeds. The area has Karst-type geology east of the Spring River and Pennsylvania shale west of the Spring River];
- Minewater discharge (this type of source includes direct minewater discharges from Lyttle Creek and boreholes);
- Historic releases from smelting operations (which has resulted in aerial dispersion of metals and direct releases of slag to river systems; at Galena, Short Creek runs through a slag pile;
- Runoff from contaminated flood plain soils (This is particularly important in Center Creek, Turkey Creek, and in the vicinity of the smelters; This source is likely to be most active during periods of high precipitation and/or high flows);
- Dust deposition from chat piles (The Quapaw Tribe has conducted air monitoring upwind and downwind of chat sales operations and observed that the levels of lead never exceeded ambient air quality standards; levels of lead were highest closest to the source. USEPA modeled air as a potential source of metals to areas that had been cleaned-up previously and concluded that air was not a significant source; and,
- Movement of streambed sediments (sediment represent an important secondary source of COPCs to downstream areas).

It was also noted that chat is currently being used in the production of asphalt, which represents an effective source control measure as encapsulation in asphalt renders the metals unavailable.

3.2 Chemicals of Potential Concern in the Study Area

The identification of COPCs represents an essential element of the problem formulation process (USEPA 1998). To initiate this process, workshop participants reviewed the available information on the various sources and releases of chemical substances in the watershed and concluded that the following should be considered as preliminary COPCs in the TSMD:

- Metals (broad suite; originating primarily from historic mining operations; also from a landfill on Turkey Creek, urban stormwater runoff, and sewage treatment plant discharges);
- Mercury (particularly in Lonnell Creek);
- Polycyclic aromatic hydrocarbons (PAHs; originating from certain NPDES permitted point sources, urban stormwater runoff, International Paper, coal mining, coal-burning smelters, and coal-fired power plants. PAH can also occur naturally in the area as tars and heavy oils, as occurs in the Tar Creek area);
- Benzene, toluene, ethyl benzene, and xylene (BTEX; i.e., Fuel storage facilities discharge to Shoal Creek);
- Nutrients (including ammonia, nitrite, nitrate, and phosphorus; originating from agricultural operations, sewage treatment plant discharges, and an explosives plant on Grove Creek. Ammonia-related fish kills have been observed in Cave Springs);
- Chlorine (i.e., associated with WWTP discharges);
- Suspended sediment;
- Major ions, particularly sulphates;
- Pesticides (including in-use insecticides, herbicides, and fungicides);

- Microbiological variables (e.g., Upper Shoal Creek is on the 303(d) list due to faecal coliform contamination;
- pH (Note: minewater is near neutral where it discharges to surface water, but can be in the 5 to 6 range in the ground; represents a potential hazard for receptors such as cave crayfish);
- Trichloroethane (TCE; in groundwater only; not in surface water);
- Dissolved oxygen (due to discharges of effluents with high BOD and due to the oxidation of iron, such as in Lyttle Creek); and,
- PCBs and other organochlorines are uncertain COPCs.

Workshop participants reviewed the preliminary list of COPCs and provided the following input on their likely environmental fate within the Spring River and Neosho River basins:

- **Metals** - Metals that are released into the environment are likely to partition into surface water, sediment, flood plain soils, and biological tissues. Downstream transport to Grand Lake and beyond can also occur. Certain metals (e.g., Pb, Cd, Zn, Hg) can accumulate in aquatic organisms and be transferred to higher trophic levels in the food web.
- **Mercury** - Mercury that is released into the environment are likely to partition primarily into sediment, flood plain soils, and biological tissues. Little partitioning into surface water is expected to occur. As methylation occurs to a lesser extent in oxic sediments than in anoxic sediment, sediment-to-biota accumulation factors (BSAFs) for fish are expected to be lower than have been observed at other sites because surficial sediments tend to be well oxygenated.
- **PAHs** - PAHs that are released into the environment are likely to partition into sediment, flood plain soils, and biological tissues. Partitioning into

sediments and flood plain soils is likely to be dependent, in large measure, on organic carbon. PAH are also known to accumulate in the tissues of aquatic invertebrates. Certain PAH (i.e., high molecular weight PAH; HMW-PAH) can also be transferred to fish.

- **Nutrients** - Nitrogen and phosphorus that is released into the environment is likely to partition primarily into surface water. However, some of the phosphorus will become associated with sediment and flood plain soils.
- **Suspended Sediments** - Downstream transport and subsequent deposition in low velocity areas (e.g., lakes, sloughs) represents the principal processes governing the fate of suspended sediments.
- **Pesticides** - In-use insecticides, pesticides, and herbicides include a broad range of substances that can behave in a variety of ways when released into aquatic ecosystems. The fate of these substances depends on the physical and chemical properties of the chemical under consideration, as well as a number of site-specific factors. More information is needed on pesticide usage patterns in the watershed before the fate of these substances can be evaluated.
- **Biological oxygen demand (BOD)** - Effluents with elevated BOD that are released into the environment are likely to partition into surface water and sediment. The substances associated with the BOD are usually broken down relatively quickly (days), resulting in depressed dissolved oxygen levels in receiving water systems.

While all of these analytes have the potential to adversely affect aquatic organisms and/or their uses, not all of them can be addressed under CERCLA. By considering the physical and chemical properties of the candidate COPCs that can be addressed under CERCLA, it is possible to identify the substances that could occur in water, sediment, soils, and/or biota at levels that pose potential risks to ecological receptors in the TSMD, including:

Toxic Substances that Partition into Water

- Metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, zinc);
- Certain herbicides, insecticides, and fungicides (identification pending pesticide use survey); and,
- Hydrogen sulfide.

Toxic Substances that Partition into Sediments or Soils

- Metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, zinc);
- Monocyclic Aromatic Hydrocarbons (MAHs; BTEX);
- PAHs (13 parent PAHs + alkylated PAHs);
- Polychlorinated Biphenyls (PCBs); and,
- Organochlorine pesticides.

Bioaccumulative Substances

- Metals (cadmium, lead, mercury, selenium and zinc);
- High molecular weight PAHs [benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene, and pyrene];
- PCBs; and,
- Organochlorine pesticides.

3.3 Areas of Interest within the Study Area

The study area is defined as those portions on Missouri, Kansas, and Oklahoma that comprise the TSMD (Figure 1). The USEPA has identified four National Priorities

List (NPL) sites within the TSMD, including Cherokee County, KS, Newton County, MO, Jasper County, MO, and Tar Creek, Ottawa County, OK. These NPL sites are contained within two main watersheds, including the Spring River basin and the Neosho River Basin. The following AoIs with respect to environmental contamination will be considered in the DERA of the TSMD (Figure 4):

Upper/Middle Spring River AoI Sub-basin

- Upper Spring River AoI
- North Fork Spring River AoI
- Middle Spring River AoI
- Cow Creek AoI
- Center Creek AoI
- Turkey Creek AoI
- Shawnee Creek AoI
- Short Creek AoI

Lower Spring River AoI Sub-basin

- Empire Lake
- Lower Spring River AoI
- Shoal Creek AoI
- Brush Creek AoI
- Willow Creek AoI
- Spring Brook AoI
- Beaver Creek AoI
- Warren Branch AoI
- Lost Creek AoI

Neosho River AoI Sub-basin

- Neosho River AoI
- Upper Tar Creek AoI
- Middle Tar Creek AoI
- Lytle Creek AoI
- Lower Tar Creek AoI
- Elm Creek AoI

Chapter 4 Environmental Fate and Ecological Effects of Chemicals of Potential Concern

4.0 Introduction

A stressor is any physical, chemical, or biological entity that has the potential to cause a change in the ecological condition of the environment (USEPA 2000a). Accurate identification of the stressor or stressors that are causing or substantially contributing to biological impairments in aquatic ecosystems is important because it provides a basis for developing strategies that are likely to improve the quality of aquatic resources (USEPA 2000a). In this way, limited human and financial resources can be directed at the challenges that are most likely to maintain or restore beneficial uses.

The DERA of the TSMD is focused on the identification of the chemical stressors that are posing a potential risk to aquatic receptors. Many physical (e.g., water temperature, salinity, dissolved oxygen, erosion and sedimentation, habitat degradation, and pH) and biological (e.g., introduced species, recreational and commercial fishing, disease) factors also have the potential to adversely affect aquatic organisms. However, quantification of the effects of these factors on key ecological receptors is outside the scope of the DERA. The strategy for addressing this apparent limitation of the DERA involves assessing risks to ecological receptors in the study areas relative to the comparable risks to those receptors in reference areas. In this way, we will estimate the incremental risks (i.e., or additional risks, which is often referred to as Δ risk) posed by COPCs above that posed by physical and biological stressors in the systems. In addition, any unaccounted effects of such factors on the measurement endpoints will be addressed in the associated uncertainty analysis (see Section 9.4). This section of the problem formulation document is intended to support the identification of exposure pathways and receptors at risk for each of the

COPCs in the TSMD. The reader is directed to Appendix 2 for more detailed information on the environmental fate and effects of the preliminary COPCs at the site.

4.1 Arsenic (As)

Arsenic is a naturally-occurring substance; nevertheless, human activities can result in releases of substantial quantities of this substance into the environment. Base metal and gold production facilities are the principle anthropogenic sources of arsenic in Canada, with other sources including use of arsenical pesticides in agriculture and wood preservation, coal-fired power generation, and disposal of domestic and industrial wastes. Arsenic compounds have also been used in paints, pharmaceuticals, and glass manufacturing (Environment Canada and Health Canada 1993). Due to its reactivity and mobility, As can cycle extensively through the biotic and abiotic components of aquatic and terrestrial ecosystems, with ocean sediments representing the ultimate sink for most environmental As (Environment Canada and Health Canada 1993).

While As may be an essential trace element in animals, it is toxic to aquatic organisms at elevated concentrations. Among the species tested, marine algae tend to be the most sensitive, with chronic toxicity thresholds of <10 µg/L reported in the literature (Environment Canada and Health Canada 1993). Exposure of marine invertebrates and fish to As concentrations of > 100 µg/L resulted in adverse effects on the survival, growth, and reproduction of exposed species (Environment Canada and Health Canada 1993). Sediment-associated As has also been shown to be toxic to marine and estuarine invertebrates, with effect concentrations in the 30 to 100 mg/kg DW range reported (Environment Canada and Health Canada 1993). Exposure to elevated levels of sediment-associated As causes acute (i.e., short-term) and

chronic (i.e., long-term) toxicity to sediment-dwelling organisms. Certain avian species have been shown to be highly sensitive to the effects of As, particularly during embryonic exposures. The adverse effects that have been documented in avian and/or mammalian wildlife in association with exposure to As include reduced egg hatchability, teratogenicity, muscular debilitation, and behavioural abnormalities. See (Environment Canada and Health Canada 1993) for more information on the environmental fate and effects of Cu.

4.2 Cadmium (Cd)

Cadmium (Cd) is released to the environment from both natural and anthropogenic sources. Small amounts of Cd enter the environment from the natural weathering of minerals, forest fires, and volcanic emissions (ATSDR 1999). Mining and smelting operations, fuel combustion, disposal of metal-containing products, and application of phosphate fertilizer or sewage sludges are major anthropogenic sources (ATSDR 1999). In the marine environment, Cd tends to become associated with biological tissues or bottom sediments.

The toxicity of Cd to aquatic species is dependent on pH, salinity, and hardness (Voyer and McGovern 1991). Cd toxicity has been extensively investigated and found to cause toxicity in aquatic plants, invertebrates, and fish, causing effects on survival, growth, and reproduction. Cd has been shown to exhibit toxicity in avian receptors, causing renal pathological changes. Mammals may be more susceptible to Cd than birds, based on critical tissue concentrations. More information on the environmental fate and effects of Cd is provided in Outridge *et al.*(1992).

4.3 Copper (Cu)

Copper may be released into the environment from a variety of agricultural, municipal, and industrial sources. In aquatic systems, Cu tends to become associated with dissolved materials or suspended particles, including both organic or inorganic substances. Over time, these forms of Cu tend to become associated with biological tissues and bottom sediments.

Copper is highly toxic to aquatic organisms (particularly the dissolved form), causing effects on the survival, growth, and reproduction of fish, invertebrates, and plants. Exposure to elevated levels of sediment-associated Cu causes acute (i.e., short-term) and chronic (i.e., long-term) toxicity to sediment-dwelling organisms. While avian and mammalian wildlife species tend to be less sensitive to the effects of Cu than are aquatic organisms, dietary exposure to elevated levels of Cu can cause organ damage, reduced growth, and death. See Appendix 2 for more information on the environmental fate and effects of Cu.

4.4 Chromium (Cr)

Chromium may be released into the environment from a number of municipal and industrial sources. Trivalent Cr, Cr(III), and hexavalent Cr, Cr(VI), are the two principal forms of Cr in the environment. The fate of Cr in aquatic systems varies depending on the form of the metal that is released and the environmental conditions in the receiving water system. Generally, Cr(III) forms associations with sediment, while Cr(VI) remains in the water column.

Both forms of Cr are toxic to aquatic organisms, with Cr(VI) being the more toxic of the two. Dissolved Cr is highly toxic to aquatic plants and invertebrates, with short-

and long-term exposures causing adverse effects on survival, growth, and reproduction. Fish are generally less sensitive to the effects of Cr than are invertebrates. Exposure to elevated levels of sediment-associated Cr causes acute and chronic toxicity to sediment-dwelling organisms. Dietary exposure to Cr can also adversely affect survival, growth, and reproduction in avian and mammalian wildlife species. See Appendix 2 for more information on the environmental fate and effects of Cr.

4.5 Lead (Pb)

Although Pb may be released into the environment from natural sources, most of the Pb that occurs in aquatic systems has been released due to human activities. Depending on the form of Pb that is discharged, Pb can remain dissolved in the water column or become associated with sediments upon release to aquatic systems.

While dissolved Pb is not highly acutely toxic to aquatic organisms, longer-term exposure to relatively low levels of this substance can adversely affect the survival, growth, and reproduction of fish, invertebrates, and, to a lesser extent, aquatic plants. Exposure to elevated levels of sediment-associated Pb causes acute and chronic toxicity to sediment-dwelling organisms. In birds and mammals, dietary exposure to elevated levels of Pb can cause damage to the nervous system and major organs, reduced growth, impaired reproduction, and death. The organic forms (i.e., associated with carbon) of Pb tend to be more toxic than the inorganic forms (i.e., Pb salts). See Appendix 2 for more information on the environmental fate and effects of Pb.

4.6 Mercury (Hg)

Natural sources, such as volcanic activity, weathering, and releases from oceans, are known to release Hg into the environment. However, far greater amounts of Hg are released due to anthropogenic activities, such as coal combustion, chemical manufacturing (e.g., chlorine and alkali production from chlor-alkali plants), and non-ferrous metal production, waste incineration, and the dumping of sewage sludge. Upon release into the environment, Hg can remain in the water column, become associated with sediments or accumulate in the tissues of aquatic and terrestrial organisms. Aquatic plants take up very little Hg from water, air, and sediments. For aquatic animals such as fish and invertebrates, the primary routes of exposure include the direct uptake of Hg from surrounding water via the gills, skin, and the gut, as well as the consumption of contaminated prey.

Mercury has the potential to cause a wide range of adverse effects in aquatic and terrestrial organisms, with methylmercury (the principal organic form of the substance) being the most toxic. The effects of Hg poisoning in fish and wildlife include altered behavior and physiology, reduced reproduction, impaired growth and development, and death. Of the forms of Hg that are present in the environment, methylmercury is the most potent form. Top level predators, especially fish-eating birds and mammals are at the highest risk of exposure and resulting adverse effects. See Appendix 2 for more information on the environmental fate and effects of Hg.

4.7 Nickel (Ni)

Nickel is released into the environment from natural sources and human activities, with the burning of fossil fuels and the processing of Ni-bearing ores being the most important sources. Unlike many other metals, Ni is considered to be highly mobile

in aquatic ecosystems, repeatedly cycling between the water column, bottom sediments, and biological tissues.

While there is little information available with which to assess the effects of sediment-associated Ni, exposure to dissolved Ni is known to adversely affect the survival, growth, and reproduction of amphibians, fish, invertebrates, and aquatic plants. In birds and mammals, dietary exposure to elevated levels of Ni can result in reduced growth and survival. See Appendix 2 for more information on the environmental fate and effects of Ni.

4.8 Selenium (Se)

Selenium (Se), is a non-metallic element with an atomic number of 34 and a molar mass of 78.96 g (ATSDR 2003). Elemental selenium is commercially produced, primarily as a by-product of copper refining. Selenium is concentrated in the sulfide minerals such as galena, chalcopyrite, arsenopyrite, sphalerite, pyrite, marcasite, and pyrrhotite (ATSDR 2003). Much of the selenium in rocks is combined with sulfide minerals or with silver, copper, lead, and nickel minerals. Of all the pollutants, selenium has the narrowest range between beneficial and detrimental concentrations for biota (USEPA 2004). Aquatic and terrestrial organisms require 0.5 µg/g dry weight (dw) of selenium in their diet to sustain metabolic processes, whereas concentrations of selenium that are only an order of magnitude greater than the required level have been shown to be toxic to fish (USEPA 2004).

The distribution and cycling of Se in the environment is heavily influenced by its oxidation state, which in turn is dependent on the range of pH, redox potential, and biological activity conditions encountered (ATSDR 2003). In surface waters, the salts (particularly sodium) of selenic and selenious acids are the dominant forms

encountered. In alkaline, oxygenated waters, sodium selenate is an important species that is very mobile due to its inability to adsorb to sediment particles (ATSDR 2003). Under acidic conditions selenite salts may be converted to elemental Se, which is stable under a wide range of pH and redox conditions (USEPA 2004). Plants, fungi, bacteria, microorganisms, and animals can produce methylated forms of Se (dimethylselenide and dimethyldiselenide) from inorganic and certain organic forms (Adriano 1986). The formation of methylated Se compounds by animals appears to be one mechanism for Se detoxification as the toxicity of dimethyl selenide is 500 to 1000 times lower than the toxicity of Se^{2-} (Vokal-Borek 1979).

Water-borne selenium can be toxic to aquatic organisms, with taxa from freshwater invertebrates being the most sensitive, followed by fish, alga and macrophytes (Nagpal and Howell 2001). The toxicity of selenium to aquatic organisms is governed by several factors, principal among them; the form and concentration of Se; the species and lifestage of the organism; the period of exposure; and water conditions (Nagpal and Howell 2001). Maier et al. (1993) studied mortality in the neonates of the water flea (*Daphnia magna*) exposed to different forms of selenium in water at pH 8.2, dissolved oxygen level of 8.6 mg/L, and 20 °C. The 48-h LC_{50} s were as follows: 2.84, 0.55, 0.31 and 2.01 for selenate-Se, selenite-Se, selenomethionine, and selenocystine, respectively. In chronic toxicity tests with invertebrates, the reported toxicity thresholds ranged from 0.002 to 15 mg Se/L (Nagpal and Howell 2001). Acute toxicity of selenium to swim-up fry (8-12 weeks) of coho salmon (*Oncorhynchus kisutch*) was observed at 7.8 mg/L of selenite-Se or 32.5 mg/L of selenate-Se; both tests conducted at pH 7.82, 12 °C, water hardness of 333 mg CaCO_3 /L (Hamilton and Buhl 1990). It was also observed that the younger life stages of both coho and chinook salmon were more sensitive to the toxic effects. The reported 4-d EC_{50} s for green algae *Selenastrum capricornutum* were 0.199 mg Se/L and 2.9 mg Se/L, for selenate-Se and selenite-Se respectively (Richter 1982).

4.9 Silver (Ag)

In 1990, about 50% of the refined silver consumed in the USA was used to manufacture photographic and X-ray products; 25% in electrical and electronic products; 10% in electroplated ware, sterling ware, and jewellery; 5% in brazing alloys; and 10% in other uses (WHO 2002). Weathering of silver-bearing rocks and soil by the wind and rain is a large natural source of silver (ATSDR 1990). Emissions from smelting operations, manufacture and disposal of certain photographic and electrical supplies, coal combustion, and cloud seeding are some of the anthropogenic sources of silver.

The global cycle of silver involves its release to the atmosphere, water, and land by natural and anthropogenic sources; transport over potentially long distances in the atmosphere; deposition (wet and dry); and, sorption to sediments (Eisler 1996). The transport and partitioning of silver in surface waters and soils is influenced by the form of the compound. Lindsay and Sadiq (1979) stated that under oxidizing conditions the primary silver compounds would be bromides, chlorides, and iodides, while under reducing conditions the free metal and silver sulfide would predominate.

Several species of freshwater plants, invertebrates and vertebrates have demonstrated the ability to bioconcentrate silver from the environment, but there is no evidence that silver biomagnifies in aquatic or aquatic-dependent food chains (Warrington 1996; Connell *et al.* 1991; Ratte 1999). Reported bioconcentration factors (BCFs) for bioavailable silver in freshwater organisms include 200 for freshwater plants (at 26 ppb silver), 21 to 240 in three species of aquatic insects, and negligible in bluegill sunfish (*Lepomis macrochirus*; WHO 2002; USEPA 1980a).

The acute toxicity of silver to aquatic species varies drastically by the chemical form, with ionic silver⁺ being one of the most toxic metals to aquatic organisms based on the results of laboratory toxicity tests (Eisler 1996). Silver is lethal to various species

of aquatic organisms, including insects, daphnids, amphipods, trout, flounders, sticklebacks, guppies, and dace plants, invertebrates, and teleosts at water concentrations as low as 1.2 to 4.9 µg/L (Eisler 1996). The 7-day LC₅₀ value for rainbow trout (*Oncorhynchus mykiss*) exposed to silver nitrate was 9.1 µg/L. Silver toxicity to aquatic species appears to be reduced by increasing water hardness between 50 and 250 mg CaCO₃/L, increasing pH between 7.2 and 8.6, increasing concentrations of humic acid and copper, and increasing salinity (Eisler 1996). As is the case with water, silver nitrate is orders of magnitude more toxic than silver chloride and silver thiosulfate in sediments (Rogers 1997). Sediment characteristics significantly affected silver bioavailability to the amphipod, *Hyalella azteca*, with 10-day LC₅₀s ranging from 1.62 mg silver/kg to 379.7 mg silver/kg (Rogers 1997).

Silver has low toxicity to avian and mammalian wildlife species, is eliminated rapidly when ingested orally, and does not accumulate in aquatic food webs (Warrington 1996). Little data were found on the effects of silver on aquatic dependent wildlife and all studied effects were on poultry and small laboratory mammals. Silver was not mutagenic, carcinogenic, or teratogenic to tested animals by normal routes of exposure (Eisler 1996).

4.10 Zinc (Zn)

Zinc is released into the environment as a result of various human activities, including electroplating, smelting and ore processing, mining, municipal wastewater treatment, combustion of fossil fuels and solid wastes, and disposal of Zn-containing materials. In aquatic systems, Zn can be found in several forms, including the toxic ionic form, dissolved forms (i.e., salts), and various inorganic and organic complexes. While Zn can form associations with particulate matter and be deposited on bottom sediments,

sediment-associated Zn can also be remobilized in response to changes in physical-chemical conditions in the water body.

The acute toxicity of dissolved Zn is strongly dependent on water hardness, however, chronic toxicity is not. Long-term exposure to dissolved Zn has been shown to adversely affect the survival, growth, and reproduction of fish, invertebrates, and aquatic plants. Exposure to sediment-associated Zn is associated with reduced survival and behavioral alterations in sediment-dwelling organisms. In birds and mammals, dietary exposure to elevated levels of Zn can cause impaired survival, growth, and health. See Appendix 2 for more information on the environmental fate and effects of Zn.

4.11 Monoaromatic Hydrocarbons (MAHs)

Monocyclic aromatic hydrocarbons are a group of widely distributed volatile organic compounds (VOCs) found in petroleum hydrocarbons. Most commonly included in this group are benzene, toluene, ethylbenzene, and xlenes (*o*-xylene, *m*-xylene and *p*-xylene), which together are referred to as BTEX.

Releases of MAHs into the environment occur almost exclusively in association with anthropogenic sources; namely the extraction, transport, storage and/or use of oil and oil-based products (Dewulf and Langenhove 1997). Contamination can occur in soil, air and water. Contamination of marine waters with MAHs is a concern due to the increase in development and industry along coastal areas. These compounds are commonly found in coastal aquifers and can find their way to marine and estuarine environments via groundwater discharge to surface water (Robinson *et. al.* 2008).

MAHs are highly soluble and volatile toxic substances. Biodegradation and volatilization in the environment depends on conditions such as temperature, presence of acclimated microorganisms, and mixing conditions, such as winds, currents and tidal influences (CCME 1999). Generally MAHs are non-persistent in the environment, are rapidly biodegraded, and tend not to be absorbed into soil or sediment. If the concentration of compounds is high, however, they can persist in the soil and water for extended periods of time (Erben *et. al.* 2002). In addition, they are persistent in groundwater because volatilization does not occur and because they are not susceptible to anaerobic biodegradation (CCME 1999).

Releases of MAHs into aquatic ecosystems have been shown to adversely effect both aquatic and terrestrial organisms. The results of many studies demonstrate that exposure to BTEX reduces the survival and/or growth of plants, algae, bacteria, amphibians, invertebrates and fish (CCME 1999). For example, MAHs are rapidly taken up by gill tissues in fish and distributed to all other organs. In addition, crustaceans and molluscs can not metabolize aromatic hydrocarbons and, as a result, these substances remain stored in the invertebrates (Erben *et. al.* 2002). In general, the most immediate harm to aquatic organisms occurs within the first one to two weeks after exposure to MAHs. Similarly, various wildlife species have been shown to be susceptible to the toxic effects of MAHs, particularly when exposed in association with oil spills or other discharges that release substantial quantities of these substances over a short period of time (Erben *et. al.* 2002)

4.12 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons are a diverse class of organic compounds that include about one hundred individual substances containing two or more fused benzene, or aromatic, rings. The term low molecular weight (LMW) PAHs is applied

to the group of PAHs with fewer than four rings, while high molecular weight (HMW) PAHs have four or more rings. The LMW PAHs include acenaphthene, acenaphthylene, anthracene, fluorene, naphthalene, 2-methylnaphthalene, and phenanthrene. The HMW PAHs include benz(a)anthracene, benzo(a)pyrene, chrysene, dibenz(a,h)anthracene, fluoranthene, and pyrene.

The behavior of PAHs in surface waters depends on a variety of chemical-specific and site-specific factors, with physical-chemical properties playing an important role in determining their fate in aquatic systems. The PAHs with high solubilities (such as naphthalene) may remain dissolved in surface water, while those with lower solubilities are likely to form associations with colloidal material or suspended particulates. Hence, PAHs are commonly associated with suspended particulates in aquatic systems. While PAHs associated with suspended particulates may be photochemically degraded, biodegraded, transported to other areas, and incorporated into aquatic biota, deposition and consolidation with bedded sediments probably represents the most important environmental fate process. Hence, sediments represent the major environmental sink for these compounds.

Releases of PAHs into aquatic ecosystems pose a number of potential risks to aquatic and terrestrial organisms. Water-borne PAHs can be acutely lethal to invertebrates, fish, and amphibians; long-term exposure to sub-lethal levels can impair survival, growth and reproduction. Similarly, exposure to sediment-associated PAHs can adversely affect the survival, growth, and reproduction of benthic invertebrates. Accumulation of PAHs in the tissues of aquatic organisms can adversely affect the survival and reproduction of aquatic-dependent avian and mammalian wildlife species (i.e., those species that consume aquatic invertebrates and/or fish). See Appendix 2 for more information on the environmental fate and effects of PAHs.

4.13 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls are synthetic substances and are released into the environment solely as a result of human activities. PCBs are widespread environmental contaminants and are commonly detected in air, precipitation, soil, surface water, groundwater, sediment, and living organisms. PCBs released to aquatic systems tend to partition into and become incorporated into sediments. PCBs have a high potential for uptake by aquatic and terrestrial organisms, including fish, birds, mammals, and other wildlife. Due to their chemical stability, PCBs are highly persistent in the environment. Hence, cycling, rather than degradation, represents the most important process affecting PCBs once released into the environment.

The PCBs that are released into aquatic ecosystems pose a number of potential risks to aquatic and terrestrial organisms. Although, water-borne PCBs can be acutely lethal to invertebrates, fish, and amphibians, the primary concerns associated with PCBs are effects on survival, growth and reproduction from long-term exposures. Similarly, exposure to sediment-associated PCBs can adversely affect the survival, growth, and reproduction of benthic invertebrates and, potentially, benthic fish species. Accumulation of PCBs in the tissues of aquatic organisms can adversely affect the survival, growth, and reproduction of aquatic-dependent avian and mammalian wildlife species (i.e., those species that consume aquatic invertebrates and/or fish). See Appendix 2 for more information on the environmental fate and effects of PCBs.

4.14 Organochlorine Pesticides

Organochlorine pesticides are a group of insecticides composed primarily of carbon, hydrogen, and chlorine. Many have been banned due to their high toxicity, adverse

human health effects, persistence in the environment, and high bioaccumulation rates in biota. The list of organochlorine pesticides that have been banned includes DDTs, mirex, aldrin, dieldrin, toxaphene, chlordane and heptachlor. Still in use today include lindane, endosulfan, methoxychlor, and pentachlorophenol. DDTs, dieldrin, mirex, and methoxychlor are profiled in greater detail below.

4.14.1 Dichlorodiphenyltrichloroethane (DDTs)

Dichlorodiphenyltrichloroethane (DDT) is a chemical that was widely used in pest control in agriculture and against insects that carry disease, such as malaria. Its use was banned in the 1970's nearly worldwide, but it is still used today in some countries to control disease spreading insects (ATSDR 2002a). Technical grade DDT is a mixture of three forms: *p,p'*-DDT (85%), *o,p'*-DDT (15%), and *o,o'*-DDT (trace amounts). DDE (dichlorodiphenyldichloroethylene) and DDD (dichlorodiphenyldichloroethane) are chemicals similar to DDT that enter the environment as contaminants or breakdown products of DDT.

DDT is persistent in the environment, with the half-life in soil usually being between 2-15 years, but can be as long as many hundreds of years depending on environmental conditions. The length of time that DDT lasts in soil depends on many factors including temperature, type of soil, and whether the soil is wet (ATSDR 2002a). DDT lasts for a shorter period in soils in tropical climates (where the chemical evaporates faster and where microorganisms degrade it faster), when soil is wet, and when it initially enters the soil (ATSDR 2002a).

DDT, DDE and DDD can enter the air when they evaporate from contaminated water and soil. They are then deposited on land or surface water. This cycle of evaporation and deposition may be repeated many times in a process known as “global distillation” (Bard 1999; Bidleman *et. al.* 1992; Goldberg 1975; Ottar 1981; Wania and MacKay 1993). As a result, DDT, DDE, and DDD can be carried long distances

in the atmosphere and have been found in bogs, snow and animals as far away as the Arctic and Antarctic (Anthony *et. al.* 1999; Harner 1997).

DDT is also highly bioaccumulative and can accumulate to high levels in fish, birds, and mammals. The highest levels of DDT are found in animal fatty adipose tissue. The bioconcentration factor (BCF) of DDT in rainbow trout has been reported to be as high as 12,000 (Oliver and Niimi 1985), and other BCFs that have been reported include: 51,000–100,000 in fish; 4,550–690,000 in mussels; and, 36,000 in snails (Davies and Dobbs 1984; Geyer *et. al.* 1982; Metcalf 1973a; Reish *et. al.* 1978; Veith *et. al.* 1979). DDT bioconcentration studies in aquatic environments with representatives of various trophic levels demonstrate that bioconcentration increases with increasing trophic levels (LeBlanc 1995). That is, DDTs tend to biomagnify in the food web.

The observed effects to wildlife are severe and numerous. For example, DDT exposure is linked to developmental abnormalities in amphibians (such as delayed metamorphosis from tadpole to frog) and birds (such as reduced growth). DDT also causes neurological effects including tremors, uncoordinated movement, hyperactivity, and weakness. DDT intake, particularly during sexual differentiation, can adversely affect the reproductive system of male animals. Many other studies have shown that DDT can adversely affect liver weight, body weight, heart weight, kidney weight, increase metabolism, development (spine abnormalities, delayed development, hatching sex ratio), and adversely effect respiration, to give a few examples (ATSDR 2002a).

4.14.2 Dieldrin

Dieldrin (CAS; Chemical Abstracts Service Number 60-57-1) is an organochlorine insecticide that is closely related structurally and chemically to aldrin. Pure dieldrin is a white powder with a mild chemical odor. The less pure commercial powders

have a tan color. Dieldrin is also known as HEOD (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-1,4-exo-5,8-dimethanonaphthalene), Compound 497, Octalox, Insecticide no.497, ENT 16225, Alvit, Dioldrex, Dioldrite, and Panoram D31 (USEPA 1979; McNeely *et al.* 1979; Windholtz *et al.* 1983; Agriculture Canada 1984). Its toxicity does not differ significantly from that of aldrin.

Dieldrin has been used in agriculture for soil and seed treatment and in public health to control disease vectors such as mosquitoes and tsetse flies. Dieldrin has also had veterinary use as a sheep dip and has been used in treatment of wood and mothproofing of woolen products (Marth 1965). Dieldrin used to be one of the most widely used domestic pesticides (Lykken 1971; Waldbott 1978; USEPA 1980). The original uses of dieldrin were as a pesticide for control of soil, fruit, and vegetable pests, as well as for control of grasshoppers, locusts and termites.

The pathways for environmental contamination by dieldrin include atmospheric dispersion, wind and water erosion of soil, and transport while sorbed onto soil particles in the silt of streams and lakes. Dieldrin can also move through the environment as residues in plants and animals, especially in fish and wildfowl (Lykken 1971).

Dieldrin is considered to be persistent in the environment. Sorption volatilization and bioaccumulation are the important processes determining its fate (USEPA 1979). Dieldrin binds to soil particles and slowly evaporates into the air. Although dieldrin is persistent in soil, environmental background levels are known to be decreasing slowly. Plants take up dieldrin from the soil and store it in their tissues. When animals take up dieldrin, it is stored in the fat and leaves the body very slowly.

The hydrolysis of dieldrin in the aquatic environment is very slow (Eichelberger and Lichtenberg 1971). However, sorption to sediments containing organic matter is

appreciable. An organic carbon partition coefficient (K_{oc}) of approximately 104 at 15°C has been reported (Weil *et al.* 1973). Experimental studies suggest that direct photolysis of dieldrin does occur; its photolytic half-life is approximately 2 months (Henderson and Crosby 1968). Volatilization of dieldrin from aquatic systems is also an important removal process. Half-lives in the order of a few hours to a few days have been determined from laboratory experiments (Singmaster 1975).

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Dieldrin may be bioaccumulated by various organisms in the aquatic environment. Bioconcentration factors of about 100 have been reported for bacteria and freshwater algae (Grimes and Morrison 1975; Neudorf and Khan 1975). Data from microcosm experiments also suggest significant bioaccumulation (Sanborn and Vu 1973; Metcalf *et al.* 1973b). Bioconcentration factors of 102 to 103 for algae, 104 to 105 for snails, and 103 for fish were reported. Biological half-lives in fish vary from 7 days in bluegill sunfish (*Lepomis macrochirus*; Gakstatter and Weiss 1967) to 40 days in rainbow trout (*Salmo gairdneri*; Macek *et al.* 1970). Very little microbial biotransformation of dieldrin occurs in the aquatic environment (Bohonos and Francis 1975; Sanborn *et al.* 1977).

Dieldrin has also shown to be highly toxic to aquatic organisms. Acute exposures to a variety of fish species (salmon, trout, minnow, catfish, bass, bluegill) have resulted in lethal concentrations in the range of 1 to 20 µg/L (USEPA 2001). Dieldrin has also been observed to illicit adverse effects to benthic organisms, such as reduced populations and species richness. Jaagumagi (1988) and Jaagumagi *et al.* (1989)

reported significant decreases in abundance of benthic organisms at sites in Humber Bay, Lake Huron compared to reference sites. Toxicity to the marine amphipod, *Rhepoxynius abronius* was observed at a concentration of 1.17 µg/g from sediments from Puget Sound, WA (Pastorok and Becker 1990).

Dieldrin is moderately to highly toxic to mammals. Acute oral LD₅₀ for rats has been reported in the range of 24 to 87 mg/kg, while those for rhesus monkeys are as low as 3 mg/kg (HSDB 2000b). Studies with animals fed dieldrin have shown that the liver can be damaged and the ability of the immune system to protect against infections can be suppressed. In addition, liver tumours, pulmonary adenomas, and pulmonary carcinomas have been reported in mice fed dieldrin for extended periods (Walker *et. al.* 1972). Adverse effects on growth and reproduction have also been observed in mammals exposed to this substance in their diets (IPCS 1989; USEPA 1980; NIOSH 1978; IARC 1974; Clayton and Clayton 1994).

4.14.3 Methoxychlor

Methoxychlor is a manufactured chemical used as an insecticide. It enters the environment when it is applied to agricultural crops, home gardens, forests, and livestock. When released into the air it eventually settles on the ground and binds strongly to soil particles (ATSDR 2002b). It does not dissolve easily in water; rather it tends to bind to particulate matter and become associated with bottom sediments. Methoxychlor breaks down slowly and may take months to biodegrade. Some breakdown products of methoxychlor can be as harmful as methoxychlor itself (ATSDR 2002b).

Bacteria and microorganisms break down methoxychlor, but very slowly. It can also be broken down by a reaction with water or materials in soil. In air and water, methoxychlor is also broken down by sunlight (ATSDR 2002b). Half-lives of <30

days in anaerobic soils and >100 days aerobic soils have been observed for methoxychlor (Fogel *et al.* 1982; Muir and Yarechewski 1984).

Methoxychlor can accumulate in aquatic organisms, including algae, bacteria, snails, clams, and some fish. However, most fish and animals change methoxychlor into other substances that are rapidly released from their bodies. Therefore methoxychlor usually does not biomagnify in the food web (Kapoor *et al.* 1970). Studies have shown that there is considerable variation between species relative to how much methoxychlor bioaccumulates, perhaps as the result of species differences in the capacity to metabolize and eliminate methoxychlor (ATSDR 2002b).

Data indicates that methoxychlor has endocrine disruptive effects on fish and amphibians. Impaired fertility, growth, and development of sea urchins has also been demonstrated in response to exposure to methoxychlor (ATSDR 2002b). Animal studies show that exposure to methoxychlor in food or water harms the ovaries, uterus, and mating cycle in females and the testes and prostate in males (ATSDR 2002b). Fertility is decreased in both male and female animals. These effects can occur both in adult and in developing animals. Such effects could also occur following inhalation or skin contact. These effects are caused by a breakdown product of methoxychlor, which acts as a natural sex hormone (ATSDR 2002b).

Exposure can also cause neurological effects similar to those caused by DDT, such as decreased locomotor activity, tremors, convulsions and death (Cannon Laboratories 1976; Dikshith *et al.* 1990).

4.15 Ammonia

Ammonia is colourless gas, with a pungent, suffocating odour and an atomic mass of 17.03 (CCME 2000). In aqueous solutions, an equilibrium exists between un-ionized (NH_3) and ionized (NH_4^+) ammonia species. Ammonia is an important component of the nitrogen cycle and because it is oxidized in the environment by microorganisms, it is a large source of available nitrogen in the environment (CCME 2000). Ammonia is used in numerous applications in the refrigeration, pulp and paper, mining, food processing, refining, and animal husbandry sectors. The principal use of ammonia in the production of nitrogenous fertilizers (ammonium nitrate, ammonium phosphate, urea, and ammonium sulphate; CCME 2000).

Ammonium is highly soluble in water, reaching saturation in water at solution concentrations of 30% (ATSDR 2004). Temperature and pH are the main factors that influence the equilibrium between un-ionized and ionized ammonia. Raising pH by one unit can cause the un-ionized ammonia concentration to increase nearly tenfold, while a 5°C temperature increase can cause an increase of 40-50% (CCME 2000).

Ammonia in the environment is a part of the nitrogen cycle. It volatilizes into the atmosphere, where it may undergo a variety of reactions. In surface waters, ammonium may undergo microbiological nitrification, which yields hydrogen and utilizes oxygen so that, in certain systems, acidification and oxygen depletion may result. Ammonia may be assimilated by aquatic plants as a nitrogen source or transferred to sediments or volatilized (WHO 1986). The ammonium cation is adsorbed on positively charged clay particles, which may subsequently settle and form bed sediments. Ammonium salts such as chloride, nitrate, and sulfate are strongly dissociated and very soluble in water; therefore, and will not form ammonium precipitates at normal pHs (ATSDR 2004). Most ammonium undergoes nitrification; the nitrate ion is mobile and is removed by leaching, plant root uptake, or denitrification.

Mean 48- and 96-hr LC₅₀ values for unionized ammonia reported for freshwater invertebrates and fish ranged from 1.10 to 22.8 mg/L for invertebrates and from 0.59 to 2.37 mg/L for fish species (Environment Canada 1999). In another acute toxicity test, *Ochromonas sociabilis*, a freshwater alga, were exposed to un-ionized ammonia concentrations to observe the effect of ammonia on growth and mortality (Bretthauer 1978). Development was reduced at 0.3 mg/L NH₃ and mortality was observed at 0.6 mg/L. Sockeye salmon (*Oncorhynchus nerka*) were exposed to total ammonia for 62 day from fertilization to hatching at 10 C and ph 8.2, with hatchability as the measured endpoint. Hatchability was 63.3%, 49% and 0% in controls, at 0.12mg/L, and 0.46 mg/L, respectively. The calculated EC20 for un-ionized ammonia was 0.057 mg/L (Environment Canada 1999). The most sensitive freshwater study identified was for the rainbow trout (*O. mykiss*). The reported lowest observed effect concentration (LOEC) for un-ionized ammonia in a five year chronic study is 0.04 mg/L, exposure to this and higher concentrations resulted in pathological lesions in the gills and tissue degradation in the kidneys (Thurston *et al.* 1984).

Chapter 5 Identification of Key Exposure Pathways for the Tri-State Mining District

5.0 Introduction

As indicated previously, ERA describes the process in which the risks associated with exposure of ecological receptors to contaminated environmental media (i.e., water, sediment, soil, or biological tissues) are estimated. Evaluation of the risks posed by COPCs in the TSMD requires a detailed understanding of the pathways through which ecological receptors are exposed to these substances. In turn, the identification of key exposure pathways requires an understanding of the sources and releases of environmental contaminants and the environmental fate of these substances.

5.1 Partitioning of Chemicals of Potential Concern

There are a number of sources of toxic and bioaccumulative substances in the TSMD. Natural sources of such substances include weathering and erosion of terrestrial soils, bacterial decomposition of vegetation and animal matter, and long-range transport of substances originating from forest fires or other natural combustion sources. Anthropogenic sources of environmental contaminants include industrial wastewater discharges, municipal wastewater treatment plant discharges, surface water recharge by contaminated groundwater, non-point source discharges, and deposition of substances that have been released into the atmosphere. An overview of the sources of environmental contaminants that have been released into the TSMD is provided in Chapter 3.

Upon release into aquatic ecosystems, these COPCs partition into environmental media (i.e., water, sediment, soils, and/or biota) in accordance with their physical and chemical properties and the characteristics of the receiving water body (see Chapter 4 and Appendix 2 for descriptions of the environmental fate of the COPCs). As a result of such partitioning, COPCs can occur at elevated levels in surface water, bottom sediments, soils and/or the tissues of aquatic organisms. To facilitate the development of conceptual models that link stressors to receptors, the COPCs can be classified into three groups based on their fate and effects in the aquatic ecosystem, including bioaccumulative substances, toxic substances that partition into sediments, and toxic substances that partition into water (including the surface microlayer).

5.2 Overview of Exposure Pathways

Once released to the environment, there are three pathways through which ecological receptors can be exposed to COPCs. These routes of exposure include direct contact with contaminated environmental media, ingestion of contaminated environmental media, and inhalation of contaminated air. The exposures routes that apply to each of the categories of COPCs are described below.

Bioaccumulative Substances – Aquatic organisms and aquatic-dependent wildlife species can be exposed to bioaccumulative substances via several pathways. However, ingestion of contaminated plant and/or animal tissues (i.e., forage or prey species) represents the most important route of exposure for the majority of aquatic organisms, aquatic-dependent wildlife species, and other terrestrial wildlife. Nevertheless, direct contact with contaminated water and/or contaminated sediment also represents an important exposure route for many aquatic organisms (e.g., benthic invertebrates, fish, amphibians). Similarly, direct contact with contaminated soil can represent an important

exposure route for certain terrestrial organisms (e.g., earthworms, amphibians). Finally, ingestion of contaminated sediment and/or ingestion of contaminated soil can result in the uptake of bioaccumulative COPCs by organisms that process these materials to obtain their food or by species that ingest them incidentally during foraging activities. Cadmium, lead, mercury, zinc, and HMW-PAH represent the principal bioaccumulative COPCs in the study area; however, PCBs, and organochlorines/pesticides may also be present in certain areas.

Toxic Substances that Partition into Sediments and Flood Plain Soils –

Aquatic organisms, aquatic-dependent wildlife species, and other organisms can be exposed to toxic substances that partition into sediments and flood plain soils through several pathways. For aquatic and terrestrial organisms, such as microbiota, aquatic and terrestrial plants, sediment-dwelling organisms, terrestrial invertebrates, benthic fish, and amphibians, direct contact with contaminated sediment (and associated pore water) and/or soil represents the most important route of exposure to toxic substances that partition into sediments and soils. However, ingestion of contaminated sediments or soils can also represent an important exposure pathway for certain species (e.g., oligochaetes that process sediments or soils to obtain food). Direct contact with contaminated sediments or soils also represents a potential exposure pathway for reptiles; however, it is less important for reptiles than for other aquatic organisms.

For aquatic-dependent wildlife species, incidental ingestion of contaminated sediments and/or soils represents the principal route of exposure to toxic substances that partition into sediments and soils. Of the wildlife species that occur in the TSMD, sediment-probing birds and birds that forage on the forest floor in riparian areas are the most likely to be exposed through this pathway.

Metals, mercury, PAHs, PCBs, BTEX, other non-polar organic compounds, and phosphorus represent the principal COPCs that partition into sediments.

For substances that are associated with fine particulates, inhalation of dust represents a potential exposure pathway for certain ecological receptors. However, air quality monitoring conducted in the vicinity of chat piles suggests that this is likely to be a minor exposure route under most circumstances. Direct exposure to chat piles may also represent an complete exposure pathway for certain ecological receptors, such as terrestrial plants, soil invertebrates, and small vertebrates that utilize chat piles for den habitats.

Toxic Substances that Partition into Surface Water – Aquatic organisms and aquatic-dependent wildlife species can be exposed to toxic substances that partition into surface water through several pathways. For aquatic organisms, such as microbiota, aquatic plants, aquatic invertebrates, fish, and amphibians, direct contact with contaminated water represents the most important route of exposure to toxic substances that partition into surface water. This exposure route involves uptake through the gills and/or through the skin.

For aquatic-dependent wildlife species, ingestion of contaminated water represents the principal route of exposure to toxic substances that partition into surface water. While virtually all aquatic-dependent wildlife species are exposed to toxic substances that partition into surface water, this pathway is likely to account for a minor proportion of the total exposure for most of these species. Metals, ammonia, nitrite, nitrate, TSS, and certain pesticides (i.e., insecticides, herbicides, and fungicides) represent the principal COPCs that partition into surface water.

Toxic Substances that Partition into the Surface Microlayer – Aquatic organisms and aquatic-dependent wildlife species can be exposed to toxic

substances that partition into surface water through several pathways. For aquatic organisms, such as aquatic invertebrates and pelagic fish, direct contact with the contaminated surface microlayer (i.e., the layer of water that is present at the water-air interface) represents the most important route of exposure to such toxic substances. This exposure route involves uptake through the gills and/or through the skin of aquatic organisms. Metals, nutrients, PAHs, BTEX, and certain pesticides (i.e., insecticides, herbicides, and fungicides) represent the principal COPCs that partition into the surface microlayer

For aquatic-dependent wildlife species (birds and mammals), inhalation of substances that volatilize from the surface microlayer represents the principal route of exposure to toxic substances that partition into this environmental medium. However, this route of exposure is likely to be of relatively minor importance under most circumstances. This pathway could become important during and following accidental spills, when such substances are present as slicks on the water surface.

Chapter 6 Identification of Receptors Potentially at Risk at the Tri-State Mining District

6.0 Introduction

A critical element of the problem formulation process is the identification of the receptors at risk that occur within the study area. USEPA guidance is available to help identify receptors at risk (USEPA 1989; 1992; 1997; 1998). The guidance states that receptors at risk include: (1) resident species or communities exposed to the highest chemical concentrations in sediments and surface water; (2) species or functional groups that are essential to, or indicative of, the normal functioning of the affected habitat; and, (3) federal or state threatened or endangered species.

In the TSMD, the ecological receptors potentially at risk include the plants and animals that utilize aquatic, wetland, and terrestrial habitats within the watershed. There are a wide variety of ecological receptors that could be exposed to contaminated environmental media in the TSMD. The aquatic and terrestrial receptor groups that were identified by workshop participants included (possible focal species are identified in parentheses):

- Aquatic and soil-resident microorganisms;
- Aquatic plants (periphyton, aquatic macrophytes, phytoplankton in lakes);
- Terrestrial plants (riparian plant species);
- Benthic invertebrates (including, but not limited to, mayflies, stoneflies, and caddisflies; i.e., EPT Taxa);
- Mollusks (freshwater mussels, snails);
- Soil invertebrates (earthworms);

- Benthic Fish (darters, sculpins, suckers, Neosho madtoms);
- Pelagic fish (smallmouth bass, other Centrarchids);
- Amphibians;
- Reptiles;
- Piscivorous birds (kingfishers, osprey, eagles);
- Carnivorous-wading birds (great blue heron, egrets);
- Sediment-probing birds (mallards, sandpipers, Canadian geese);
- Raptors (bald eagles, hawks);
- Herbivorous mammals (deer, rabbits, muskrat, beaver):
- Carnivorous mammals (fox, mink);
- Omnivorous mammals (mice, raccoons)
- Vermivorous mammals (shrews);
- Piscivorous mammals (otters).

The various groups of ecological receptors that occur within the TSMD are further described in the following sections.

6.1 Microbial Community

Microbial communities consist of bacteria, protozoans, and fungi and play several essential roles in freshwater and terrestrial ecosystems. First, the microbial community represents an important food source for many organisms, such as worms, bivalves, and snails (Apple *et al.* 2001). In addition, microbial communities also play a number of key roles in the cycling and transformation of nutrients in soils, sediments, and the water column (Odum 1975). For example, the microbial

community is an essential component of the nitrogen cycle, in which atmospheric nitrogen is converted, through a series of steps, into nitrates, nitrites, and ammonia. These forms of nitrogen represent essential plant nutrients and are the basic building blocks for protein synthesis (Colinvaux 1973). The sulfur cycle in aquatic environments, in which hydrogen sulfide is converted to sulfate (which is incorporated into plant and animal tissues), is also mediated by the microbial community (Odum 1975). The microbial community also supports primary productivity by transforming phosphorus into forms that can be readily used by aquatic plants (i.e., phosphate). Finally, carbon cycling (i.e., between the dissolved and particulate forms) in aquatic and terrestrial ecosystems is dependent on the microbial community. Although specific information on the composition of microbial communities in the TSMD was not located, it is certain that the microbial community plays an essential ecological role in this watershed.

6.2 Plant Communities

The plant communities in the TSMD consist of phytoplankton, periphyton, aquatic macrophytes, and riparian and upland vegetation. Phytoplankton, the small non-vascular plants that are suspended in the water column, are comprised of several types of algae. While periphyton are also non-vascular plants, they tend to be larger than the plankton forms of algae and grow on other aquatic plants or on the bottom of the watercourse. Aquatic macrophytes is the general term applied to either large vascular or non-vascular plants that grow in freshwater systems (including both submergent and emergent plants). Riparian vegetation is the term that is applied to the vascular plants that grow along the waters edge. Upland vegetation include the plant species that grow in areas outside the river channel and floodplain.

As primary producers, aquatic plants transform the sun's energy into organic matter. Aquatic, riparian, and terrestrial plants represent a primary food source for a variety of plant-eating invertebrates (i.e., herbivores, which are also known as primary consumers). In addition, aquatic, riparian, and terrestrial plants provide habitats for a wide variety of species, including aquatic and terrestrial invertebrates, fish, and wildlife. Hence, plants represent essential components of aquatic, riparian, and terrestrial ecosystems.

6.2.1 Phytoplankton Communities

Phytoplankton represent an essential component of aquatic food webs because they convert the sun's energy into organic matter, which can then be consumed by zooplankton (i.e., the tiny animals that are suspended in the water column; Odum 1975). There are many different species of algae that can comprise phytoplankton communities, which generally fall into seven main groups. The blue-green algae (cyanophyta) are the most primitive group of algae, with a cell structure like that of bacteria (i.e., the cells lack certain membranous structures, such as nuclear membranes, mitochondria, and chloroplasts; Bell and Woodcock 1968). Blue-green algae can occur in unicellular, filamentous, and colonial forms, many of which are enclosed in gelatinous sheaths. Many species of blue-green algae can utilize nitrogen from the atmosphere as a nutrient (termed nitrogen fixation), which makes them adaptable to a variety of environmental conditions.

Green algae (chlorophyta) encompass a large and diverse group of phytoplankton species that are largely confined to freshwater ecosystems. Green algae can occur as single cells, colonies, or filaments of cells. The chrysophytes are comprised of three groups of algae (diatoms - bacillariophyceae; yellow-green algae - xanthophyceae; golden-brown algae - chrysophyceae) which are linked by a common set of features, including a two-part cell wall, the presence of a flagella, the deposition of silica in the cell wall, and the accumulation of the food reserve, leucosin (Bell and Woodcock

1968). The four other groups of phytoplankton include the desmids and the dinoflagellates (i.e., pyrophytes; which are unicellular, flagellate algae), cryptomonads (i.e., cryptophytes; which are typically flagellate algae that grow well under cold, low light conditions), euglenoids (i.e., euglenophytes; which are unicellular, flagellate algae that are only rarely planktonic), brown algae (i.e., phaeophytes), and red algae (i.e., rhodophytes; Bell and Woodcock 1968).

Within the TSMD, phytoplankton production is likely to represent an important component of overall primary productivity in lake and pond ecosystems (e.g., Empire Lake). Phytoplankton production is not expected to be significant within the various stream systems that comprise the majority of the study area. Information on the phytoplankton communities that exist in the vicinity of the TSMD will be compiled at a later date.

6.2.2 Periphyton Communities

Periphyton are non-vascular aquatic plants that grow on firm substrates, such as sand, gravel, rocks, shells, and aquatic macrophytes (Bell and Woodcock 1968). Like phytoplankton, periphyton are autotrophic organisms that use the sun's energy to convert inorganic materials (such as carbon, nitrogen, and phosphorus) into organic matter, such as proteins, lipids, and sugars. Periphyton represent an important source of food for benthic and epibenthic invertebrates that feed by grazing on small plants (Odum 1975). Periphyton communities can be comprised of diverse assemblages of algal species, including members of all of the seven groups of algae that comprise phytoplankton communities (Bell and Woodcock 1968).

Within the stream systems of the TSMD, periphyton production is likely to represent a substantial component of the overall primary productivity of aquatic ecosystems. Information on the periplankton communities that exist in the vicinity of the TSMD will be compiled at a later date.

6.2.3 Aquatic Macrophyte Communities

Aquatic macrophyte communities are comprised of large vascular and non-vascular plants that grow in a waterbody. Aquatic macrophytes can grow under the surface of the water (i.e., submergent plants, such as milfoil) or emerge from the surface of the water (i.e., emergent plants, such as bulrushes; Bell and Woodcock 1968).

Aquatic macrophytes play several important roles in freshwater and estuarine ecosystems. As autotrophic organisms, aquatic macrophytes can account for much of the primary productivity in aquatic systems, particularly in wetlands and other shallow areas that favor the establishment of marsh plants. In this role, macrophytes represent an important food source for aquatic organisms, either for grazers that can process these plant materials directly or those species that consume the bacteria that decompose these plant tissues following their death (Odum 1975). In addition, aquatic macrophytes provide habitats that are utilized by a variety of aquatic invertebrate species. These habitats can also represent important spawning and nursery areas for many fish species, and are frequently used by diverse wildlife species. Information on the aquatic macrophyte communities that exist in the vicinity of the TSMD will be compiled at a later date.

6.2.4 Riparian Plant Communities

The term riparian plants is used to describe a broad range of vascular and non-vascular plant species that grow along the margins of stream channels (i.e. within flood plain areas). Riparian plants play several important roles in riparian ecosystems. As autotrophic organisms, riparian plants account for most of the primary productivity in riparian areas. In this role, riparian plants represent important food source for many invertebrate and vertebrate species that utilize these habitats. In addition, those species that consume the bacteria that decompose these plant tissues following their death are also indirectly sustained by riparian plants (Odum 1975).

Furthermore, riparian plants provide habitats that are utilized by a variety of wildlife species, such as invertebrates, amphibians, reptiles, birds, and mammals. Information on the riparian plant communities that exist in the vicinity of the TSMD will be compiled at a later date.

6.2.5 Terrestrial Plant Communities

Terrestrial plants is used to describe a broad range of vascular and non-vascular plant species that grow in upland areas within the study area. Terrestrial plants play several important roles in upland ecosystems. As autotrophic organisms, riparian plants account for most of the primary productivity in upland areas. In this role, terrestrial plants represent important food source for many invertebrate and vertebrate species that utilize upland habitats. In addition, those species that consume the bacteria that decompose these plant tissues following their death are also indirectly sustained by terrestrial plants (Odum 1975). Furthermore, terrestrial plants provide habitats that are utilized by a variety of wildlife species, such as invertebrates, amphibians, reptiles, birds, and mammals. Information on the terrestrial plant communities that exist in the vicinity of the TSMD will be compiled at a later date.

6.3 Invertebrate Communities

The aquatic invertebrate communities in study area consist primarily of zooplankton communities and benthic macroinvertebrate communities. Riparian and floodplain soils are also populated by invertebrates that play essential roles in ecosystem functioning. Zooplankton is the term used to describe the small animals that remain suspended in the water column in aquatic systems. In contrast, benthic macroinvertebrates are the small animals that live in (i.e., infaunal species) or on (i.e., epibenthic species) the sediments in aquatic systems. Terrestrial invertebrates is the

term that is applied to the animals that utilize soil habitats within riparian and flood plain areas and within upland areas. Aquatic and terrestrial invertebrates (i.e., primary consumers) represent essential elements of aquatic food webs because they consume aquatic plants (i.e., primary producers) and provide an important food source for fish and many other aquatic organisms. Riparian and terrestrial invertebrates play similar roles in riparian and upland habitats.

6.3.1 Zooplankton Communities

Zooplankton communities in freshwater ecosystems can be comprised of a wide variety of animals. Some of the groups of animals that are commonly found in the water column of such systems include protozoa (which are single-celled animals) and the early life history stages of mollusks (e.g., mussels; Wetzel 1983). In addition, several classes of arthropods are commonly encountered in zooplankton communities, including rotifers, crustaceans (e.g., cladocerans and copepods), arachnids (i.e., spiders and mites), and insects (such as midges and mayflies; Wetzel 1983). Finally, the early larval stages of certain fish species are often planktonic; this group of animals is commonly referred to as nekton. Information on the zooplankton communities that exist in the vicinity of the TSMD (i.e., in Empire Lake) will be compiled at a later date.

6.3.2 Benthic Macroinvertebrate Community

Benthic invertebrates are the animals that live in and on the sediments in freshwater ecosystems. Benthic animals are extremely diverse and are represented by nearly all taxonomic groups from protozoa to large invertebrates. The groups of organisms that are commonly associated with benthic communities include protozoa, sponges (i.e., Porifera), coelenterates (such as *Hydra* sp.), flatworms (i.e., Platyhelminthes), bryozoans, aquatic worms (i.e., oligochaetes), crustaceans (such as ostracods,

isopods, and amphipods), mollusks (such as mussels), and aquatic insects (such as dragonflies, mayflies, stoneflies, true flies, caddisflies, and aquatic beetles). Because benthic invertebrate communities are difficult to study in a comprehensive manner, benthic ecologists often focus on the relatively large members of benthic invertebrate communities, which are known as benthic macroinvertebrates. These organisms are usually operationally defined, for example, as those that are retained on a 0.5 mm sieve.

Benthic invertebrates represent key elements of aquatic food webs because they consume aquatic plants (i.e., such as algae and aquatic macrophytes) and detritus. In this way, these organisms facilitate energy transfer to fish, birds, and other organisms that consume aquatic invertebrates. The EPT taxa (i.e., Ephemeroptera - mayflies; Plecoptera - stoneflies; Tricoptera - caddisflies) have been identified as key indicator species of water quality and benthic conditions in stream systems, both in the TSMD and elsewhere in the United States.

Crayfish are among the largest benthic invertebrate species that occur in the Spring River basin. Crayfish feed on a variety of plant and animal species, including algae, decomposing plant matter, snails, insects, dead fish. Crayfish are also consumed by a variety of fish and aquatic-dependent wildlife species, making them important components of aquatic food webs. A total of five crayfish species have been recorded in the Spring River Basin, including bristley cave crayfish (*Cambarus stetosus*), Neosho midget crayfish (*Orconectes macrus*), ringed crayfish (*Oroconectes neglectus*), northern crayfish (*Orconectes virilis*), and grassland crayfish (*Procambarus gracilis*). Information on the benthic invertebrate communities that exist in the vicinity of the TSMD will be compiled at a later date.

6.3.3 Mussel Community

Freshwater mussels are bivalve mollusks that utilize habitats in stream and lake ecosystems within the study area. Mussels are filter-feeding invertebrates that tend to be very sensitive to polluted waters, a characteristic that has led to their decline in many areas throughout the United States (including the Spring River Basin (MWIN 2007)). Various wildlife species, including raccoons and otters, feed on mussels, making them important components in aquatic and aquatic-dependent food webs. According to MWIN (2007) at least 35 mussel species have been recorded in the Spring River Basin (Table 2).

6.3.4 Riparian and Terrestrial Invertebrate Communities

Riparian and terrestrial invertebrate communities are terms that describe a diverse range of species. The groups of organisms that are commonly associated with riparian and terrestrial invertebrate communities include many species that utilize habitats in riparian and upland areas throughout their life cycle (e.g., springtails, bristletails, grasshoppers, earwigs, isopods), as well as species that utilize aquatic habitats for a portion of their lives (e.g., mayflies, caddisflies, midges).

Riparian and terrestrial invertebrates represent key elements of riparian and upland food webs because they consume plants and detritus. In this way, these organisms facilitate energy transfer to amphibians, reptiles, birds, mammals, and other organisms that consume invertebrates. Information on the riparian and terrestrial invertebrate communities that exist in the vicinity of the TSMD will be compiled at a later date.

6.4 Fish Community

Fish are key elements of freshwater ecosystems for a number of reasons. As one of the most diverse groups of vertebrates, fish are able to occupy a wide range of ecological niches and habitats (Hoese and Moore 1998). As such, fish represent important components of aquatic food webs by processing energy from aquatic plants (i.e., primary producers), zooplankton and benthic macroinvertebrate species (i.e., primary consumers), or detritivores. Fish represent important prey species for piscivorous (fish-eating) wildlife, including reptiles, birds, and mammals.

A total of 86 fish species have been collected within the Spring River Basin (Table 3; MWIN 2007). The fish communities within the study area are diverse because the basin includes both the Ozark-Neosho and Prairie-Neosho communities. The sportfish species that are commonly encountered within the watershed include smallmouth bass (*Micropterus salmoides*), largemouth bass (*Micropterus dolomieu*), spotted bass (*Micropterus punctulatus*), white crappie (*Poxomis annularis*), rock bass (*Ambloplites constellatus*), channel catfish (*Ictalurus punctatus*), and rainbow trout (*Oncorhynchus mykiss*; which was introduced to the watershed). A listing of some of the sportfish and non-sportfish species that have been recorded in the Spring River basin is provided in Table 3.

The fish species that are encountered in the eastern portion of the watershed are characterized as Ozark-Neosho fish communities. The species that are unique to this fish community include redbspot chub (*Nocomis asper*), bluntface shiners (*Cypinella camura*), cardinal shiners (*Luxilus cardinalis*), southwestern mimic shiners (*Notropis volucellus*), western slim minnow (*Pimephales tenellus*), Neosho madtom (*Noturus placidus*), Arkansas darters (*Etheostoma cragini*), Neosho orangethroat darters (*Etheostoma spectabile*), redbfin darters (*Etheostomo whipplei*), and channel darters (*Percina copelandi*; MWIN 2007)

The fish species that are encountered in the western portion of the watershed are characterized as Prairie-Neosho fish communities. These fish communities are typically comprised of fish species that are commonly found in prairie streams. The fish species that are unique to this community include spotted sucker (*Minytrema melanops*) and brindled madtom (*Noturus miurus*).

6.5 Amphibians

Amphibians are important elements of freshwater components of estuarine ecosystems. The early life history stages of amphibian species are aquatic, feeding primarily on zooplankton to meet their energy requirements. As they mature, most amphibians develop lungs and can utilize both aquatic and terrestrial habitats. Both larval and adult amphibians represent prey species for aquatic-dependent wildlife, including fish, reptiles, birds, and mammals.

Within the Spring River Basin, a total 13 species of salamanders and 15 species of frogs and toads have been recorded (MWIN 2007). The species that have been observed within the watershed are listed in Table 4.

6.6 Reptiles

Reptiles, including snakes, lizards, and turtles, represent important components of freshwater and riparian ecosystems. While lizards are most commonly found in riparian and upland habitats, turtles and, to a lesser extent, snakes frequently utilize aquatic habitats. Reptiles feed on a wide range of aquatic and terrestrial species, including plants, invertebrates and fish. Some reptiles occupy relatively high trophic

levels in the food web, in some cases as apex predators (e.g., alligator snapping turtles). In this role, reptiles process energy primarily from fish, birds and small mammals. Certain species and life stages of reptiles also represent important prey items for birds and mammals.

A total of 14 species of turtles have been recorded in the Spring River Basin (MWIN 2007). In addition, 11 species of lizards and 32 species of snakes have been observed in the watershed (MWIN 2007). The water moccasin, or cottonmouth (*Agkistrodon piscivorus*), is the only poisonous water snake that occurs in the watershed. A listing of the reptilian species that have been recorded in the Spring River Basin is presented in Table 5.

6.7 Birds

Although most birds are primarily terrestrial, many species utilize aquatic and/or riparian habitats through portions or all of their life history. These species consume a variety of aquatic organisms and, hence, are often termed aquatic-dependent bird species. Birds can process energy from aquatic plants, invertebrates, fish, amphibians, and reptiles. In turn, avian species may be consumed by other avian, reptilian, or mammalian predator species. As such, birds represent critical components of ecological systems.

For the purposes of identifying key exposure pathways, the aquatic-dependent bird community has been classified into four feeding guilds, including piscivorous birds (e.g., belted kingfisher, osprey), carnivorous-wading birds (e.g., great blue heron, great egret), sediment-probing birds (e.g., spotted sandpipers), and aerial-feeding insectivorous birds (e.g., purple martin, tree swallow). By comparison, the terrestrial and upland bird communities were classified into the following feeding guilds:

carnivorous birds (e.g., hawks, turkey vulture, bald eagle), omnivorous birds (e.g., turkey, starling), ground-feeding insectivorous birds (e.g., warblers, robins). Table 6 provides a list of aquatic-dependent and terrestrial birds that have been observed in the TSMD.

6.8 Mammals

Like birds, mammals play an important role in the TSMD area food web, both as prey (e.g., rabbit, *Sylvilagus* sp.) and predators (e.g., river otter, *Lutra canadensis*). They are numerically less dominant than birds in the TSMD area, but nevertheless represent important components of aquatic and riparian ecosystems. For the purposes of identifying key exposure pathways, the mammals that occur within the Spring River basin were classified into five feeding guilds, including: herbivorous mammals (e.g., deer, rabbits, muskrat, beaver), carnivorous mammals (fox, mink), omnivorous mammals (mice, raccoons), vermivorous mammals (shrews), insectivorous mammals (e.g., gray bats), and, piscivorous mammals (otters). A list of aquatic-dependent and terrestrial mammals that have been observed in the TSMD is provided in Table 7.

6.9 Rare, Threatened and Endangered Species

Threatened and endangered species are receptors that require special consideration in the study area. Endangered species are at risk of becoming extinct throughout all or a significant portion of their range, while threatened species are likely to become endangered in the foreseeable future (USFWS 2001). The current status of these species indicates that they may be more vulnerable than other species to the presence of contaminants and/or other stressors.

The United States Endangered Species Act enacted in 1973, provides federal legislative authority to list a species as threatened or endangered. The purpose of the Act is to 'protect these endangered and threatened species and to provide a means to conserve the ecosystems' of which they are a part (USFWS 2001). The USFWS has the responsibility to administer the law for terrestrial and freshwater organisms. The plant and animals that have been listed as threatened or endangered under federal legislative authority that utilize or may utilize habitats within the study area are listed in Table 8. The rare or threatened species that have been identified by one or more states in the TSMD and the species on state watch lists are also shown in Table 8.

Chapter 7 Overview of Conceptual Site Model

7.0 Introduction

In accordance with USEPA guidance, the problem formulation for the DERA is intended to provide three main products, including: assessment endpoints, conceptual models, and a risk analysis plan (USEPA 1997; 1998). The conceptual site model (CSM) represents a particularly important component of the problem formulation because it enhances the level of understanding regarding the relationships between human activities and ecological receptors at the site under consideration. Specifically, the conceptual model describes key relationships between stressors and assessment endpoints. In so doing, the CSM provides a framework for predicting effects on ecological receptors and a template for generating risk questions and testable hypotheses (USEPA 1997; 1998). The CSM also provides a means of highlighting what is known and what is not known about a site. In this way, the conceptual model provides a basis for identifying data gaps and designing monitoring programs to acquire the information necessary to complete the assessment.

Conceptual site models consist of two main elements, including: a set of hypotheses that describe predicted relationships between stressors, exposures, and assessment endpoint responses (along with a rationale for their selection); and, diagrams that illustrate the relationships presented in the risk hypotheses. The following sections of this chapter summarize information on the sources and releases of COPCs, the fate and transport of these substances, the pathways by which ecological receptors are exposed to the COPCs, and the potential effects of these substances on the ecological receptors that occur in the TSMD. In turn, this information is used to develop a series of hypotheses that provide predictions regarding how ecological receptors will be exposed to and respond to the COPCs.

7.1 Sources and Releases of Chemicals of Potential Concern

There are a number of natural and anthropogenic sources of toxic and bioaccumulative substances in the TSMD. Anthropogenic sources of environmental contaminants in the watershed include releases and discharges associated with historic mining, milling, and smelting operations, industrial wastewater discharges, municipal wastewater treatment plant discharges, stormwater discharges, surface-water recharge by contaminated groundwater, non-point source discharges, spills associated with production and transport activities, and deposition of substances that were originally released into the atmosphere. A summary of the available information on the sources of environmental contaminants in the TSMD is presented Chapter 3.

Based on the information provided by participants at the January 17 and 18, 2007 workshop (MESL and CH2M Hill 2007), a wide variety of substances have been released into aquatic ecosystems located within the TSMD. Using information on the environmental fate and transport of these substances, it is reasonable to suggest that the following substances represent the principal COPCs at the TSMD (Chapter 3):

- Metals (arsenic, cadmium, chromium, copper, mercury, lead, nickel, selenium, zinc);
- MAHs (i.e., BTEX);
- PAHs (13 parent PAHs + alkylated PAHs);
- PCBs;
- Organochlorine pesticides; and,
- Ammonia.

7.2 Environmental Fate of Contaminants of Concern

Upon release into aquatic ecosystems, the COPCs partition into environmental media (i.e., water, sediment, soil, and/or biota) in accordance with their physical and chemical properties and the characteristics of the receiving water body. As a result of such partitioning, elevated levels of COPCs can occur in surface water (including the surface microlayer), bottom sediments, and/or the tissues of aquatic organisms. Accordingly, information on the environmental fate can be used to classify the COPCs into three groups (Table 9), including:

- Bioaccumulative substances (i.e., substances that accumulate in the tissues of aquatic organisms);
- Toxic substances that partition into sediments and/or soils; and,
- Toxic substances that partition into surface waters (including pore water and the surface microlayer).

Detailed information on the environmental fate and transport of the COPCs is provided in Appendix 2, while brief summaries of the environmental fate of the COPCs at the TSMD are provided in Chapter 4.

7.3 Potential Exposure Pathways

Once released to the environment, there are three pathways through which ecological receptors can be exposed to COPCs. These routes of exposure include direct contact with contaminated environmental media, ingestion of contaminated environmental media, and inhalation of contaminated air. For bioaccumulative substances, the ingestion of contaminated prey species represents the most important route of exposure for the majority of aquatic organisms and aquatic-dependent wildlife

species. Direct contact with contaminated water and/or contaminated sediment and ingestion of contaminated sediment also represent an important route of exposure to bioaccumulative COPCs for many aquatic organisms (Table 10).

For toxic substances that partition into sediments and soils, direct contact with contaminated sediments and pore water) represents the most important route of exposure for exposure for most aquatic organisms. However, ingestion of contaminated sediments and/or soil can also represent an important exposure pathway for certain aquatic organisms (e.g., oligochaetes that process sediments to obtain food) and aquatic-dependent wildlife species (e.g., sediment-probing birds, such as sandpipers; Table 10).

For toxic substances that partition into surface water, direct contact with contaminated water represents the most important route of exposure for aquatic organisms (i.e., uptake through the gills and/or through the skin). For aquatic-dependent wildlife species, ingestion of contaminated water represents the principal route of exposure to toxic substances that partition into surface water (Table 10).

For toxic substances that partition into the surface microlayer, direct contact with the contaminated surface microlayer represents the most important route of exposure for aquatic organisms (i.e., uptake through the gills and/or through the skin). However, aquatic-dependent wildlife species can be exposed to substances that volatilize from the surface microlayer through inhalation. This route of exposure could become important during and following accidental spills of volatile organic compounds (VOCs), when such substances are present as slicks on the water surface such spills of VOCs are not expected to occur in the study area, however (Table 10). A more detailed description of the pathways through which ecological receptors can be exposed to environmental contaminants is presented in Chapter 5.

7.4 Ecological Receptors at Risk

There are a wide variety of ecological receptors that could be exposed to contaminated environmental media in the TSMD. The receptor groups for which potentially complete exposure pathways exist in aquatic ecosystems within the TSMD can be classified into seven main receptor groups (Table 11), including:

- Microbiota (e.g., bacteria, fungi and protozoa);
- Aquatic plants (including phytoplankton, periphyton, and aquatic macrophytes);
- Aquatic invertebrates (including zooplankton and benthic invertebrates);
- Fish (including benthic and pelagic fish);
- Amphibians;
- Terrestrial plants (including riparian plants and other terrestrial plants that inhabit floodplain areas); and,
- Terrestrial invertebrates.

By comparison, potentially complete exposure pathways exist for five receptor groups in the riparian and/or terrestrial portions of the study area, including:

- Aquatic-dependent reptiles (e.g., turtles, water snakes);
- Aquatic-dependent birds (including a number of feeding guilds); and,
- Aquatic-dependent mammals (including a number of feeding guilds).

The DERA will focus on the five receptor groups that occur within the aquatic portions of the TSMD. Figures 5 to 8 present examples of a riverine food webs for Ozark stream ecosystems at various times of the year. These food web models have been integrated to illustrate the exposure pathways for the groups of organisms that

occupy various trophic levels and the linkages between groups at various trophic levels in the food web (Figure 9). Refinement of this food web model to reflect the receptors that occur in the TSMD and key linkages between groups at various trophic levels provides a basis for identifying ecological receptors at risk in the study area.

The COPCs in the TSMD were classified into four categories based on their predicted environmental fate (MESL and CH2M Hill 2007). By considering this information, in conjunction with the exposure pathways that apply to these groups of COPCs, it is possible to identify the receptors that are potentially at risk due to exposure to contaminated environmental media. For bioaccumulative substances, the groups of aquatic organisms that are most likely to be exposed to tissue-associated contaminants include benthic invertebrates, carnivorous fish, and amphibians (Table 11).

Toxic substances that partition into sediments and soils pose a potential risk to a variety of aquatic organisms and aquatic-dependent wildlife species. The groups of aquatic organisms that are most likely to be exposed to sediment-associated contaminants include decomposers (i.e., microbiota), aquatic plants (i.e., rooted aquatic macrophytes), benthic invertebrates, benthic fish, and amphibians. Although reptiles can come in contact with contaminated sediments, it is unlikely that significant dermal uptake would occur (Table 11).

For toxic substances that partition into surface water, aquatic plants, aquatic invertebrates, fish, and amphibians represent the principal groups of exposed aquatic organisms. By comparison, aquatic invertebrates and pelagic fish, are likely to have the highest potential for exposure to toxic substances that partition into the surface microlayer (Table 11)

7.5 Hypotheses Regarding the Potential Fate and Effects of Chemicals of Potential Concern

Exposure to environmental contaminants has the potential to adversely affect aquatic organisms utilizing habitats within the study area. The nature and severity of such effects are dependent on the substance under consideration, bioavailability, characteristics of the exposure medium, duration of exposure, species and life stage of the exposed biota, and several other factors. Evaluation of the environmental fate of COPCs and identification of the types of effects that could occur in the various groups of organisms found in the TSMD (Table 12) provides a basis for developing fate and effects hypotheses (i.e., using the information presented in Appendix 2). In turn, these hypotheses provide a basis for evaluating the logical consequences of exposing ecological receptors to environmental contaminants (i.e., predicting the responses of assessment endpoints when exposed to chemical stressors; USEPA 1998).

Certain metals (cadmium, copper, lead, mercury, and zinc), certain PAHs (e.g., benzo(a)pyrene), PCBs, and organochlorine pesticides are the bioaccumulative substances of greatest concern at the TSMD. Short- and long-term exposure to these substances have been demonstrated to adversely affect the survival, growth, and/or reproduction of aquatic invertebrates, fish, and amphibians. Extended exposure to some of these substances can also result in tumor induction and/or immune system suppression (see Chapter 4 and Appendix 2 for more information). The following fate and effects hypothesis was developed to identify the key stressor-effect relationships that need to be evaluated during the analysis phase of the assessment:

- Based on the physical-chemical properties (e.g., K_{ow}s) of the bioaccumulative substances of concern, the nature of food web in the TSMD, and the effects that have been documented in field and laboratory studies, cadmium, copper, lead, mercury, zinc, certain PAHs, PCBs, and

organochlorine pesticides, that are released into the aquatic environment will accumulate in the tissues of aquatic organisms to levels that will adversely affect the survival, growth, and/or reproduction of benthic invertebrates, fish, and/or amphibians. Although not addressed in the DERA, the survival, growth, and/or reproduction of aquatic-dependent wildlife will also be adversely affected by food web transfer of bioaccumulative substances.

Many of the COPCs in the TSMD were classified as toxic substances that partition into sediments or soils, including metals (arsenic; cadmium; chromium; copper; lead, mercury; nickel; zinc), PAHs (13 parent PAHs + alkylated PAHs), PCBs, BTEX, phthalates, phenol, chlorophenols, and organochlorine pesticides. Adverse effects on the survival, growth, and/or reproduction have been observed in aquatic plants, aquatic invertebrates, fish, and amphibians exposed to one or more of these substances in sediments (see Chapter 4 and Appendix 2 for more information). Exposure to sediment-associated contaminants also has the potential to adversely affect the microbial community (i.e., decomposers). The following fate and effect hypothesis was developed to identify the key stressor-effect relationships that need to be evaluated during the analysis phase of the assessment:

- Based on the environmental fate of the toxic substances that partition into sediments and the effects that have been documented in laboratory studies, metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, zinc), PAHs (13 parent PAHs + alkylated PAHs), PCBs, BTEX, phthalates, phenol, chlorophenols, and/or organochlorine pesticides will accumulate in whole sediments and/or pore water, to levels that will adversely affect the activity of the microbial community (e.g., reduce the rate of carbon processing by decomposers), the survival and/or growth of aquatic plants, and/or the survival, growth, and/or reproduction of benthic invertebrates, fish, and/or amphibians. Although not addressed in the DERA, the

survival, growth, and/or reproduction of terrestrial plants, terrestrial invertebrates, reptiles, birds, and/or mammals will also be adversely affected by exposure to toxic substances that partition into floodplain soils.

The toxic substances of greatest concern (i.e., COPCs) that partition into water in the TSMD include arsenic, cadmium, chromium, copper, mercury, lead, nickel, and zinc. Adverse effects on survival, growth, and/or reproduction have been observed in aquatic plants, aquatic invertebrates, and fish exposed to one or more of these substances in water (Chapter 4). The following fate and effect hypothesis was developed to identify the key stressor-effect relationships that need to be evaluated during the analysis phase of the assessment:

- Based on the environmental fate of the toxic substances that partition into water (including pore water and the surface microlayer) and the effects that have been documented in laboratory studies, arsenic, cadmium, chromium, copper, mercury, lead, nickel, and/or zinc will occur in surface water at levels that will adversely affect the survival, growth, and/or reproduction of aquatic plants, aquatic invertebrates, fish, and/or amphibians.

7.6 Conceptual Site Model Diagrams

As indicated previous, the conceptual modeling process for hazardous waste sites is intended to culminate in the development of:

- A series of hypotheses that describe the predicted relationships between stressors, exposures, and assessment endpoint responses (along with the rationale for their selection); and,

- Diagrams that illustrate the relationships presented in the risk hypotheses.

Accordingly, conceptual model diagrams were developed to illustrate the linkages between sources and releases of COPCs and the potential responses of ecological receptors for all four categories of COPCs (i.e., bioaccumulative COPCs, COPCs that partition in sediments; and COPCs that partition in water; Figure 10 to 12, respectively). In addition, Figure 13 integrates the linkages that were identified for all four categories of COPCs. Furthermore, Figure 14 provides a more explicit linkage diagram that highlight the potentially complete exposure pathways that need to be evaluated in the DERA.

Chapter 8 Selection of Assessment and Measurement Endpoints for Evaluating Risks to Ecological Receptors

8.0 Introduction

In the environment, a variety of plant and animal species can be exposed to COPCs (these species are referred to as receptors potentially at risk). Each of these receptors can be exposed to a chemical through different exposure routes and have the potential to exhibit different types and severities of effects. While information on the effects of each COPC on each component of the ecosystem would provide comprehensive information for evaluating ecological risks, it is neither practical nor feasible to directly evaluate risks to all of the individual components of the ecosystem that could be adversely affected by environmental contamination at a site (USEPA 1997). For this reason, risk assessment activities should be focused on the receptors that represent valued ecosystem components (e.g., sportfish species) and on the receptors that support valued ecosystem functions (e.g., carbon processing by the microbial community, which is needed to support healthy fish populations). Of particular interest are those receptors that are most likely to be adversely affected by the presence of COPCs at the site (USEPA 1998). This chapter describes the process that was used to select assessment and measurement endpoints for evaluating risks to ecological receptors in the TSMD.

8.1 Considerations for Selecting Assessment Endpoints

An assessment endpoint is an ‘explicit expression of the environmental value that is to be protected’ (USEPA 1997). The selection of assessment endpoints is an essential element of the overall ERA process because it provides a means of focusing assessment activities on the key environmental values (e.g., reproduction of sediment-probing birds) that could be adversely affected by exposure to environmental contaminants.

Assessment endpoints must be selected based on the ecosystems, communities, and species that occur, have historically occurred, or could potentially occur at the site (USEPA 1997). The following factors need to be considered during the selection of assessment endpoints (USEPA 1997):

- The COPCs that occur in environmental media and their concentrations;
- The mechanisms of toxicity of the COPCs to various groups of organisms;
- The ecologically-relevant receptor groups that are potentially sensitive or highly exposed to the contaminant, based upon their natural history attributes; and,
- The presence of potentially complete exposure pathways.

Thus, the fate, transport, and mechanisms of ecotoxicity for each contaminant or group of contaminants must be considered to determine which receptors are likely to be most at risk. This information must include an understanding of how the adverse effects of the contaminant could be expressed (e.g., eggshell thinning in birds) and how the form of the chemical in the environment could influence its bioavailability and toxicity.

The primary contaminants of concern in the study area were identified in Chapter 3 of this document. Brief overviews of the environmental fate and ecological effects of each of these COPCs were also provided to describe what happens to each chemical when it is released into the environment and how adverse effects could be expressed on various ecological receptors (Chapter 4). Importantly, the information on fate and transport of these COPCs facilitated identification of the environmental media in which each chemical is most likely to be found at elevated concentrations (i.e., in water, sediment, or biota; Chapter 4). The review of the available toxicological data provided a basis for identifying which groups of ecological receptors are most sensitive to the effects of each substance (Chapter 4 and Appendix 2). Chapter 5 of this report provided more detailed descriptions of the various exposure pathways, while the ecological receptors that occur within the study area were identified in Chapter 6. Integration of this information provides a means of developing a conceptual model of the site that clearly identifies linkages between contaminant discharges and effects on key ecological receptors (Chapter 7). This CSM and associated information provide the basis for selecting the assessment endpoints that are most relevant for inclusion in the DERA for the TSMD.

8.2 Identification of Candidate Assessment Endpoints

An assessment endpoint is an ‘explicit expression of the environmental value that is to be protected’ (USEPA 1997). The selection of assessment endpoints is an essential element of the overall ecological risk assessment (ERA) process because it provides a means of focusing assessment activities on the key environmental values (e.g., reproduction of sediment-probing birds) that could be adversely affected by exposure to environmental contaminants. Assessment endpoints must be selected based on the ecosystems, communities, and species that occur, have historically occurred, or could potentially occur at the site (USEPA 1997). Using the results of the ERA workshop

that was conducted in Joplin, MO during January 17 and 18, 2007 (MESL and CH2M Hill 2007), a number of candidate assessment endpoints were identified for application in the BERA of the TSMD (if required), including:

- Survival and growth of aquatic and terrestrial plants;
- Survival and growth, and reproduction of aquatic invertebrates;
- Survival and growth, and reproduction of terrestrial invertebrates;
- Survival, growth and reproduction of fish;
- Survival, growth and reproduction of amphibians
- Survival, growth and reproduction of reptiles
- Survival, growth and reproduction birds; and,
- Survival, growth and reproduction of mammals.

8.3 Preliminary Risk Questions

Selection of assessment endpoints represents an essential element of the overall problem formulation process for a BERA. While such assessment endpoints are essential for defining the environmental values that need to be protected at the TSMD, it is difficult or impossible to measure the effects on all of the members of a receptor group that are associated with exposure to chemicals of potential concern (COPCs) at the site. For this reason, it is necessary to articulate specific risk questions (i.e., testable hypotheses) that can be answered through the collection of focused data and information at the site. The preliminary list of assessment endpoints and associated risk questions that should be considered in a BERA include:

- 1. Survival and Growth of Aquatic and Terrestrial Plants*

- Are the levels of COPCs in surface water, whole sediments and/or soils from the site greater than benchmarks for the survival, growth, or reproduction of aquatic or terrestrial plants?
 - Is the survival, growth, or reproduction of aquatic and/or terrestrial plants exposed to surface water, sediments, or soil from the site significantly lower than that for aquatic and/or terrestrial plants exposed to media from reference sites?
2. *Survival, Growth, and Reproduction of Aquatic Invertebrates*
- Are the levels of COPCs in surface water, whole sediments, and/or pore water from the site greater than benchmarks for the survival, growth, or reproduction of aquatic invertebrates?
 - Is the survival, growth or reproduction of aquatic invertebrates exposed to whole sediments from the site significantly lower than that in reference sediments?
 - Is the structure of aquatic invertebrate communities sediments from the site outside the normal range (i.e., 95th percentile) for aquatic invertebrate communities in reference areas?
3. *Survival, Growth, and Reproduction of Terrestrial Invertebrates*
- Are the levels of COPCs in soil from the site greater than benchmarks for the survival, growth, or reproduction of terrestrial invertebrates?
 - Is the survival, growth or reproduction of terrestrial invertebrates exposed to soils from the site significantly lower than that in reference soils?
 - Is the structure of terrestrial invertebrate communities in soils from the site outside the normal range (i.e., 95th percentile) for terrestrial invertebrate communities in reference areas?

4. *Survival, Growth and Reproduction of Fish*

- Are the levels of COPCs in surface water and/or whole sediments from the site greater than benchmarks for the survival, growth, or reproduction of fish?
- Is the survival, growth or reproduction of fish exposed to surface water or sediments from the site significantly lower than that for reference media?
- Is the frequency of deformities, eroded fins, lesions, or tumors (DELT) abnormalities significantly higher in fish from the site than in fish from reference areas?
- Are the levels of COPCs in fish tissues from the site greater than critical tissue values for the survival, growth, or reproduction of fish?

5. *Survival, Growth and Reproduction of Amphibians*

- Are the levels of COPCs in surface water, whole sediments and/or soil from the site greater than benchmarks for the survival, growth, or reproduction of amphibians?
- Is the survival, growth or reproduction of amphibians exposed to surface water, whole sediments and/or soils from the site significantly lower than that for reference media?
- Is the frequency of abnormalities significantly higher in amphibians from the site than in amphibians from reference areas?
- Is the sex ratio of amphibians significantly different between the site and reference areas?

6. *Survival, Growth and Reproduction of Reptiles*

- Are the levels of COPCs in surface water, whole sediments and/or soil from the site greater than benchmarks for the survival, growth, or reproduction of reptiles?

- Is the frequency of abnormalities significantly higher in reptiles from the site than in reptiles from reference areas?

7. *Survival, Growth and Reproduction Birds*

- Does the daily dose of COPCs received by birds from consumption of the tissues of prey species and from other media at the site exceed the toxicity reference values (TRVs) for survival, growth or reproduction of birds? If yes, what are the probabilities of effects of differing magnitude for survival and/or reproduction of sediment-probing birds?
- Are the concentrations of COPCs in bird eggs from the site greater than benchmarks for the survival, growth, or reproduction of birds?
- Is the reproduction of birds utilizing the habitats in the vicinity of the site significantly impaired compared to that measured for reference areas?

8. *Survival, Growth and Reproduction of Mammals*

- Does the daily dose of COPCs received by mammals from consumption of the tissues of prey species and from other media at the site exceed the TRVs for survival, growth or reproduction of mammals? If yes, what are the probabilities of effects of differing magnitude for survival and/or reproduction of sediment-probing birds?
- Are the concentrations of COPCs in mammal tissues from the site greater than benchmarks for the survival, growth, or reproduction of mammals?

8.4 Identification of Candidate Measurement Endpoints

A measurement endpoint is defined as ‘a measurable ecological characteristic that is related to the valued characteristic that is selected as the assessment endpoint’ and it is a measure of biological effects (e.g., mortality, reproduction, growth; USEPA 1997). Measurement endpoints are frequently numerical expressions of observations (e.g., toxicity test results, community diversity measures) that can be compared to similar observations at a control and/or reference site. Such statistical comparisons provide a basis for evaluating the effects that are associated with exposure to a contaminant or group of COPCs at the site under consideration. Measurement endpoints can include measures of exposure (e.g., contaminant concentrations in water or sediments) or measures of effects (e.g., survival or growth of amphipods in 10-d toxicity tests). The relationship between an assessment endpoint, a risk question, and a measurement endpoint must be clearly described within the conceptual model and must be based on scientific evidence (USEPA 1997).

After identifying receptors of concern and selecting assessment endpoints, it is helpful to describe the linkages that are likely to exist between exposure media (i.e., stressors) and receptors within the site. The results of this process provide a basis for identifying focal species for each group of receptors and each group of chemical substances. In turn, this information was used to identify measurement endpoints that could be used to evaluate the status of each assessment endpoint. As it would not be practical nor possible to incorporate all of the possible measurement endpoints into the remedial investigation (RI), it is necessary to identify the measurement endpoints that would provide the most useful information for evaluating the ecological risks associated with exposure to environmental COPCs in the study area. Accordingly, the candidate measurement endpoints for inclusion in a BERA of the site include:

AE: Survival and Growth of Aquatic and Terrestrial Plants

RQ: Are the levels of COPCs in surface water, whole sediments and/or soils from the site greater than benchmarks for the survival, growth, or reproduction of aquatic or terrestrial plants?

ME: COPC concentrations in surface water, whole sediments and soils, and associated physical/chemical measurements.

RQ: Is the survival, growth, or reproduction of aquatic and/or terrestrial plants exposed to surface water, sediments, or soil from the site significantly lower than that for aquatic and/or terrestrial plants exposed to media from reference sites?

ME: Survival, growth, and/or reproduction of aquatic and/or terrestrial plants in laboratory toxicity tests.

AE: Survival, Growth, and Reproduction of Aquatic Invertebrates

RQ: Are the levels of COPCs in surface water, sediment pore water, or invertebrate tissue samples from the site greater than benchmarks for the survival, growth, or reproduction of aquatic invertebrates?

ME: COPC concentrations in surface water, sediment pore water, invertebrate tissues, and associated physical/chemical measurements.

RQ: Is the survival, growth or reproduction of aquatic invertebrates exposed to whole sediments from the site significantly lower than that in reference sediments?

ME: Survival, growth, and/or reproduction of aquatic invertebrates in laboratory toxicity tests.

RQ: Is the structure of aquatic invertebrate communities in sediments from the site outside the normal range (i.e., 95th percentile) for aquatic invertebrate communities in reference areas?

ME: Species richness of freshwater mussels for habitats within the site and for similar habitat types in reference areas.

AE: Survival, Growth, and Reproduction of Terrestrial Invertebrates

RQ: Are the levels of COPCs in soil from the site greater than benchmarks for the survival, growth, or reproduction of terrestrial invertebrates?

ME: COPC concentrations in soils and associated physical/chemical measurements.

RQ: Is the survival, growth or reproduction of terrestrial invertebrates exposed to soils from the site significantly lower than that in reference soils?

ME: Survival, growth, and/or reproduction of terrestrial invertebrates in laboratory toxicity tests.

RQ: Is the structure of terrestrial invertebrate communities in soils from the site outside the normal range (i.e., 95th percentile) for terrestrial invertebrate communities in reference areas?

ME: Standardized measures of terrestrial invertebrate community structure for various habitat types within the site and reference areas.

AE: Survival, Growth and Reproduction of Fish

RQ: Are the levels of COPCs in surface water and/or whole sediments from the site greater than benchmarks for the survival, growth, or reproduction of fish?

ME: COPC concentrations in surface water and/or whole sediments, and associated physical/chemical measurements.

RQ: Is the survival, growth or reproduction of fish exposed to surface water or sediments from the site significantly lower than that for reference media?

ME: Survival, growth, and/or reproduction of fish in laboratory toxicity tests.

RQ: Is the frequency of DELT abnormalities significantly higher in fish from the site than in fish from reference areas?

ME: Frequency of frequencies of DELT in fish within the site and reference areas.

RQ: Are the levels of COPCs in fish tissues from the site greater than critical tissue values for the survival, growth, or reproduction of fish?

ME: COPC concentrations in the tissues (whole body and liver) of fish from the site and reference areas, and associated variables (e.g., percent lipids, fish species, fish length, weight, age).

AE: Survival, Growth and Reproduction of Amphibians

RQ: Are the levels of COPCs in surface water, whole sediments and/or soil from the site greater than benchmarks for the survival, growth, or reproduction of amphibians?

ME: COPC concentrations in water, whole sediments and soil, and associated physical/chemical measurements.

RQ: Is the survival, growth or reproduction of amphibians exposed to surface water, whole sediments and/or soils from the site significantly lower than that for reference media?

ME: Survival, growth, and/or reproduction of amphibians in laboratory toxicity tests.

RQ: Is the frequency of abnormalities in amphibians from the site significantly higher than that in amphibians from reference areas?

ME: Frequency of abnormalities in amphibians collected at the site and in those collected from reference areas (i.e., biological surveys).

ME: Fetal and embryonic toxicity in amphibians (African clawed toad) as measured using standard laboratory toxicity testing (e.g., frog embryo teratogenesis assay-xenopus; FETAX).

RQ: Is the sex ratio of amphibians significantly different between the site and reference areas?

ME: Sex ratio of adult amphibians collected within the site and of those collected at reference sites (i.e., biological surveys).

AE: Survival, Growth and Reproduction of Reptiles

RQ: Are the levels of COPCs in surface water, whole sediments and/or soil from the site greater than benchmarks for the survival, growth, or reproduction of reptiles?

ME: COPC concentrations in water, whole sediments and soil, and associated physical/chemical measurements.

RQ: Is the frequency of abnormalities in reptiles from the site significantly higher than that in reptiles from reference areas?

ME: Frequency of physical abnormalities in reptiles collected from the site and in those collected from reference areas (i.e., biological surveys).

AE: Survival, Growth and Reproduction Birds

RQ: Does the daily dose of COPCs received by birds from consumption of the tissues of prey species and from other media at the site exceed the TRVs for survival, growth or reproduction of birds? If yes, what are the probabilities of effects of differing magnitude for survival and/or reproduction of sediment-probing birds?

ME: Concentrations of COPCs in the tissues of prey species (i.e., whole body tissue residues) and associated measurements (e.g., prey size).

RQ: Are the concentrations of COPCs in bird eggs from the site greater than benchmarks for the survival, growth, or reproduction of birds?

ME: Concentrations of COPCs in the eggs of selected bird species and associated information (e.g., species, location; i.e., targeted biological surveys).

RQ: Is the reproduction of birds utilizing the habitats in the vicinity of the site significantly impaired compared to that measured for reference areas?

ME: Concentrations of COPCs in the eggs of selected bird species (and/or other measures of exposure) and measures of reproductive success (e.g., hatching and fledgling success).

AE: Survival, Growth and Reproduction of Mammals

RQ: Does the daily dose of COPCs received by mammals from consumption of the tissues of prey species and from other media at the site exceed the TRVs for survival, growth or reproduction of mammals? If yes, what are the probabilities of effects of differing magnitude for survival and/or reproduction of sediment-probing birds?

ME: Concentrations of COPCs in the tissues of prey species (i.e., whole body tissue residues) and associated measurements (e.g., prey size).

RQ: Are the concentrations of COPCs in mammal tissues from the site greater than benchmarks for the survival, growth, or reproduction of mammals?

ME: Concentrations of COPCs in the tissues of selected mammalian species and associated information (e.g., species, location; i.e., targeted biological surveys).

If the assessment of the site proceeds to a BERA, the preceding list may provide a basis for selecting AEs, RQs, and MEs that should be considered in a more thorough assessment of risks to ecological receptors in the study area.

8.5 Selection of Measurement Endpoints

Baseline ecological risk assessments of the TSMD as a whole or portions thereof could address many or all of the assessment endpoints identified in Section 8.2. This DERA is focused on evaluating risks to the benthic invertebrate community

associated with exposure to COPCs in the study area. Accordingly, the following MEs were selected to evaluate risks to the benthic invertebrate community:

AE: Survival, Growth, and Reproduction of Aquatic Invertebrates

RQ: Are the levels of COPCs in surface water, sediment pore water, or invertebrate tissue samples from the site greater than benchmarks for the survival, growth, or reproduction of aquatic invertebrates?

ME: COPC concentrations in surface water, sediment pore water, invertebrate tissues and associated physical/chemical measurements.

RQ: Is the survival, growth or reproduction of aquatic invertebrates exposed to whole sediments from the site significantly lower than that in reference sediments?

ME: Survival, growth, and/or reproduction of aquatic invertebrates in laboratory toxicity tests.

RQ: Is the structure of aquatic invertebrate communities in sediments from the site outside the normal range (i.e., 95th percentile) for aquatic invertebrate communities in reference areas?

ME: Species richness of freshwater mussels for habitats within the site and for similar habitat types in reference areas.

Chapter 9 Risk Analysis Plan and Uncertainty Analysis

9.0 Introduction

The development of a risk analysis plan represents the final stage of the problem formulation process. During risk analysis planning, risk questions and testable hypotheses are developed and evaluated to determine how they will be assessed using available and new data (USEPA 1997). The risk analysis plan includes four components, including descriptions of the assessment design, the data requirements, the measurements that will be made, and the methods for conducting the analysis phase of the risk assessment (USEPA 1997). Procedures for addressing outstanding data gaps and uncertainties associated with the risk assessment are also identified during risk analysis planning.

In the DERA of the TSMD, ecological risks associated with exposure to contaminated environmental media will be evaluated for aquatic organisms only. The ecological receptor groups that will be implicitly evaluated include the microbial community, aquatic plant community, benthic invertebrate community, fish community, and amphibian community. This assessment will be designed to answer the following questions:

- Does the presence of COPCs in surface water, whole sediments, pore water or benthic invertebrate tissues pose potential risks to aquatic organisms?
- Which COPCs, by media type, and AoI occur at concentrations sufficient to pose potential risks to aquatic organisms?

As designed, the DERA will be conducted by comparing the measured concentrations of COPCs in environmental media to conservative benchmarks for the protection of

aquatic organisms. Accordingly, assessment of the potential risks to aquatic organisms associated with exposure to COPCs in surface water, sediments, and associated pore water within the TSMD will require six types of data, including surface-water chemistry data, sediment chemistry data, sediment-toxicity data, pore-water chemistry data, invertebrate-tissue chemistry data, and freshwater mussel species richness data. The DERA will consist of three main components, including exposure assessment, effects assessment, and risk estimation. The objectives of the exposure characterization are to identify the receptors that will be evaluated, to describe the pathway of the stressor from the source to each aquatic receptor, and to describe the intensity and areal extent of contact with the stressor (USEPA 1998). The objectives of the effects characterization are to describe the effects elicited by the stressor, to link those effects to the aquatic assessment endpoints, and to evaluate how the effects change at various levels (i.e., concentrations) of the stressor (USEPA 1998). Integration of the exposure and effects characterizations provides a basis for estimating risks to ecological receptors and identifying COPC concentrations below which risks are considered to be negligible. The procedures that will be used to conduct these assessments are described below.

9.1 Exposure Assessment

As indicated above, six types of data (i.e., surface-water chemistry data, sediment chemistry data, sediment toxicity data, pore-water chemistry data, invertebrate-tissue chemistry data, and freshwater mussel species richness data) will be used to evaluate the potential risks to aquatic organisms associated with exposure to COPCs within the TSMD. These media types were selected because complete exposure pathways from COPC sources to the receptors that occur at the site are thought to exist within the TSMD. To ensure that potential ecological threats are not missed, the 95th percentile concentration of each COPC that has been measured in samples of each media type

from the TSMD will be used to estimate the exposure point concentration for the DERA. Such exposure point concentrations (EPCs) will be calculated for each AoI and for the study area as a whole.

The exposure assessment will include estimates of exposure to each individual COPC and to mixtures of COPCs with similar modes of toxicity. For surface water, the chemical mixture model will be applied by calculating a hazard index (HIs) for metals. The hazard index for each surface water sample will be calculated by summing the hazard quotients (HQs) that are determined for individual divalent metals (where $HQ = \text{measured concentration} \div \text{conservative benchmark}$). The 95th percentile HI that is calculated for all of the water samples collected within an AoI and for the TSMD as a whole will be selected as the EPCs for the chemical mixture.

For whole sediments, several chemical mixture models will be evaluated during the DERA. Exposure to metals will be evaluated using a total of six chemical mixture models (based on measures of total metal concentrations - TM, acid volatile sulfide concentrations - AVS, simultaneously extracted metal concentrations - SEM, and probable effect concentration quotients (PEC-Qs), including:

- Mean PEC-Q metals;
- Mean PEC-Q metals (DW@1%OC);
- SEM-AVS;
- $SEM-AVS/f_{oc}$
- $\Sigma SEM-AVS$;
- $\Sigma SEM-AVS/f_{oc}$;
- $\Sigma PEC-Q_{Cd, Pb, Zn}$; and,
- Mean $PEC-Q_{Cd, Pb, Zn}$.

These metal mixture models will be calculated using the methods described by MacDonald *et al.* (2000); USEPA (2000b); Ingersoll *et al.* (2001); MacDonald *et al.* (2002); USEPA (2005), and MacDonald *et al.* (2009). In addition, exposure to non-polar organic compounds will be evaluated using the equilibrium partitioning sediment benchmark toxic units model (ESB-TUs), using the procedures described in USEPA (2003). The maximum value that is calculated for each chemical mixture model for all of the whole-sediment samples collected within an AoI and for the TSMD as a whole will be selected as the EPCs for the chemical mixture.

For pore water, the chemical mixture model will be applied by calculating a HI) for metals. The hazard index for each surface water sample will be calculated by summing the HQs that are determined for individual metals (where HQ = measured concentration ÷ conservative benchmark). The maximum HI that is calculated for all of the pore-water samples collected within an AoI and for the TSMD as a whole will be selected as the EPCs for the chemical mixture.

For benthic invertebrate tissues, the results of 28-d laboratory bioaccumulation tests (which were conducted in 20 of the 70 sediment samples from the TSMD) will be evaluated and, if found to be acceptable, used to estimate exposure of benthic invertebrates to COPCs. First, sediment-to-biota accumulation functions will be developed for each COPC. These accumulation functions will be used to estimate the concentration of each bioaccumulative COPC in tissues of benthic invertebrates for each sediment sample from the study area. HQs will then be calculated for each COPC in each sample, with the maximum HQ for each AoI and for the TSMD as a whole selected as the EPC.

9.2 Effects Assessment

As indicated above, surface-water chemistry, whole-sediment chemistry, and pore-water chemistry data will be used to evaluate exposure of aquatic receptors to COPCs in the TSMD. Accordingly, effects information will need to be compiled for all three media types. Appendix 2 provides a summary of the information that has been compiled to date on the effects of each of the COPCs in the TSMD.

Surface Water - Ambient water quality criteria (i.e., final chronic values; FCVs) will be used to evaluate the surface-water chemistry data. Such values represent lowest observed adverse effect levels (LOAELs) for each COPC in surface water (USEPA 1997).

Whole Sediment - The consensus-based threshold effect levels (TECs) represent conservative benchmarks for whole sediment, below which adverse effects on aquatic organisms are unlikely to be observed. Accordingly, these and comparable sediment quality guidelines (SQGs) will be applied in the DERA. It is anticipated that the use of these SQGs will provide a relevant basis for screening out many of the substances that were initially identified as COPCs. However, such conservative benchmarks will result in exceedances for metals throughout the study area. Hence, the DERA will provide little additional information for focusing further investigations in the watershed.

There are a number of factors that influence the bioavailability of metals in freshwater sediments, including AVS, TOC, and grain size. As the existing data indicate that AVS, TOC, and grain size are highly variable in sediments within the TSMD, it is possible that metals may be less bioavailable and/or less toxic in certain portions of the watershed than would be expected based on total metal concentrations alone. For this reason, a field sampling program will be designed and implemented in 2007 to facilitate the collection of matching whole-sediment chemistry, pore-water chemistry,

and whole-sediment toxicity data at 70 locations throughout the TSMD. These data will be used to derive site-specific sediment toxicity thresholds (SSTTs) for assessing risks to ecological receptors (i.e., benthic invertebrates) in the study area. This process consists of three main steps, including:

- Compilation of matching whole-sediment chemistry and toxicity data;
- Development and selection of preliminary SSTTs for each COPC; and,
- Evaluation and final selection of SSTTs.

Each of these steps in the sediment toxicity threshold derivation process is briefly described below. More information on these methods are provided in MacDonald *et al.* (2002; 2003; 2004; 2005; 2007a).

As part of the 2007 field sampling program, a total of 70 whole-sediment samples will be collected from the study area. All of these samples will undergo chemical characterization to determine the concentrations of COPCs in whole sediment and pore water. In addition, toxicological assessment will be conducted by evaluating survival and growth of the amphipod, *Hyalella azteca*, in 28-d exposures, the survival and growth of midge, *Chironomus dilutus*, in 10-d exposures, and the survival and growth of mussels, *Lampsilis siliquoidea*, in 28-d exposures (with about 35 of the 70 samples). These chemistry and toxicity data will be evaluated to ensure that they meet the performance criteria for measurement data specified in the project quality assurance project plan (QAPP; Ingersoll *et al.* 2007). Acceptable data will be compiled in the project database and used to derive the SSTTs.

The COPCs in whole sediments within the study area include metals, PAHs, BTEX, phthalates, phenol, chlorophenols, PCBs, and organochlorine pesticides. As a first step, correlations between toxicity and chemistry will be evaluated by conducting Spearman-Rank correlation analysis on the resultant data. Preliminary SSTTs for the

benthic invertebrate community will be established for each of the COPCs or groups of COPCs that are found to be significantly negatively correlated with the results of one or more toxicity tests. More specifically, such SSTTs will be derived based on site-specific concentration-response relationships derived from matching sediment chemistry and sediment toxicity data.

The procedures that will be used to derive SSTTs will be consistent with those described by MacDonald *et al.* (2002; 2003; 2004; 2005). More specifically, SSTTs for the benthic invertebrate community will be derived using the matching sediment chemistry and toxicity data from the study area. The site-specific chemistry and toxicity data will be used to develop concentration-response relationships for each COPC, based on the magnitude of toxicity (i.e., % survival; % growth; % biomass) to the amphipods, midge, and/or mussels. Development of the concentration-response relationships will involve summarizing the concentration and response data, determining the numerical relationships between concentration and response (e.g., conducting logistic regression analysis), and plotting the resultant relationships. The SSTT-LRs (i.e., thresholds for low risk) and SSTT-HRs (i.e., thresholds for high risk) will be determined by calculating the concentration of each COPC that corresponds with 10% and a 20% reduction in survival, growth, or biomass of the test organisms, respectively (i.e., compared to reference conditions; see Appendix E2 of the MacDonald *et al.* 2002 for a more detailed description of these procedures).

The evaluation of the SSTTs will consist of several steps. In the first step of the process, all of the whole-sediment samples will be designated as posing a low, intermediate, or high risk to benthic invertebrates, based on the predicted magnitude of the response of toxicity test organisms (i.e., as predicted by comparing COPC concentrations to the preliminary SSTTs). To evaluate the low-risk SSTTs, individual sediment samples will be classified into either a low risk group and an intermediate risk group based on the concentration of the selected COPC (e.g., zinc; i.e., below the SSTT-LR and above the STT-LR). The samples that are classified into the low risk

group based on chemical concentration will be predicted to pose a low risk to benthic invertebrates. The accuracy of these predictions will then be evaluated by determining the proportion of samples within the low risk group that actually posed a low risk to benthic invertebrates, based on the results of the whole-sediment toxicity tests. A similar procedure will be used to assess the reliability of SSTT-HRs.

Criteria for evaluating the reliability of the SSTT-IRs and SSTT-HRs were established on an a priori basis, based on the criteria that had been established previously for evaluating SSTTs at other sites. These criteria will be used to select the SSTTs that are most applicable for assessing risks to benthic invertebrates associated with exposure to contaminated sediments in the study area. More specifically, the SSTT-LRs will be considered to be reliable if the incidence of toxicity is $< 80\%$ at COPC concentrations below the SSTT-LR (i.e., the probability of false negative results was less than 20%) and if the incidence of toxicity is $> 50\%$ at COPC concentrations above the SSTT-LR (i.e., the probability of false positive results was less than 50%). The SSTT-HRs will be considered to be reliable if the incidence of toxicity is $> 80\%$ at COPC concentrations above the SSTT-HR (i.e., the probability of false positive results was less than 20%) and if the incidence of toxicity is $< 50\%$ at COPC concentrations below the SSTT-HR (i.e., the probability of false negative results was less than 50%).

In this evaluation, the number of criteria that are met by each of the candidate SSTTs will be determined and compared. The SSTT-LR that meets the most criteria will be selected as the final SSTT-LR for that substance (i.e., SSTT-LRs will be developed using the data for all three toxicity tests and multiple endpoints, resulting in up to six SSTT-LRs for each COPC). Likewise, the SSTT-HR that meets the most criteria will be selected as the final SSTT-HR for that substance. In the event of a tie, the higher of the SSTTs will be selected as the final SSTT for that substance, unless such a selection results in the SSTT-LR being higher than the SSTT-HR. Completion of this evaluation process will result in the selection of two benthic SSTTs for each COPC

and COPC group, including a SST-LR and a SSTT-HR. Given that AVS is frequently low in sediments from the TSMD, it is anticipated that the SSTTs for COPC groups (e.g., mean PEC-Q metals (DW@1%OC) will be among the most reliable SSTTs and will ultimately be selected to facilitate evaluations of risks to benthic invertebrates exposed to contaminated sediments in the study area.

Pore Water - Ambient water quality criteria (i.e., final chronic values; FCVs) will be used to evaluate the pore-water chemistry data. More specifically, PW-TU_{S_{Zn}} will be used to evaluate pore-water chemistry data from the TSMD.

Invertebrate-Tissue Chemistry - Invertebrate-tissue chemistry data will be evaluated using toxicity thresholds selected from a compendium of critical body residues summarized from the published literature (Jarvinen and Ankley 1999).

9.3 Risk Characterization

In the risk calculation step of the DERA, the exposure estimate is integrated with the effects information for each COPC to estimate risks to ecological receptors at the site. In this assessment, hazard quotients (HQs) will be calculated for each COPC in each media type. The HQs will be calculated by dividing the highest measured concentration of each COPC in each media type by the corresponding toxicity threshold. For surface water and pore water, the site-specific toxicity threshold for pore water will be used to calculate the HQs. For sediments, the site-specific toxicity thresholds for sediment will be used to calculate the HQs. In addition, hazard indices will be calculated for the groups of COPCs with common modes of toxicity for each media type (i.e., using the various toxic units models and chemical mixture models described earlier in this document). As part of this assessment, the adequacy of the existing data for conducting the evaluation of potential risks to ecological receptors

will be evaluated and reported upon. Accordingly, the results of the risk estimation step of the DERA will provide the risk managers with the information needed to select from among three possible decisions:

- 1) There is adequate information to conclude that risks to aquatic receptors are negligible and, therefore, there is no need for remediation based on aquatic risks in the TSMD;
- 2) The information is not adequate to make a decision at this point in the process and the ecological risk assessment process for the TSMD will continue to Step 3; or,
- 3) The information indicates a potential for adverse effects on aquatic receptors in the TSMD and a more thorough ecological risk assessment is warranted.

It is important to note that the results of the DERA are likely to support the identification of COPCs that require further evaluation. In addition, the COPC concentrations in sediment that correspond to low risk and high risk thresholds for aquatic receptors (i.e., benthic invertebrates) will be identified at this stage of the process. The SSTs-LR and SSTs-HR that are derived to support the DERA will also define the range of concentrations of individual COPCs and/or COPC mixtures within which the preliminary remediation goals (PRGs) for aquatic receptors would likely be established (see MacDonald *et al.* 2004 for more information). Hence, the results of the DERA will likely provide a basis for evaluating early action and source control alternatives at the site (i.e., if risks to aquatic receptors are found to be likely unacceptable). Importantly, the DERA will not provide a basis for evaluating risks to:

- Aquatic organism exposed to COPCs in surface water or sediments, with the exception of benthic invertebrates;

- Aquatic-dependent wildlife exposed to COPCs in surface water, sediments, or biological tissues within the stream channel;
- Any terrestrial species exposed to COPCs in soils or biological tissues within the flood plain or within source areas; or,
- Human health associated with exposure to COPCs from any exposure route.

9.4 Uncertainty Analysis

Ecological risk assessments are uncertain because of the complexity of ecological systems and the economic costs associated with collection of the data required to predict the behavior of such systems. However, the vast majority of ERAs conducted to date have been based on conservative quotients that have not been supported by a quantitative uncertainty analysis. An uncertainty analysis, if performed, has been typically restricted to a list of sources of uncertainty and perhaps qualitative statements of believability or confidence in the estimated quotients. As a result, risk managers and interested parties are not aware of the extent of uncertainty in the risk assessment and its consequences to the decision-making process. An open and explicit process of uncertainty analysis can reduce suspicion and misunderstandings. The objective of this section is to describe sources of uncertainty and describe how they will be dealt with in the DERA of the TSMD.

There are a number of sources of uncertainty in assessments of risk to aquatic receptors, including uncertainties in the CSM, in the exposure assessment, and in the effects assessment. As each of these sources of uncertainty can influence the estimations of risk, it is important to describe and, when possible, quantify the magnitude and direction of such uncertainties. In this way, it is possible to evaluate

the level of confidence that can be placed in the assessments conducted using the various lines of evidence. The various sources of uncertainty are discussed below.

Uncertainties in the CSM - The CSM is intended to define the linkages between stressors, potential exposure, and predicted effects on ecological receptors. As such, the CSM provides the scientific basis for selecting assessment and measurement endpoints to support the risk assessment process. Potential uncertainties arise from lack of knowledge regarding ecosystem functions, failure to adequately address spatial and temporal variability in the evaluations of sources, fate, and effects, omission of stressors, and overlooking secondary effects (USEPA 1998). In this analysis, uncertainties associated with the conceptual model will be explicitly identified and their impact on the results of the risk assessment will be discussed. The types of uncertainties that are likely to be identified in this analysis include uncertainties associated with the identification of COPCs, environmental fate and transport of COPCs, exposure pathways, receptors at risk, and ecological effects.

Uncertainties in the Exposure Assessment - The exposure assessment is intended to describe the actual or potential co-occurrence of stressors with receptors. As such, the exposure assessment identifies the exposure pathways and the intensity and extent of contact with stressors for each receptor or group of receptors at risk. There are a number of potential sources of uncertainty in the exposure assessment, including measurement errors, extrapolation errors, and data gaps.

In this assessment, two types of measurements will be used to evaluate exposure of aquatic receptors to COPCs, including chemical analyses of environmental media and toxicity tests conducted using indicator species. Relative to the surface-water, sediment, and pore-water chemistry data, analytical errors and descriptive errors represent potential sources of

uncertainty. Three approaches will be used to address concerns relative to these sources of uncertainty. First, analytical errors will be evaluated using information on the accuracy, precision, and detection limits (DL) that are generated to support the sampling programs (i.e., data quality will be evaluated using the performance criteria for measurement data that are documented in the QAPP). Second, all data entry, data translation, and data manipulations will be audited to assure their accuracy. Finally, statistical analyses of resultant data will be conducted to evaluate data distributions, identify the appropriate summary statistics to generate, and evaluate the variability in the observations. Potential measurement errors associated with toxicity tests will be evaluated using negative control results, positive control results, and the results obtained from samples collected at the reference locations.

There are several potential sources of extrapolation errors in the DERA. First, indicator species have been selected to evaluate the potential for effects on certain groups of aquatic receptors (e.g., information on the amphipod, *H. azteca*, *C. dilutus*, and/or *L. siligoidea*, will be used to assess effects on sediment-dwelling organisms associated with sediment-associated contaminants). The implications of such extrapolations on the results of the DERA will be described and, to the extent possible, quantified in the uncertainty analysis.

Data gaps also represent a source of uncertainty in the assessments of exposure for aquatic receptors. For example, limitations on the available data on the chemical composition of surface waters will constrain the assessment of exposure due to direct contact with or ingestion of surface waters. Because it is difficult to fully characterize the temporal and spatial variability of surface water quality during short-duration sampling programs, further collection of water quality data during the 2007 field sampling program was not recommended for the sampling program. Rather, focused water quality

sampling in conjunction with detailed source identification activities may be conducted in the future to evaluate loadings of COPCs from each source and associated effects on surface water quality. Such data will be useful for prioritizing the various sources and developing early action alternatives. Likewise, there are difficulties associated with the collection of data on the chemical composition of the surface microlayer and, therefore, collection of such data is not recommended for the sampling program. As a result, it will not be possible to estimate exposure to COPCs via this pathway. The implications of such data gaps will be described and, to the extent possible, quantified in the uncertainty analysis.

Uncertainties in the Effects Assessment - The effects assessment is intended to describe the effects that are caused by stressors, link them to the assessment endpoints, and evaluate how effects change with fluctuations in the levels (i.e., concentrations) of the various stressors. There are several sources of uncertainty in the assessment of effects on aquatic receptors, including measurement errors, extrapolation errors, and data gaps.

Two types of measurements will be used to evaluate the effects on aquatic receptors that are associated with exposure to COPCs. First, chemical analyses of environmental media will be used, in conjunction with laboratory-derived dose-response relationships and analyses of field-collected data, to evaluate the potential effects on aquatic receptors associated with exposure to contaminated environmental media. These types of measurements are subject to analytical errors and descriptive errors, both of which represent potential sources of uncertainty. Three approaches will be used to address concerns relative to these sources of uncertainty. First, analytical errors will be evaluated using information on the accuracy, precision, and DLs that are generated to support the sampling program. Second, all data entry, data translation, and data manipulation will be audited to ensure their accuracy.

Finally, statistical analyses of resultant data will be conducted to evaluate data distributions, identify the appropriate summary statistics to generate, and evaluate the variability in the observations. Potential measurement errors associated with toxicity tests will be evaluated using negative control results, positive control results, and the results obtained from samples collected in the reference areas.

There are several sources of extrapolation errors in the effects assessment for the DERA. First, indicator species have been selected to evaluate the potential for exposure effects on certain groups of aquatic receptors. Uncertainties associated with the application of this approach will be evaluated by examining the sensitivities of various species within each group (i.e., using information contained in the USEPA AQUIRE database and elsewhere). These data will be used to develop cumulative distribution functions to evaluate differences in species sensitivities and, hence, the potential implications of using the selected indicator species (i.e., *H. azteca*, *C. dilutus*, and *L. siligoidea*). In addition, the application of multiple lines of evidence to evaluate effects on assessment endpoints will help to minimize implications associated with this type of extrapolation error. Second, in some cases, environmental samples will be collected from areas that may not reflect the conditions that exist in the areas that effects actually occur (e.g., for rooted aquatic plants). The implications of these uncertainties will be described and, to the extent possible, quantified in the uncertainty analysis.

Uncertainty in the exposure and effects assessments for aquatic receptors is also increased by data gaps. To the extent possible, this source of uncertainty will be addressed by collecting information on the effects of COPCs in the TSMD during the 2007 field season. In addition, the use of multiple lines of evidence provides a basis for minimizing the influence of data gaps on the effects assessment. Nevertheless, limitations on certain types of data, such as

information on the chemical composition of the surface microlayer, will necessarily constrain assessments of effects due to direct contact with or ingestion of waters associated with the surface microlayer and due to inhalation of COPCs from the surface microlayer. In addition, data were not located on the effects of many COPCs on amphibians; therefore, this group of receptors will not be directly addressed in the effects assessment for aquatic receptors. The implications of such data gaps, on the results of the risk assessment will be discussed and, to the extent possible, quantified in the uncertainty analysis.

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Tables

Table 1. Listing of National Pollutant Discharge Elimination System (NPDES) permitted facilities within the Tri-State Mining District.

Facility Name	Area of Interest	Facility NPDES ID Number	Facility Type	Likely Chemicals of Potential Concern Associated with Facility
<i>Oklahoma Portion of the TSMD</i>				
Cardin Special Utilities	Tar Creek	OK0038962	Sewerage system	Metals, PAHs, nutrients (N and P), phthalates, chlorinated benzenes, other SVOCs, pesticides, fecal coliforms, TOC, suspended solids and phenol
City of Commerce	Tar Creek	OK0020320	Sewerage system	Metals, PAHs, nutrients (N and P), phthalates, chlorinated benzenes, other SVOCs, pesticides, fecal coliforms, TOC, suspended solids and phenol
City of Miami-Southeast WTF	Neosho River	OK0031798	Sewerage system	Metals, PAHs, nutrients (N and P), phthalates, chlorinated benzenes, other SVOCs, pesticides, fecal coliforms, TOC, suspended solids and phenol
City of Picher	Tar Creek	OK0032263	Sewerage system	Metals, PAHs, nutrients (N and P), phthalates, chlorinated benzenes, other SVOCs, pesticides, fecal coliforms, TOC, suspended solids and phenol
Ottawa County W&S District #1	Lost Creek	OK0028291	Sewerage system	Metals, PAHs, nutrients (N and P), phthalates, chlorinated benzenes, other SVOCs, pesticides, fecal coliforms, TOC, suspended solids and phenol
Quapaw Public Works Authority	Spring River Mainstem	OK0028258	Sewerage system	Metals, PAHs, nutrients (N and P), phthalates, chlorinated benzenes, other SVOCs, pesticides, fecal coliforms, TOC, suspended solids and phenol
EaglePicher Technology LLC Boron	Spring River Mainstem	OK0040142	Boron isotope enrichment facility	Boron, zinc, lithium
Midwest Minerals - Quarry No. 32	Spring River Mainstem	OK0042927	Limestone quarry	Suspended solids, PAHs, pH, BOD, COD, NH ₄ , NO ₃

Missouri Portion of the TSMD

As noted by Mark Doolan at the January 17-19 2007 workshop, this data will be compiled by Black and Veatch.

Kansas Portion of the TSMD

As noted by Mark Doolan at the January 17-19 2007 workshop, this data will be compiled by Black and Veatch.

PAHs = Polycyclic aromatic hydrocarbons; N = nitrogen; P = phosphorous; TOC = total organic carbon; BOD = biological oxygen demand; COD = chemical oxygen demand; NO₃ = nitrate, NH₄ = ionized ammonia.

Table 2. Mussels collected in the Spring River Basin in Missouri (Oesch 1984).

Common Name	Scientific Name
Paper floater	<i>Anodonta imbecilis</i>
Giant floater	<i>Anodonta grandis grandis</i>
Squaw foot	<i>Strophitus undulatus undulatus</i>
Elk toe	<i>Alasmidonta marginata</i>
Slipper shell	<i>Alasmidonta viridis</i>
White heel-splitter	<i>Lasmigona complanata</i>
Fluted shell	<i>Lasmigona costata</i>
Pistol-grip	<i>Tritogonia verrucosa</i>
Maple leaf	<i>Quadrula quadrula</i>
Rabbit's foot	<i>Quadrula cylindrica cylindrica</i>
Monkey face	<i>Quadrula metanevra</i>
Pimple-back	<i>Quadrula pustulosa</i>
Three-ridge	<i>Amblema plicata plicata</i>
Wabash pig-toe	<i>Fusconaia flava</i>
Ozark shell	<i>Fusconaia ozarkensis</i>
Round pig-toe	<i>Pleurobema coccineum</i>
Lady-finger	<i>Elliptio dilata</i>
Kidney-shell	<i>Ptychobranthus occidentalis</i>
Western fanshell	<i>Cyprogenia aberti</i>
Mucket	<i>Actinonaias ligamentina carinata</i>
Plea's mussel	<i>Venustaconcha ellipsiformis</i>
Fawn's foot	<i>Truncilla donaciformis</i>
Deer-toe	<i>Truncilla truncata</i>
Fragile paper shell	<i>Leptodea fragilis</i>
Liliput shell	<i>Toxolasma parvus</i>
Little purple	<i>Toxolasma lividus glans</i>
Pond mussel	<i>Ligumia subrostrata</i>
Slough sand shell	<i>Lampsilis teres teres</i>
Yellow sand shell	<i>Lampsilis teres anodontoides</i>
Fat mucket	<i>Lampsilis radiata luteola</i>
Neosho mucket	<i>Lampsilis rafinesqueana</i>
Pocketbook	<i>Lampsilis ventricosa</i>
Broken rays	<i>Lampsilis reeviana brevicula</i>
Purple pimpleback	<i>Cyclonaias tuberculata</i>
Black sand shell	<i>Ligumia recta</i>

Table 3. Fish species found in the Spring River Basin (MDC 1991 and Beckman 1995).

Common Name	Scientific Name
<i>Percidae (Perches)</i>	
Arkansas darter	<i>Etheostoma cragini</i>
Fantail darter	<i>Etheostoma flabellare</i>
Orangethroat darter	<i>Etheostoma spectabile</i>
Stippled darter	<i>Etheostoma punctulatum</i>
<i>Cyprinidae (Minnows or carps)</i>	
Cardinal shiner	<i>Luxilus cardinalis</i>
Common carp	<i>Cyprinus carpio</i>
Creek chub	<i>Semotilus atromaculatus</i>
Southern redbelly dace	<i>Phoxinus erythrogaster</i>
Stoneroller	<i>Campostoma sp.</i>
<i>Lepisosteidae (Gars)</i>	
Longnose gar	<i>Lepisosteus osseus</i>
Shortnose gar	<i>Lepisosteus platostomus</i>
<i>Catostomidae (Suckers)</i>	
Black buffalo	<i>Ictiobus niger</i>
Black redhorse	<i>Moxostoma duquesnei</i>
Golden redhorse	<i>Moxostoma erythrurum</i>
Northern hog sucker	<i>Hypentelium nigricans</i>
River carpsucker	<i>Carpionodes carpio</i>
River redhorse	<i>Moxostoma carinatum</i>
Shorthead redhorse	<i>Moxostoma macrolepidotum</i>
Spotted sucker	<i>Minytrema melanops</i>
White sucker	<i>Catostomus commersoni</i>
<i>Centrarchidae (Sunfishes)</i>	
Green sunfish	<i>Lepomis cyanellus</i>
Warmouth	<i>Lepomis gulosus</i>
<i>Ictaluridae (North American freshwater catfishes)</i>	
Blue catfish	<i>Ictalurus punctatus</i>
Black bullhead	<i>Ameiurus melas</i>
Flathead catfish	<i>Pylodictis olivaris</i>
Yellow bullhead	<i>Ameiurus natalis</i>
Neosho madtom	<i>Noturus placidus</i>
<i>Salmonidae (Salmonids)</i>	
Rainbow trout	<i>Oncorhynchus mykiss</i>
<i>Clupeidae (Herrings, shads, sardines, menhadens)</i>	
Gizzard shad	<i>Dorosoma cepedianum</i>

Table 4. Amphibian species found in the Spring River Basin (Johnson 1987).

Common Name	Scientific Name	Range
<i>Salamanders</i>		
Ringed salamander	<i>Ambystoma annulatum</i>	Basinwide
Spotted salamander	<i>Ambystoma maculatum</i>	Basinwide
Marbled salamander	<i>Ambystoma opacum</i>	Eastern counties of the basin
Smallmouth salamander	<i>Ambystoma texanum</i>	Western counties of the basin
Eastern tiger salamander	<i>Ambystoma tigrinum tigrinum</i>	Basinwide
Central newt	<i>Notophthalmus viridescens louisianensis</i>	Basinwide
Longtail salamander	<i>Eurycea longicauda</i>	Basinwide
Cave salamander	<i>Eurycea lucifuga</i>	Basinwide
Graybelly salamander	<i>Eurycea multiplicata griseogaster</i>	Basinwide
Oklahoma salamander	<i>Eurycea tynerensis</i>	Basinwide
Ozark zigzag salamander	<i>Plethodon dorsalis angusticlavius</i>	Basinwide
Slimy salamander	<i>Plethodon glutinosus glutinosus</i>	Basinwide
Grotto salamander	<i>Typhlotriton spelaeus</i>	Basinwide
Red River mudpuppy	<i>Necturus maculosus louisianensis</i>	Basinwide
<i>Frogs and Toads</i>		
Dwarf American toad	<i>Bufo americanus charlesmithi</i>	Basinwide
Fowler's toad	<i>Bufo woodhousei fowleri</i>	Basinwide
Woodhouse's toad	<i>Bufo woodhousei woodhousei</i>	possibly in Newton County
Blanchard's cricket frog	<i>Acris crepitans blanchardi</i>	Basinwide
Northern spring peeper	<i>Hyla crucifer crucifer</i>	Basinwide
Cope's gray treefrog	<i>Hyla chrysoscelis</i>	Basinwide
Western chorus frog	<i>Pseudacris triseriata</i>	Basinwide
Eastern narrowmouth toad	<i>Gastrophryne carolinensis</i>	Basinwide
Great Plains narrowmouth toad	<i>Gastrophryne olivacea</i>	Western counties of the basin
Northern crawfish frog	<i>Rana areolata circulosa</i>	Western counties of the basin
Bullfrog	<i>Rana catesbeiana</i>	Basinwide
Green frog	<i>Rana clamitans</i>	Basinwide
Pickerel frog	<i>Rana palustris</i>	Basinwide
Southern leopard frog	<i>Rana sphenoccephala</i>	Basinwide
Wood frog	<i>Rana sylvatica</i>	Eastern counties of the basin

Table 5. Reptile species found in the Spring River Basin (Johnson 1987).

Common Name	Scientific Name	Range
Turtles		
Common snapping turtle	<i>Chelydra serpentina serpentina</i>	Basinwide
Alligator snapping turtle	<i>Macrolemys temminckii</i>	Southern counties of the basin
Yellow mud turtle	<i>Kinosternon flavescens</i>	Western counties of the basin
Stinkpot	<i>Sternotherus odoratus</i>	Basinwide
Western painted turtle	<i>Chrysemys picta bellii</i>	Basinwide
Common Map turtle	<i>Graptemys geographica</i>	Basinwide
Mississippi map turtle	<i>Graptemys kohnii</i>	Basinwide
Ouachita map turtle	<i>Graptemys pseudogeographica ouachitensis</i>	Basinwide
River cooter	<i>Pseudemys concinna concinna</i>	Basinwide
Three-toed box turtle	<i>Terrapene carolina triunguis</i>	Basinwide
Ornate box turtle	<i>Terrapene ornata ornata</i>	Basinwide
Red-eared slider	<i>Trachemys scripta elegans</i>	Basinwide
Midland smooth softshell	<i>Apalone mutica mutica</i>	Basinwide
Eastern spiny softshell	<i>Apalone spinifera spinifera</i>	Basinwide
Lizards		
Eastern collared lizard	<i>Crotaphytus collaris collaris</i>	Basinwide
Texas horned lizard	<i>Phrynosoma cornutum</i>	Western counties of the basin
Northern fence lizard	<i>Sceloporus undulatus hyacinthinus</i>	Basinwide
Southern coal skink	<i>Eumeces anthracinus pluvialis</i>	Basinwide
Five-lined skink	<i>Eumeces fasciatus</i>	Basinwide
Broadhead skink	<i>Eumeces laticeps</i>	Basinwide
Great Plains skink	<i>Eumeces obsoletus</i>	Western counties of the basin
Northern Prairie Skink	<i>Eumeces septentrionalis</i>	Western counties of the basin
Ground skink	<i>Scincella lateralis</i>	Basinwide
Six-lined racerunner	<i>Cnemidophorus sexlineatus sexlineatus</i>	Basinwide
Western slender glass lizard	<i>Ophisaurus attenuatus attenuatus</i>	Basinwide
Snakes		
Western worm snake	<i>Carphophis vermis</i>	Basinwide
Eastern yellowbelly racer	<i>Coluber constrictor flaviventris</i>	Basinwide
Prairie ringneck snake	<i>Diadophis punctatus arnyi</i>	Basinwide
Great Plains rat snake	<i>Elaphe guttata emoryi</i>	Basinwide
Black rat snake	<i>Elaphe obsoleta obsoleta</i>	Basinwide
Eastern hognose snake	<i>Heterodon platirhinos</i>	Basinwide
Prairie kingsnake	<i>Lampropeltis calligaster calligaster</i>	Basinwide
Speckled kingsnake	<i>Lampropeltis getula holbrookii</i>	Basinwide
Red milk snake	<i>Lampropeltis triangulum sypila</i>	Basinwide
Eastern coachwhip	<i>Masticophis flagellum flagellum</i>	Basinwide

Table 5. Reptile species found in the Spring River Basin (Johnson 1987).

Common Name	Scientific Name	Range
Blotched water snake	<i>Nerodia erythrogaster transversa</i>	Basinwide
Diamondback water snake	<i>Nerodia rhombifer rhombifer</i>	Western counties of the basin
Midland water snake	<i>Nerodia sipedon pleuralis</i>	Basinwide
Rough green snake	<i>Opheodrys aestivus</i>	Basinwide
Bullsnake	<i>Pituophis catenifer sayi</i>	Basinwide
Graham's crayfish snake	<i>Regina grahamii</i>	Western counties of the basin
Ground snake	<i>Sonora semiannulata</i>	Basinwide
Midland brown snake	<i>Storeria dekayi wrightorum</i>	Eastern counties of the basin
Texas brown snake	<i>Storeria dekayi texana</i>	Basinwide
Northern redbelly snake	<i>Storeria occipitomaculata occipitomaculata</i>	Basinwide
Flathead snake	<i>Tantilla gracilis</i>	Basinwide
Western ribbon snake	<i>Thamnophis proximus proximus</i>	Basinwide
Eastern garter snake	<i>Thamnophis sirtalis sirtalis</i>	Basinwide
Red-sided garter snake	<i>Thamnophis sirtalis parietalis</i>	Western counties of the basin
Lined snake	<i>Tropidoclonion lineatum annectens</i>	Western counties of the basin
Rough earth snake	<i>Virginia striatula</i>	Basinwide
Western earth snake	<i>Virginia valeriae elegans</i>	Basinwide
Osage copperhead	<i>Agkistrodon contortrix phaeogaster</i>	Northwest counties of the basin
Southern copperhead	<i>Agkistrodon contortrix contortrix</i>	Southern counties of the basin
Western cottonmouth	<i>Agkistrodon piscivorus leucostoma</i>	Southern counties of the basin
Timber rattlesnake	<i>Crotalus horridus</i>	Basinwide
Western pygmy rattlesnake	<i>Sistrurus miliarius streckeri</i>	Southeast counties of the basin

Table 6. Bird species found in the Spring River Basin, based on bird checklists from the George Washington Carver National Monument, Missouri (USFWS, unknown) and the Osage Hills and Tallgrass Prairie region, Oklahoma (Droege 1995).

Loons & grebes

Common Loon
Eared Grebe
Horned Grebe
Pied-billed Grebe

Pelicans & Cormorants

American White Pelican
Double-crested Cormorant
White Pelican

Wadingbirds

American Bittern
Black-crowned Night-Heron
Cattle Egret
Great Blue Heron
Great Egret
Green Heron
Least Bittern
Little Blue Heron
Snowy Egret
White-faced Ibis
Yellow-crowned Night-Heron

Waterfowl

American Wigeon
Blue-winged Teal
Bufflehead
Canada Goose
Canvasback
Cinnamon Teal
Common Goldeneye
Common Merganser
Gadwall
Greater Scaup
Greater White-fronted Goose
Green-winged Teal
Hooded Merganser
Lesser Scaup
Mallard
Northern Pintail
Northern Shoveler
Red-breasted Merganser
Redhead

Waterfowl (cont)

Ring-necked Duck
Ross' Goose
Ruddy Duck
Snow Goose
Tundra Swan
White-fronted Goose
Wood Duck

Vultures, Hawks & Falcons

American Kestrel
Bald Eagle
Broad-winged Hawk
Cooper's Hawk
Ferruginous Hawk
Golden Eagle
Merlin
Mississippi Kite
Northern Goshawk
Northern Harrier
Osprey
Peregrine Falcon
Prairie Falcon
Red-shouldered Hawk
Red-tailed Hawk
Rough-legged Hawk
Sharp-shinned Hawk
Swainson's Hawk
Turkey Vulture

Gallinaceous birds / Upland Game Birds

Greater Prairie-Chicken
Northern Bobwhite
Wild Turkey

Marshbirds

American Coot
King Rail
Sora

Shorebirds, Gulls, & Terns

American Avocet
American Golden-Plover
American Woodcock
Baird's Sandpiper

Table 6. Bird species found in the Spring River Basin, based on bird checklists from the George Washington Carver National Monument, Missouri (USFWS, unknown) and the Osage Hills and Tallgrass Prairie region, Oklahoma (Droege 1995).

Shorebirds, Gulls, & Terns (cont)

Black Tern
 Black-bellied Plover
 Bonaparte's Gull
 Buff-breasted Sandpiper
 Caspian Tern
 Common Snipe
 Common Tern
 Dunlin
 Forster's Tern
 Franklin's Gull
 Greater Yellowlegs
 Herring Gull
 Hudsonian Godwit
 Killdeer
 Least Sandpiper
 Least Tern
 Lesser Yellowlegs
 Long-billed Dowitcher
 Marbled Godwit
 Pectoral Sandpiper
 Piping Plover
 Red Knot
 Ring-billed Gull
 Ruddy Turnstone
 Sanderling
 Semipalmated Plover
 Semipalmated Sandpiper
 Short-billed Dowitcher
 Solitary Sandpiper
 Spotted Sandpiper
 Stilt Sandpiper
 Upland Sandpiper
 Western Sandpiper
 White-rumped Sandpiper
 Willet
 Wilson's Phalarope

Doves & Cuckoos

Black-billed Cuckoo
 Greater Roadrunner
 Mourning Dove
 Rock Dove
 Yellow-billed Cuckoo

Owls

Barn Owl
 Barred Owl
 Eastern Screech-Owl
 Great Horned Owl
 Long-eared Owl
 Short-eared Owl

Pipits & Waxwings

American Pipit
 Cedar Waxwing
 Sprague's Pipit

Nightjars, Swifts & Hummingbirds

Chimney Swift
 Chuck-will's-widow
 Common Nighthawk
 Common Poorwill
 Ruby-throated Hummingbird
 Whip-poor-will

Kingfishers

Belted Kingfisher

Woodpeckers

Downy Woodpecker
 Hairy Woodpecker
 Northern Flicker
 Pileated Woodpecker
 Red-bellied Woodpecker
 Red-headed Woodpecker
 Yellow-bellied Sapsucker

Flycatchers

Acadian Flycatcher
 Alder Flycatcher
 Eastern Kingbird
 Eastern Phoebe
 Eastern Wood-Pewee
 Great Crested Flycatcher
 Least Flycatcher
 Olive-sided Flycatcher
 Scissor-tailed Flycatcher
 Western Kingbird
 Willow Flycatcher
 Yellow-bellied Flycatcher

Table 6. Bird species found in the Spring River Basin, based on bird checklists from the George Washington Carver National Monument, Missouri (USFWS, unknown) and the Osage Hills and Tallgrass Prairie region, Oklahoma (Droege 1995).

<i>Larks</i>	<i>Mockingbirds & Thrashers</i>
Horned Lark	Brown Thrasher
	Gray Catbird
	Northern Mockingbird
<i>Swallows</i>	<i>Shrikes</i>
Bank Swallow	Loggerhead Shrike
Barn Swallow	
Cliff Swallow	<i>Starlings</i>
Northern Rough-winged Swallow	European Starling
Purple Martin	
Tree Swallow	
<i>Jays & Crows</i>	<i>Vireos</i>
American Crow	Bell's Vireo
Blue Jay	Philadelphia Vireo
Fish Crow	Red-eyed Vireo
	Solitary Vireo
<i>Titmice, Chickadees, Nuthatches & Creepers</i>	Warbling Vireo
Brown Creeper	White-eyed Vireo
Carolina Chickadee	Yellow-throated Vireo
Red-breasted Nuthatch	
Tufted Titmouse	<i>Warblers</i>
White-breasted Nuthatch	American Redstart
<i>Wrens</i>	Bay-breasted Warbler
Bewick's Wren	Black-and-white Warbler
Carolina Wren	Blackburnian Warbler
House Wren	Blackpoll Warbler
Marsh Wren	Black-throated Green Warbler
Sedge Wren	Blue-winged Warbler
Winter Wren	Canada Warbler
	Cerulean Warbler
<i>Kinglets, Thrushes & Gnatcatchers</i>	Chestnut-sided Warbler
American Robin	Common Yellowthroat
Blue-gray Gnatcatcher	Golden-winged Warbler
Eastern Bluebird	Kentucky Warbler
Golden-crowned Kinglet	Louisiana Waterthrush
Gray-cheeked Thrush	Magnolia Warbler
Hermit Thrush	Mourning Warbler
Ruby-crowned Kinglet	Nashville Warbler
Swainson's Thrush	Northern Parula
Veery	Northern Waterthrush
Wood Thrush	Orange-crowned Warbler
	Ovenbird
	Palm Warbler
	Pine Warbler

Table 6. Bird species found in the Spring River Basin, based on bird checklists from the George Washington Carver National Monument, Missouri (USFWS, unknown) and the Osage Hills and Tallgrass Prairie region, Oklahoma (Droege 1995).

Warblers (cont)

Prairie Warbler
 Prothonotary Warbler
 Tennessee Warbler
 Wilson's Warbler
 Worm-eating Warbler
 Yellow Warbler
 Yellow-breasted Chat
 Yellow-rumped Warbler
 Yellow-throated Warbler

Tanagers

Scarlet Tanager
 Summer Tanager

Grosbeaks & Buntings

Blue Grosbeak
 Dickcissel
 Indigo Bunting
 Northern Cardinal
 Painted Bunting
 Rose-breasted Grosbeak

Towhees, Sparrows & Longspurs

American Tree Sparrow
 Chestnut-collared Longspur
 Chipping Sparrow
 Clay-colored Sparrow
 Dark-eyed Junco
 Field Sparrow
 Fox Sparrow
 Grasshopper Sparrow
 Harris' Sparrow
 Henslow's Sparrow
 Lapland Longspur
 Lark Sparrow
 Le Conte's Sparrow
 Lincoln's Sparrow
 Rufous-sided Towhee
 Savannah Sparrow
 Smith's Longspur
 Song Sparrow
 Swamp Sparrow
 Vesper Sparrow
 White-crowned Sparrow
 White-throated Sparrow

Blackbirds & Orioles

Bobolink
 Brewer's Blackbird
 Brown-headed Cowbird
 Common Grackle
 Eastern Meadowlark
 Great-tailed Grackle
 Northern Oriole
 Orchard Oriole
 Red-winged Blackbird
 Rusty Blackbird
 Western Meadowlark
 Yellow-headed Blackbird

Finches & Weaverfinches

American Goldfinch
 Evening Grosbeak
 House Finch
 Pine Siskin
 Purple Finch
 House Sparrow

Table 7. Mammal species found in the Spring River Basin (MWIN 2007).

Common Name	Scientific Name
Badger	<i>Taxidea taxus</i>
Beaver	<i>Castor canadensis</i>
Black-tailed jack rabbit	<i>Lepus californicus</i>
Bobcat	<i>Felis rufus</i>
Chipmunk	<i>Eutamias spp.</i>
Coyote	<i>Canis latrans</i>
Deer	<i>Odocoileus spp.</i>
Gray bat	<i>Myotis grisescens</i>
Gray fox	<i>Urocyon cinereoargenteus</i>
Long-tailed weasel	<i>Mustela frenata</i>
Mink	<i>Mustela vison</i>
Muskrat	<i>Ondatra zibethicus</i>
Opossum	<i>Monodelphis spp.</i>
Rabbit	<i>Oryctolagus cuniculus</i>
Raccoon	<i>Procyon lotor</i>
Red fox	<i>Vulpes vulpes</i>
River otter	<i>Lontra canadensis</i>
Skunk	<i>Mephitis spp</i>
Squirrel	<i>Spermophilus spp.</i>

Table 8. List of plant and animal species as risk, based on federal and state legislation (MWIN 2007).

Common Name	Latin Name	Threatened and Endangered Plants & Animals (Federal Level)	Rare or Threatened (State Level)	Species of the Spring River Basin on the State Watch List
Mammals				
Black-tailed jack rabbit	<i>Lepus californicus</i>	✓		
Gray bat	<i>Myotis grisescens</i>	✓		
Long-tailed weasel	<i>Mustella frenata</i>		✓	
Plains spotted skunk	<i>Spilogale putorius intempta</i>	✓		
Swamp rabbit	<i>Sylvilagus aquaticus</i>		✓	
Birds				
Barn owl	<i>Tyto alba</i>		✓	
Cooper's hawk	<i>Accipiter cooperii</i>		✓	
Greater prairie-chicken	<i>Tympanuchus cupido</i>		✓	
Henslow's sparrow	<i>Ammodramus henslowii</i>		✓	
Northern harrier	<i>Circus cyaneus</i>	✓		
Ozark wake robin	<i>Trillium pusillum var ozarkanum</i>		✓	
Pied-billed grebe	<i>Podilymbus podiceps</i>		✓	
Upland sandpiper	<i>Bartramia longicauda</i>			✓
Fish				
Arkansas darter	<i>Etheostoma cragini</i>		✓	
Bluntnose shiner	<i>Cyprinella camura</i>		✓	
Ghost shiner	<i>Notropis buechanani</i>			✓
Least darter	<i>Etheostoma microperca</i>			✓
Neosho madtom	<i>Noturus placidus</i>	✓		
Ozark cavefish	<i>Amblyopsis rosae</i>	✓		

Table 8. List of plant and animal species as risk, based on federal and state legislation (MWIN 2007).

Common Name	Latin Name	Threatened and Endangered Plants & Animals (Federal Level)	Rare or Threatened (State Level)	Species of the Spring River Basin on the State Watch List
<i>Fish (cont)</i>				
Pugnose minnow	<i>Opsopoeodus emiliae</i>			✓
Redfin darter	<i>Etheostoma whipplei</i>	✓		
Western slim minnow	<i>Pimephales tenellus tenellus</i>		✓	
<i>Reptiles/Amphibians</i>				
Great plains skink	<i>Eumeces obsoletus</i>		✓	
Grotto salamander	<i>Typhlotriton spelaeus</i>			✓
Northern crayfish frog	<i>Rana areolata circulosa</i>			✓
<i>Invertebrates</i>				
Bristly cave crayfish	<i>Cambarus setosus</i>			✓
Neosho mucket	<i>Lampsilis rafinesqueana</i>		✓	
Rabbits foot (bivalve)	<i>Quadrula cylindrica cylindrica</i>	✓		
Western fanshell (bivalve)	<i>Cyprogenia aberti</i>		✓	
<i>Insects</i>				
Arkansas snaketail dragonfly	<i>Ophiogomphus westfalli</i>		✓	
Prairie mole cricket	<i>Grylotalpa major</i>		✓	
Regal fritillary (butterfly)	<i>Speyeria idalia</i>			✓
<i>Plants</i>				
False foxglove spp.	<i>Agalinis auriculata</i>		✓	✓
Moss spp.	<i>Leska polycarpa</i>		✓	
Venus' looking glass spp.	<i>Triodanis lamprosperma</i>		✓	

Table 8. List of plant and animal species as risk, based on federal and state legislation (MWIN 2007).

Common Name	Latin Name	Threatened and Endangered Plants & Animals (Federal Level)	Rare or Threatened (State Level)	Species of the Spring River Basin on the State Watch List
<i>Plants (cont.)</i>				
Wild pea spp.	<i>Lathyrus pusillus</i>	✓		
Alabama lip-fern	<i>Chalanthes alabamensis</i>	✓		
Adder's tongue fern spp.	<i>Ophioglossum vulgatum</i>			✓
Brush's poppy mallow	<i>Callirhoe bushii</i>			✓
Drummond's halfchaff sedge	<i>Lipocarpa drummondii</i>	✓		
Geocarpon	<i>Geocarpon minimum</i>	✓		
Green false foxglove	<i>Agalinis viridis</i>	✓		
Joint grass	<i>Coelorachis cylindrica</i>	✓		
Kansas arrowhead	<i>Sagittaria ambigua</i>	✓		
Lake-bank sedge	<i>Carex lacustris</i>	✓		
Low prickly pear <i>Opuntia macrorhiza</i>	<i>Opuntia macrorhiza</i>		✓	
Marsh bellflower	<i>Campanula aparinoides</i>	✓		
Mead's milkweed	<i>Asclepias meadii</i>	✓		
Mudbank paspalum	<i>Paspalum dissectum</i>	✓		
Oklahoma sedge	<i>Carex oklahomensis</i>		✓	
Pinnate dog shade	<i>Limnoscadium pinnatum</i>	✓		
Prairie false foxglove	<i>Agalinis heterophylla</i>	✓		
Purple lilliput	<i>Toxolasma lirudus</i>			✓
Royal catchfly	<i>Silene regia</i>			✓
Running buffalo clover	<i>Trifolium stoloniferum</i>	✓		
Sixteenweeks three-awn	<i>Aristida adscensionis</i>			✓
Slender ladies' tresses	<i>Spiranthes lacera var gracilis</i>			✓
Slender pondweed	<i>Potamogeton pusillus var pusillus</i>	✓		

Table 8. List of plant and animal species as risk, based on federal and state legislation (MWIN 2007).

Common Name	Latin Name	Threatened and Endangered Plants & Animals (Federal Level)	Rare or Threatened (State Level)	Species of the Spring River Basin on the State Watch List
<i>Plants (cont)</i>				
Small spike rush	<i>Eleocharis parvula var anachaeta</i>		✓	
Soapberry	<i>Sapindus drummondii</i>			✓
Tansy mustard	<i>Descurainia pinnata</i>	✓		
Tradescant aster	<i>Aster dumosus var strictior</i>		✓	
Water hyssop	<i>Mecardonia acuminata</i>	✓		
Western prairie fringed orchid	<i>Planthera praeclara</i>	✓		
Yellow-eyed grass	<i>Xyris torta</i>	✓		
Yellow false mallow	<i>Malvastrum</i>			✓
Yellow-flowered leafcup	<i>Smallanthus wedalius</i>			✓

Table 9. Classification of chemicals of potential concern in the Tri-State Mining District, based on their environmental fate and effects.

Classification	Chemical Class/Substance	
Toxic substances that partition into water (including pore water and the surface microlayer)	Metals Arsenic, boron, cadmium, chromium, copper, lead, lithium, mercury, nickel, selenium, zinc	
	Certain herbicides, insecticides, and fungicides Identification pending pesticide use survey	
	Nutrients NO ₂ , NO ₃ , NH ₃ , P	
	TSS (total suspended solids)	
	BOD (biological oxygen demand)	
	Hydrogen sulfide (H₂S)	
Toxic substances that partition into sediments and/or soils	Metals Arsenic, boron, cadmium, chromium, copper, lead, lithium, mercury, nickel, selenium, zinc	
	PAHs Parent PAHs (<i>Acenaphthene, Acenaphthylene, Anthracene, Fluorene, 2-Methylnaphthalene, Naphthalene, Phenanthrene, Benz(a)anthracene, Benzo(a)pyrene, Chrysene, Dibenz(a,h)anthracene, Fluoranthene, Pyrene</i>), Alkylated PAHs, Total PAHs	
	BTEX Benzene, toluene, ethylbenzene, xylene	
	PCBs Aroclors, PCB congeners, Total PCBs	
	Chlorinated phenols	
	Organochlorine pesticides	
	Phenol	
	Phthalates	
	Bioaccumulative substances	Metals Cadmium, lead, mercury, zinc
		PAHs High molecular weight PAHs <i>Benz(a)anthracene, Benzo(a)pyrene, Chrysene, Dibenz(a,h)anthracene, Fluoranthene, Pyrene</i>
PCBs Aroclors, PCB congeners, Total PCBs		
Organochlorine pesticides		

PCBs = Polychlorinated biphenyls; PAHs = Polycyclic aromatic hydrocarbons; NO₂ = nitrite; NO₃ = nitrate, NH₃ = unionized ammonia; P = phosphorous.

Table 10. Key exposure routes for various classes of chemicals of potential concern (COPCs) in the Tri-State Mining District.

Classification	Substances	Exposure Route - Aquatic		Exposure Route - Wildlife		
		Contact	Ingestion	Inhalation	Contact	Ingestion
Toxic substances that partition into surface water (including pore water and the surface microlayer)	Arsenic, boron, cadmium, chromium, copper, lead, lithium, mercury, nickel, selenium, zinc, certain herbicides, insecticides, and fungicides, nutrients (NO ₂ , NO ₃ , NH ₃ , P), TSS, BOD, H ₂ S	✓				✓
Toxic substances that partition into sediments and/or soils	Arsenic, boron, cadmium, chromium, copper, lead, lithium, mercury, nickel, selenium, zinc, PAHs (parent and alkylated), BTEX (benzene, toluene, ethylbenzene, xylene), PCBs, chlorinated phenols, OC pesticides, phenol, phthalates	✓	✓			✓
Bioaccumulative substances	Cadmium, lead, mercury, zinc, high molecular weight PAHs, PCBs, OC pesticides	✓	✓			✓

PCBs = Polychlorinated biphenyls; PAHs = Polycyclic aromatic hydrocarbons; OC = organochlorine; NO₂ = nitrite; NO₃ = nitrate, NH₃ = ammonia; P = phosphorous; TSS = total suspended solids; BOD = biological oxygen demand; H₂S = hydrogen sulfide.

Table 11. Receptor groups exposed to various classes of chemicals of potential concern (COPCs) in the Tri-State Mining District.

Classification	Substances	Ecological Receptors		
		Aquatic Organisms	Birds	Mammals
Toxic substances that partition into surface water (including pore water and the surface microlayer)	Arsenic, boron, cadmium, chromium, copper, lead, lithium, mercury, nickel, selenium, zinc, certain herbicides, insecticides, and fungicides, nutrients (NO ₂ , NO ₃ , NH ₃ , P), TSS, BOD, and H ₂ S	Aquatic plants, Aquatic invertebrates, Fish, Amphibians		
Toxic substances that partition into sediments and/or soils	Arsenic, boron, cadmium, chromium, copper, lead, lithium, mercury, nickel, selenium, zinc, PAHs (parent and alkylated), BTEX (benzene, toluene, ethylbenzene, xylene), PCBs, chlorinated phenols, OC pesticides, phenol, phthalates	Decomposers, Aquatic plants, Benthic invertebrates, Benthic fish, Reptiles, Amphibians	Sediment-probing birds	
Bioaccumulative substances	Cadmium, lead, mercury, zinc, high molecular weight PAHs, PCBs, OC pesticides	Benthic invertebrates, Carnivorous fish, Amphibians, Reptiles	Insectivorous birds, Sediment-probing birds, Carnivorous-wading birds, Piscivorous birds	Piscivorous mammals, Omnivorous mammals

PCBs = Polychlorinated biphenyls; PAHs = Polycyclic aromatic hydrocarbons; OC = organochlorine; NO₂ = nitrite; NO₃ = nitrate, NH₃ = ammonia; P = phosphorous; TSS = total suspended solids; BOD = biological oxygen demand; H₂S = hydrogen sulfide.

Table 12. Documented effects of chemicals of potential concern in the Tri-State Mining District on aquatic organisms.

Chemical of Potential Concern (COPC)	Aquatic Plants			Zooplankton			Benthic Invertebrates			Fish		
	S	G	R	S	G	R	S	G	R	S	G	R
Arsenic				✓			✓			✓		
Boron	✓	✓	P	P	P	P	✓			✓	✓	✓
Cadmium				✓	✓	✓	✓	✓	✓	✓	✓	✓
Chromium	✓	✓	✓	✓	✓	✓	✓			✓	✓	
Copper	✓	✓	✓	✓	✓	✓	✓			✓	✓	✓
Lead				✓	✓	✓	✓					
Lithium				?			?			?		
Mercury		✓		✓			✓		✓	✓	✓	✓
Nickel	✓	✓	✓	✓	✓	✓				✓		✓
Selenium	?	?	?	?	?	?	P	P	P	P	P	✓
Zinc	✓	✓	✓	✓	✓	✓	✓			✓		✓
PAHs				✓	✓	✓	✓	✓	✓	✓	✓	✓
PCBs				✓	✓	✓	✓	✓	✓	✓	✓	✓
OC pesticides				✓			✓		✓	✓		
BTEX				✓			✓			✓		
Phthalates				✓						✓		
Chlorinated phenols				✓			✓			✓		
Phenol				✓			✓			✓		
Certain herbicides, insecticides, and fungicides	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓
Nutrients (NO ₂ , NO ₃ , NH ₃ , P)		✓		✓	✓	✓	✓	✓	✓	✓	✓	✓

Table 12. Documented effects of chemicals of potential concern in the Tri-State Mining District on aquatic organisms.

Chemical of Potential Concern (COPC)	Aquatic Plants			Zooplankton			Benthic Invertebrates			Fish		
	S	G	R	S	G	R	S	G	R	S	G	R
TSS				✓			✓	✓	✓	✓	✓	
BOD				✓			✓			✓		

Effects: S = survival; G = growth; R = reproduction; ✓ = effects documented; P = effects indicated but not clearly demonstrated.

BTEX = benzene, toluene, ethylbenzene, xylene; PCBs = Polychlorinated biphenyls; PAHs = Polycyclic aromatic hydrocarbons; OC = organochlorine; NO₂ = nitrite;

NO₃ = nitrate, NH₃ = ammonia; P = phosphorous; TSS = total suspended solids; BOD = biological oxygen demand.



Figures



Figure 2. The framework for ecological risk assessment (modified from USEPA 1997).

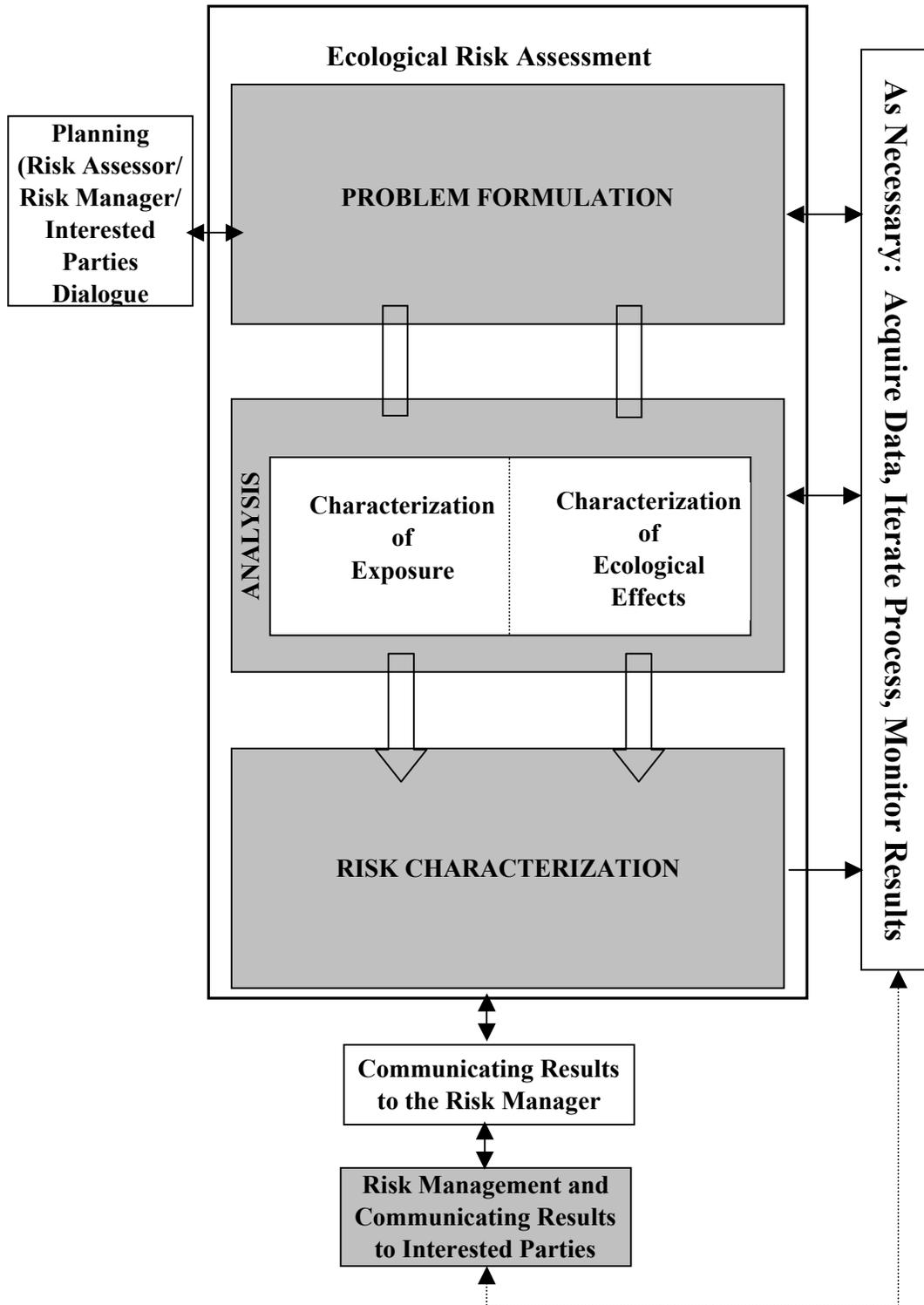
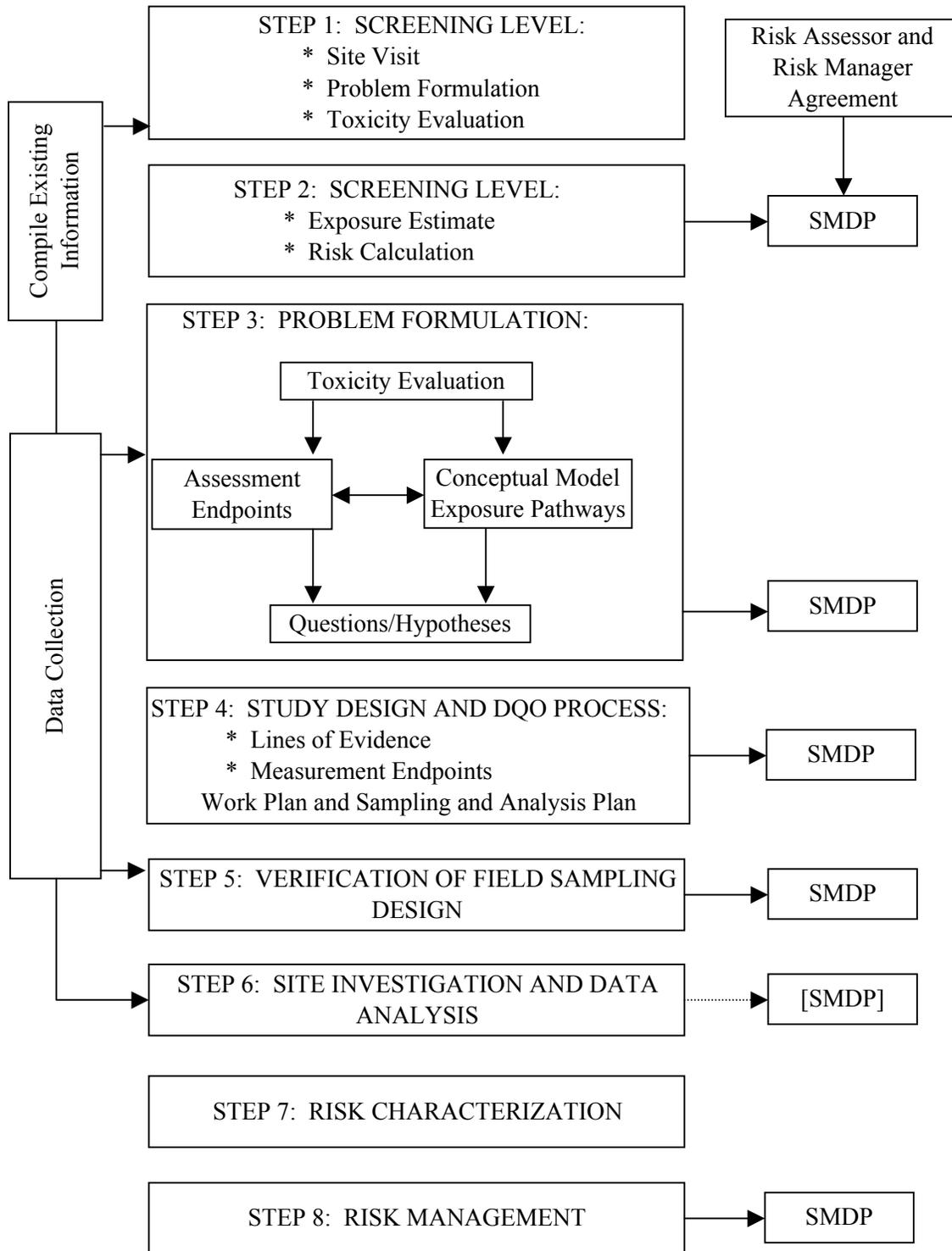


Figure 3. Eight-step ecological risk assessment process for Superfund (USEPA 1997).



SMDP = Scientific/Management Decision Point

Figure 4. Map of Study Area, showing Areas of Interest (AoI).

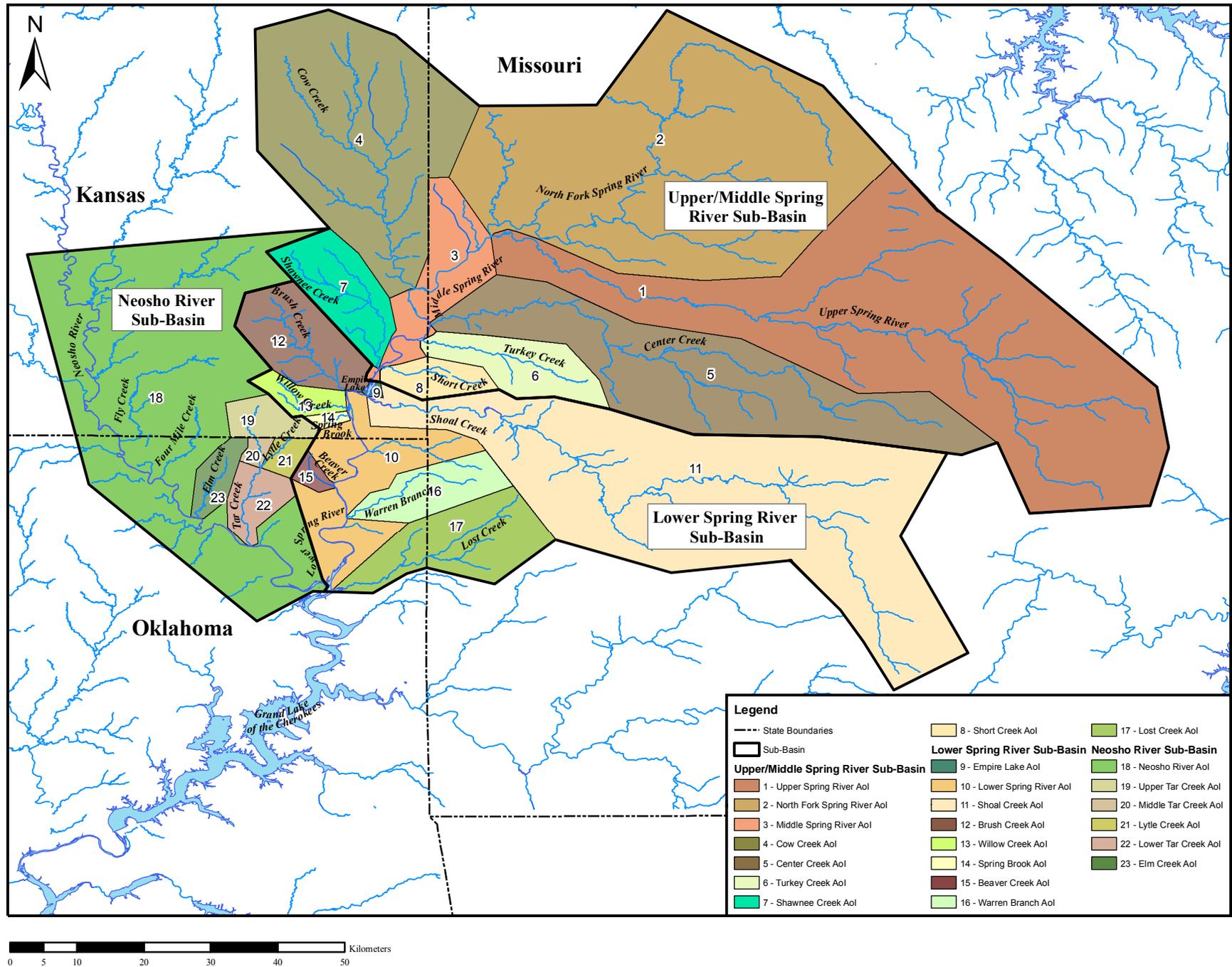


Figure 5. Simplified aquatic food web for a low order, cool water Ozark stream (Meyer, unknown).

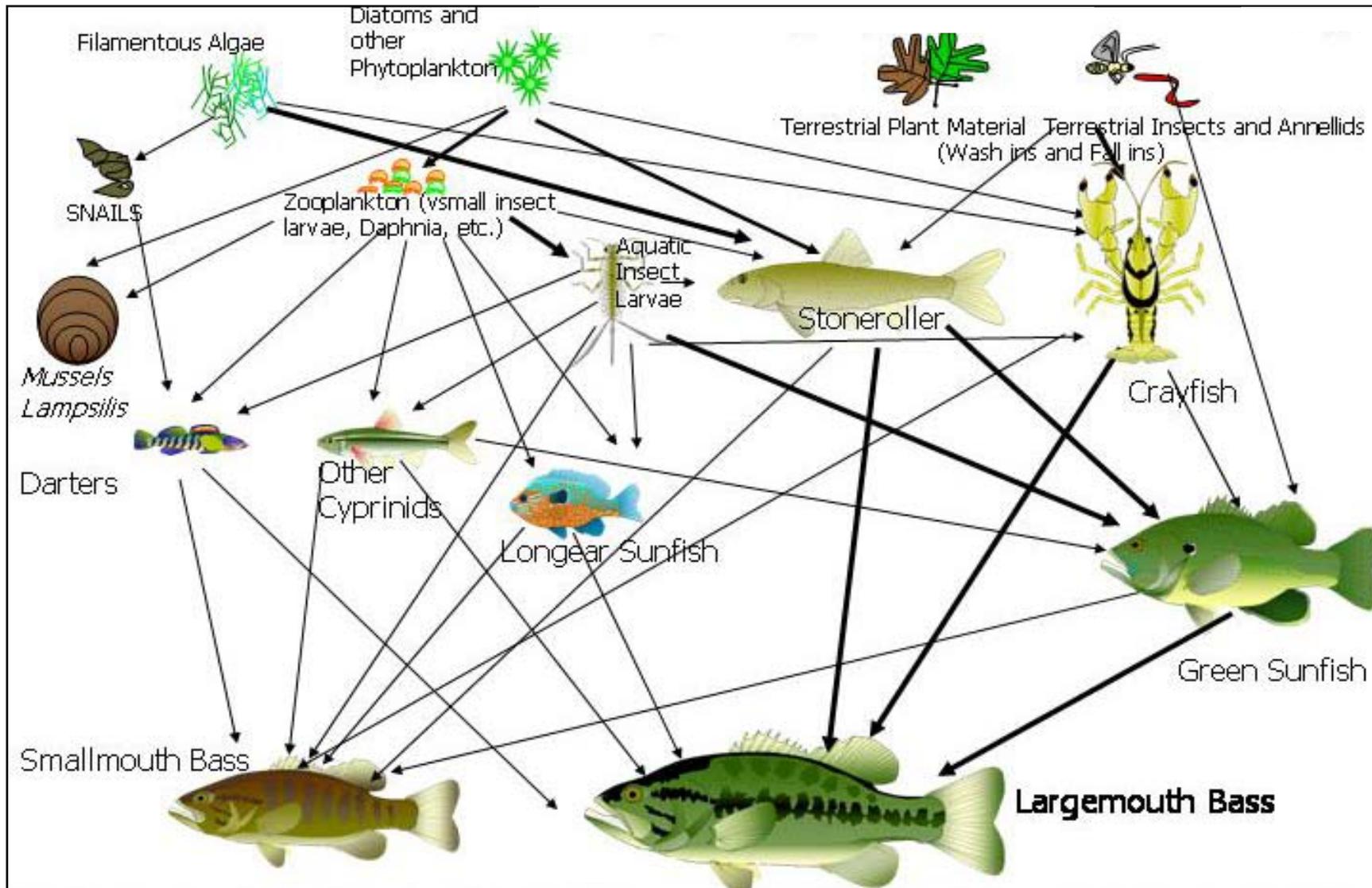


Figure 6. Simplified aquatic food web for a moderate order Ozark stream, after spring warming (Meyer, unknown).

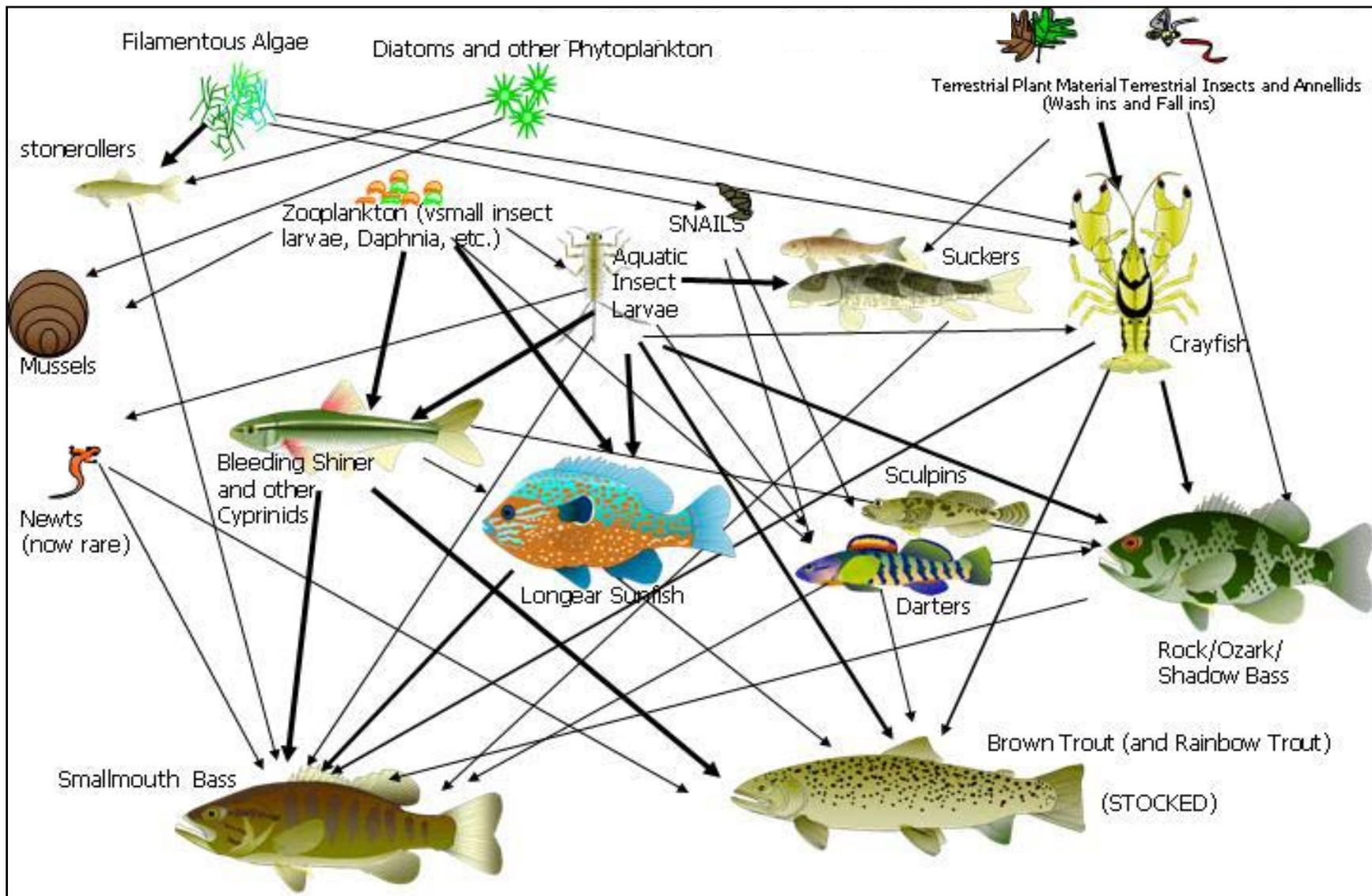


Figure 7. Simplified aquatic food web for a moderate order Ozark stream, after fall cooling (Meyer, unknown).

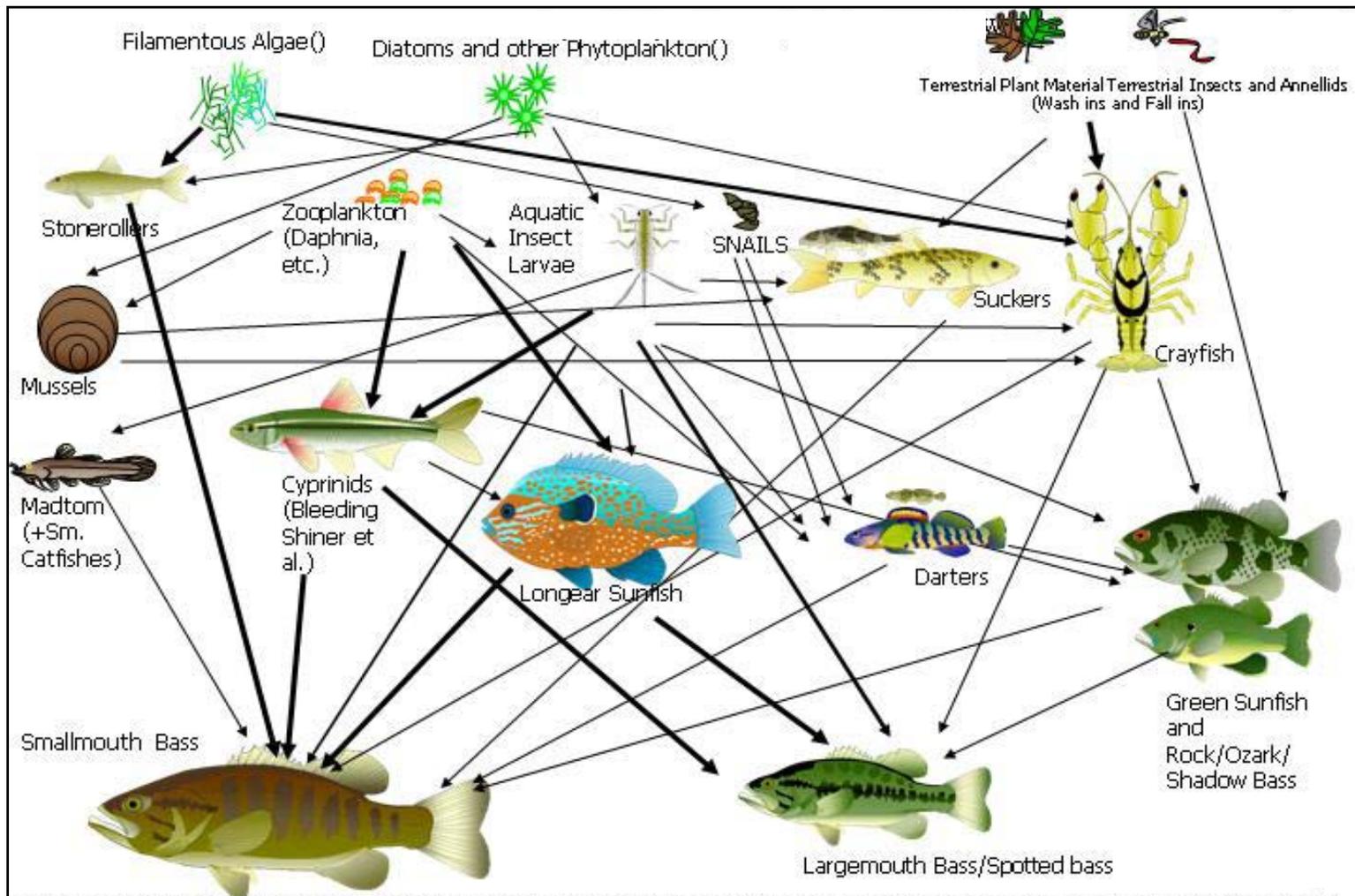


Figure 8. Simplified aquatic food web for Ozark streams, near springs or spring riffles (Meyer, unknown).

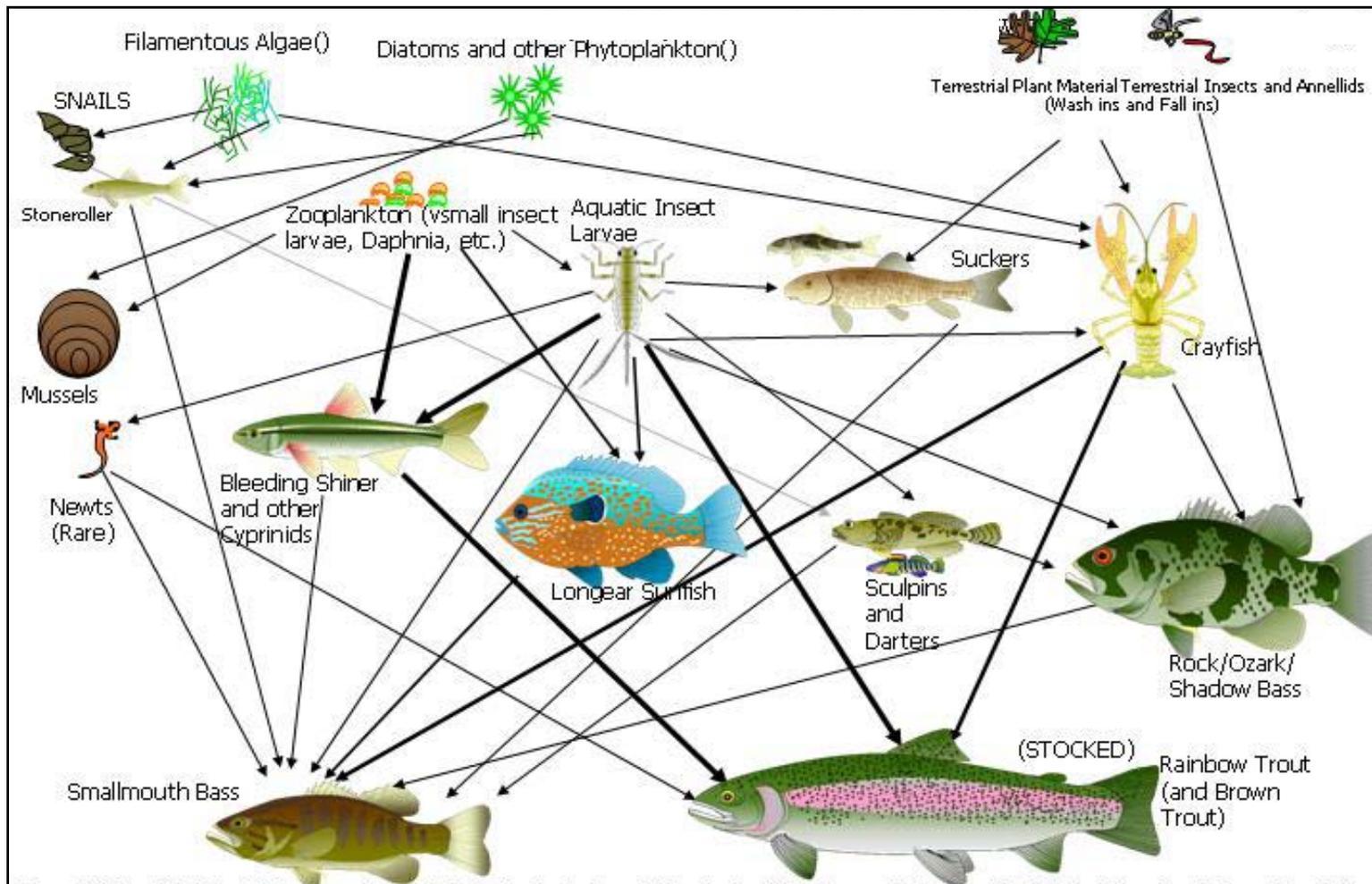
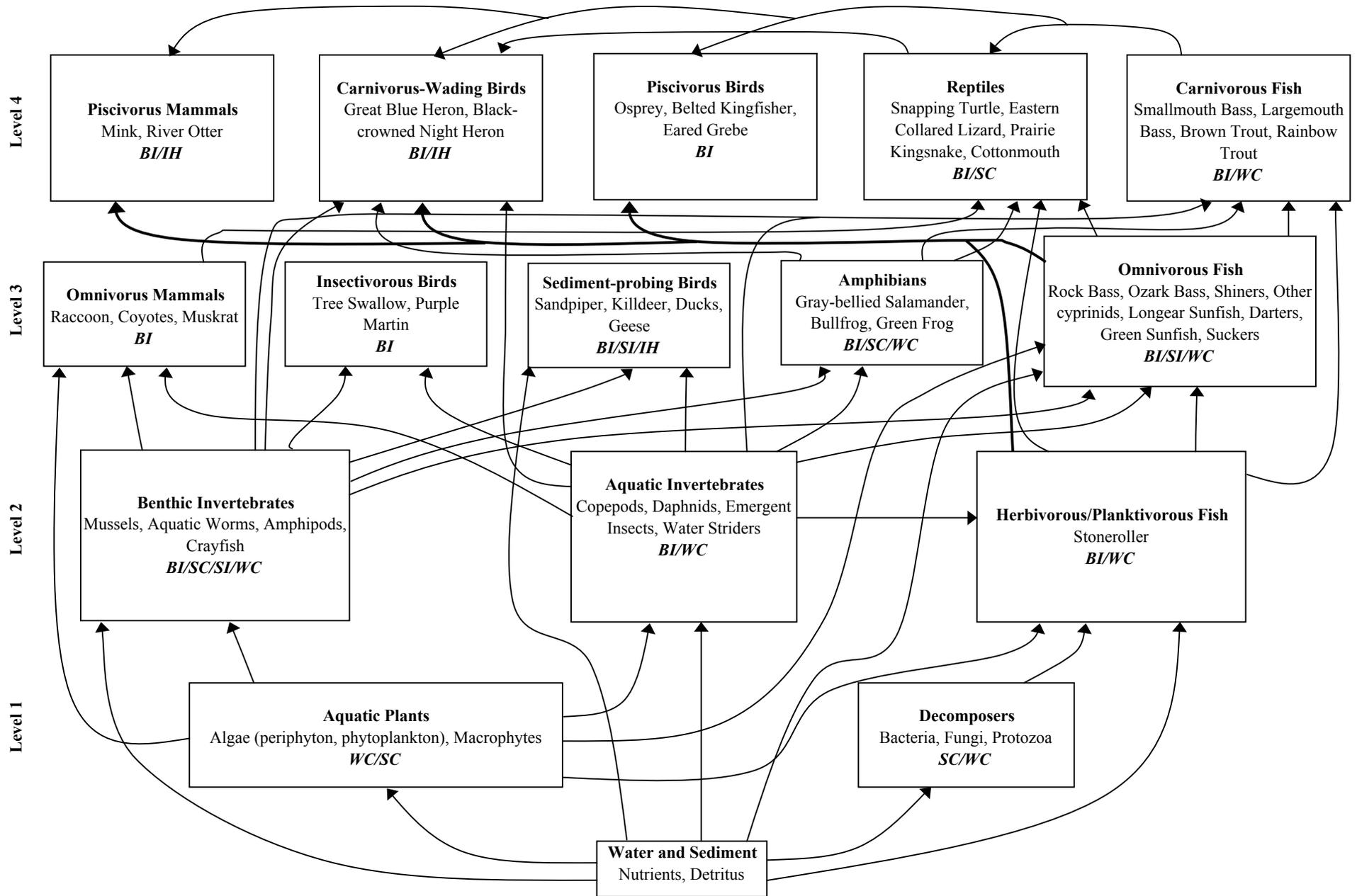


Figure 9. A generalized aquatic food web for the study area, showing the principal routes of exposure to contaminated water, sediment and biota.



Principal Exposure Routes (note: surface waters tend to have high salinity, reducing the potential for water ingestion by ecological receptors): BI = Biota Ingestion; WC = Water Contact; WI = Water Ingestion; SC = Sediment Contact; SI = Sediment Ingestion; IH = Inhalation

Figure 10. Conceptual model diagram illustrating exposure pathways and potential effects for bioaccumulative substances.

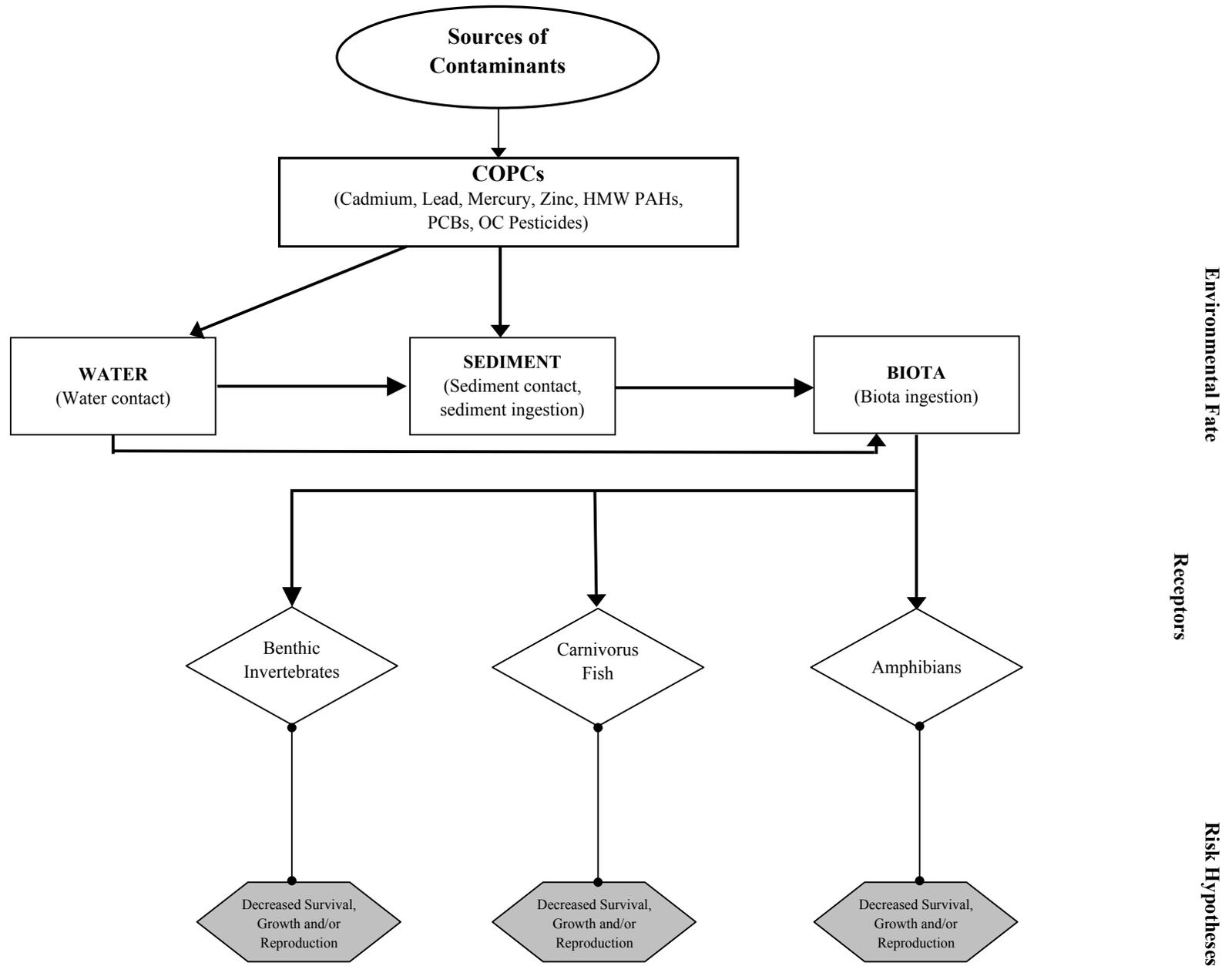


Figure 11. Conceptual model diagram illustrating exposure pathways and potential effects for toxic substances that partition into sediments.

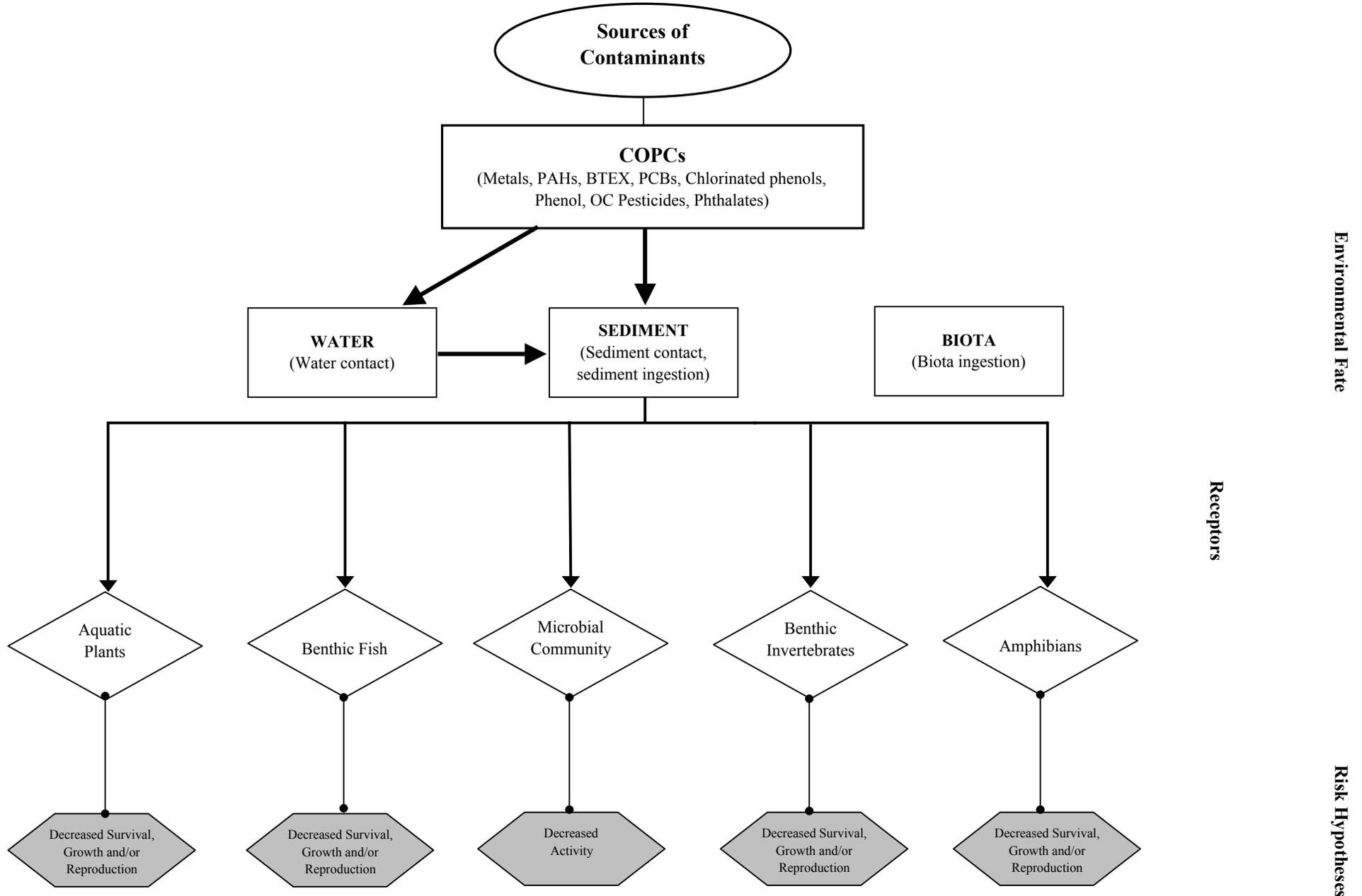


Figure 12. Conceptual model diagram illustrating exposure pathways and potential effects for toxic substances that partition into overlying water.

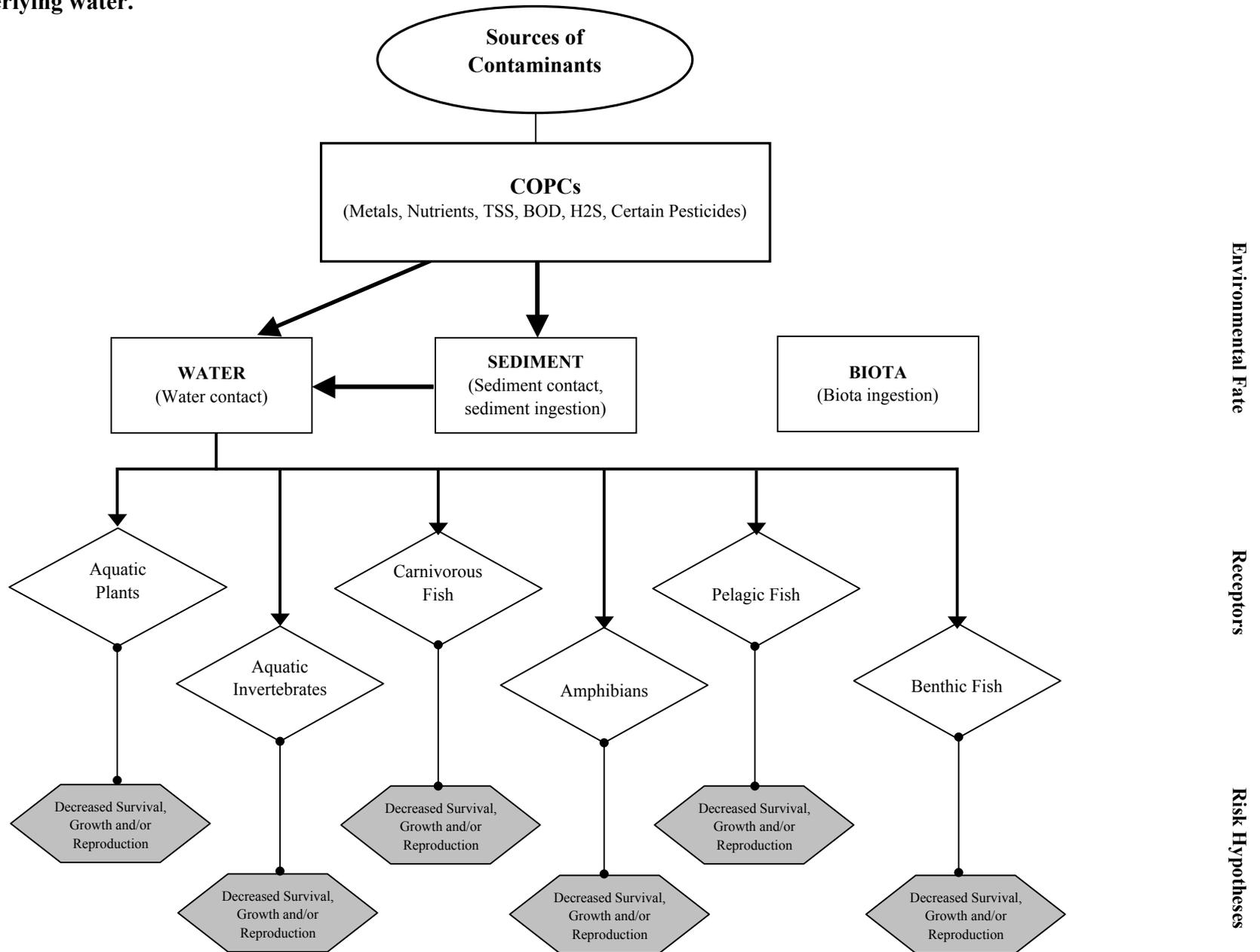


Figure 13. Conceptual model diagram illustrating exposure pathways and potential effects for all categories of COPCs.

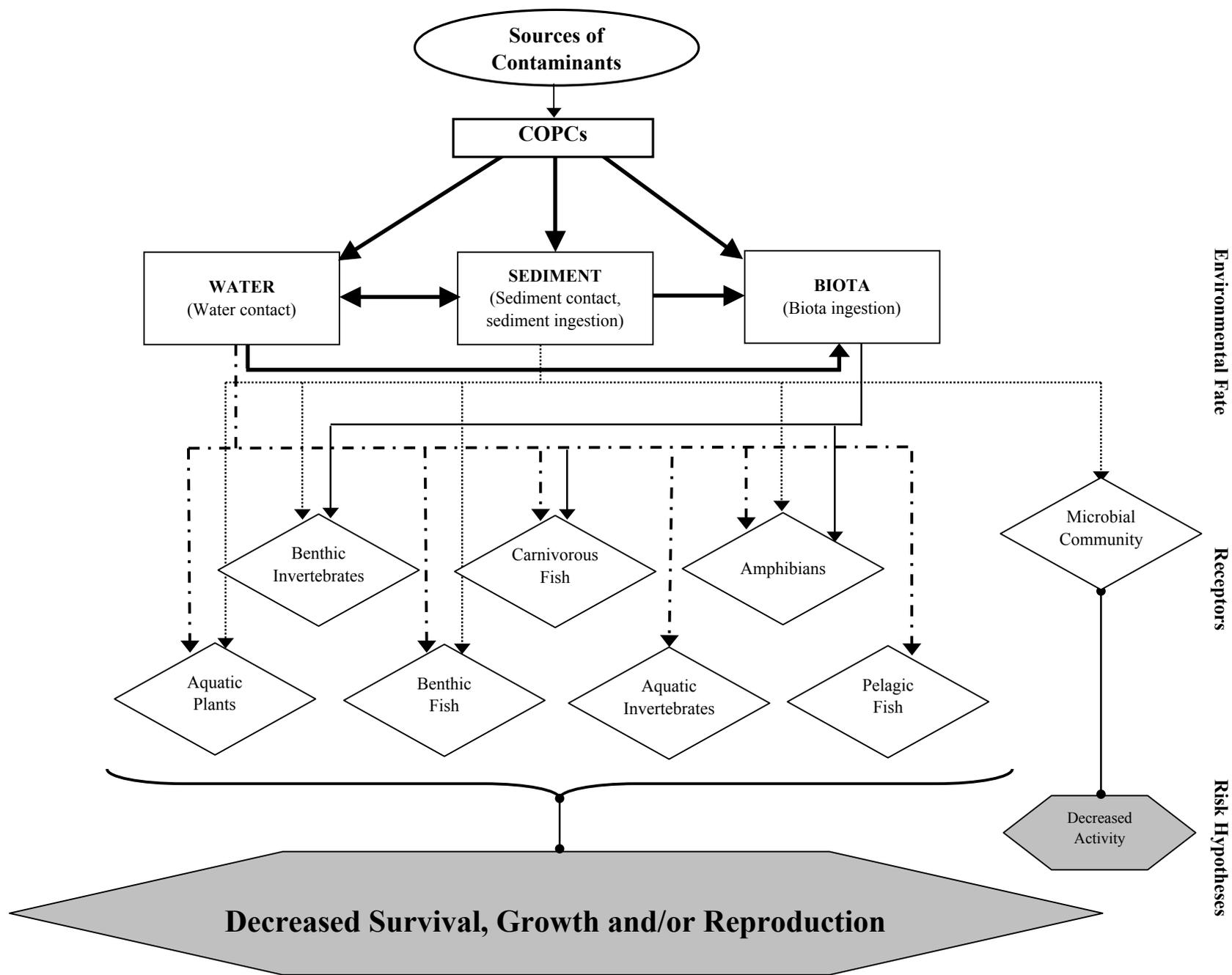
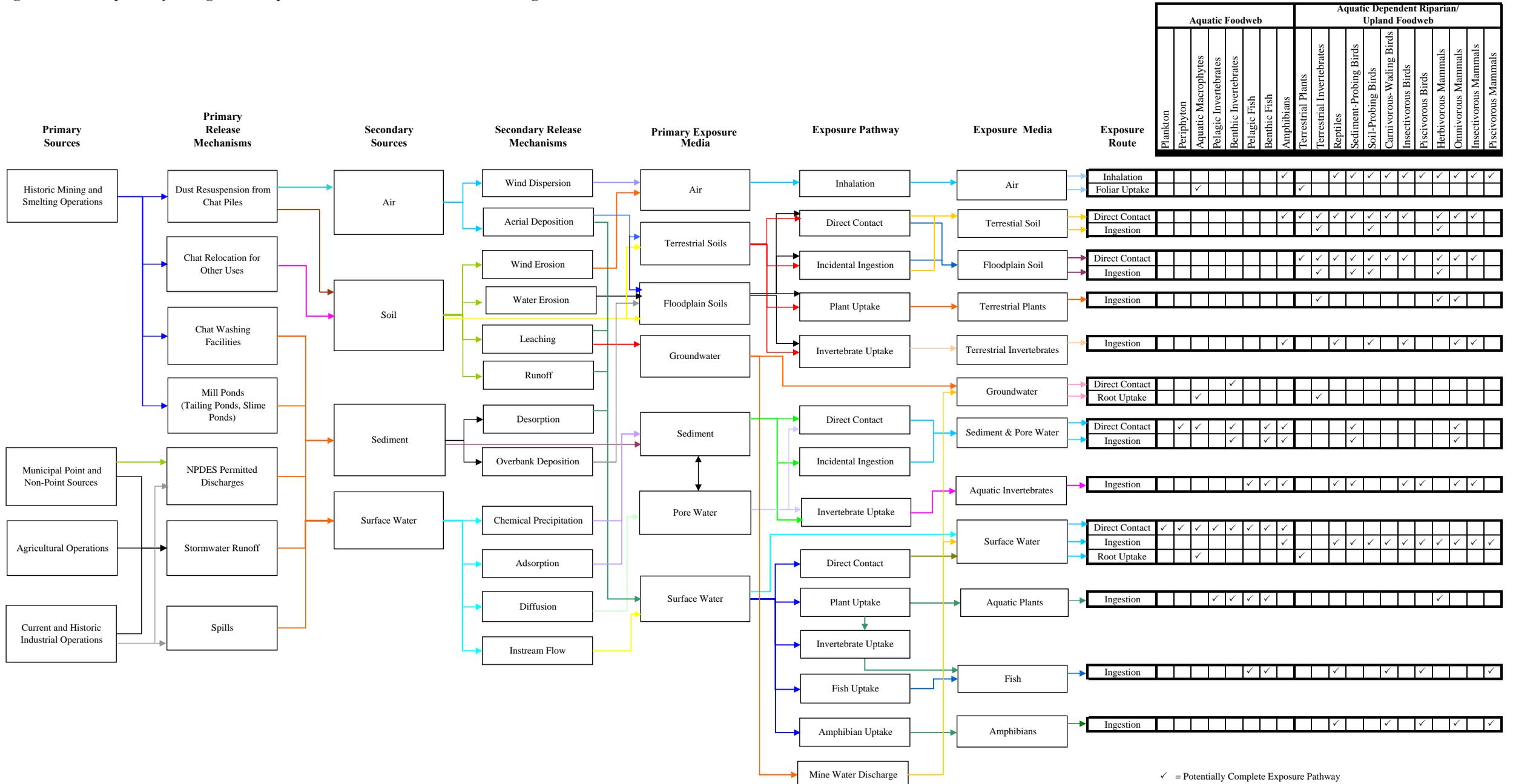


Figure 14. Multi-pathway ecological conceptual site model for the Tri-State Mining District.



**Appendix 2 - Overview
of the Fate and Effects
of COPCs in the Tri-
State Mining District**

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1.0 An Overview of the Environmental Fate and Effects of Arsenic

Arsenic (As) is a naturally-occurring substance; nevertheless, human activities can result in releases of substantial quantities of this substance into the environment. Base metal and gold production facilities are the principal anthropogenic sources of arsenic in Canada, with other sources including use of arsenical pesticides in agriculture and wood preservation, coal-fired power generation, and disposal of domestic and industrial wastes. Arsenic compounds have also been used in paints, pharmaceuticals, and glass manufacturing (Environment Canada and Health Canada 1993). Due to its reactivity and mobility, As can cycle extensively through the biotic and abiotic components of aquatic and terrestrial ecosystems, with ocean sediments representing the ultimate sink for most environmental As (Environment Canada and Health Canada 1993).

While As may be an essential trace element in animals, it is toxic to aquatic organisms at elevated concentrations. Among the species tested, marine algae tend to be the most sensitive, with chronic toxicity thresholds of <10 g/L reported in the literature (Environment Canada and Health Canada 1993). Exposure of marine invertebrates and fish to As concentrations of >100 g/L resulted in adverse effects on the survival, growth, and reproduction of exposed species (Environment Canada and Health Canada 1993). Sediment-associated As has also been shown to be toxic to marine and estuarine invertebrates, with effect concentrations in the 30 to 100 mg/kg DW range reported (Environment Canada and Health Canada 1993). Exposure to elevated levels of sediment-associated As causes acute (i.e., short-term) and chronic (i.e., long-term) toxicity to sediment-dwelling organisms. Certain avian species have been shown to be highly sensitive to the effects of As, particularly during embryonic exposures. The adverse effects that have been documented in avian and/or mammalian wildlife in association with exposure to As include reduced egg hatchability, teratogenicity, muscular debilitation, and behavioural abnormalities. See (Environment Canada and Health Canada 1993) for more information on the environmental fate and effects of As.

1.1 General Information

Arsenic (As) is a gray, shiny, brittle, metallic-looking trace metal with an atomic number of 33 and a molar mass of 74.92 g (Budavari *et al.* 1989). It ranks 20th in abundance in the earth's crust and is found at concentrations ranging from 0.2 to 15 mg/kg (NRCC 1978; WHO 2001). Arsenic occurs naturally as both inorganic and organic arsenic compounds. The most common rock-bound arsenic mineral is arsenopyrite (FeAsS; WHO 2001).

The commercial use and production of arsenic compounds have raised local concentrations in the environment far above the natural background concentrations (Eisler 1988).

1.2 Uses

Although its use has diminished because of its toxicity, arsenic is still used in the production of various metals, in rat poisons, insecticides, weedkillers, lead shot for guns, glassmaking, and in certain types of electrical equipment (MacDonald 1997). Until recently, chromated copper arsenate (CCA) was widely used in wood preservatives. In 2003, the wood treatment industry in Canada stopped treating wood with CCA for use in residential applications. Wood treatment still accounts for nearly 70% of arsenic useage world-wide (WHO 2001). Other uses include certain veterinary medicines, and the formulation of pigments for paints used in the early 1900's (MacDonald 1997).

1.3 Sources

Natural releases of arsenic occur from the weathering of rocks and soils, volcanic activity, and low-temperature volatilization (WHO 2001). Mining, smelting, and refining industries are major anthropogenic sources, with lesser amounts contributed by the burning of fossil fuels (CCME 1999a; WHO 2001). In the Canadian north, gold and base metal mining have the largest potential to release arsenic into the environment. Arsenic is released as arsenic trioxide (As_2O_3) through the roasting, smelting, and refining of arsenious ores (MacLatchy 1992). More than 1500 kg of arsenic was released into the atmosphere daily from gold roasters at the Giant mine near Yellowknife between 1949 and 1958 (MacDonald 1997). Over the next 20 years (i.e., 1959 to 1977), atmospheric emissions of arsenic from the mine averaged roughly 360 kg/day and in 1997 it was estimated that annual releases from this facility were in the order of 8.8 tonnes (MacDonald 1997). Deposition of atmospheric arsenic on the landscape could be a major (historic) source of arsenic to surface waters along with released decant-water from tailing ponds at operating metal and gold mines. Runoff from contaminated unused mine workings could also be a significant source of arsenic to surface waters (MacDonald 1997).

1.4 Physical and Chemical Properties

Elemental arsenic has a density of 5.72 g/cm³ at 20 °C, a melting point of 817 °C, and sublimates at 613°C (Eisler 1988). Arsenic exists in four oxidation states: As^{3-} , As^0 , As^{3+} , and As^{5+} (ATSDR 2001). Elemental As is insoluble, but it forms many inorganic salts and organic compounds with varying solubilities. The solubilities of some As compounds commonly encountered in the environment are arsenic trioxide (37 g/L at 20 °C), calcium arsenate (0.13 g/L at 20 °C), sodium arsenite (very soluble), methylarsonic acid (soluble) and dimethylarsinic acid (660 g/L at 25 °C; ATSDR 2001; WHO 2001).

1.5 Environmental Transport and Fate

Major pathways for arsenic entering the aquatic environment include atmospheric fallout from smelting of non-ferrous metals and burning of fossil fuels, leachate from mining sites, erosion

of arsenic-containing rocks and soils, and run-off from agricultural fields (ATSDR 2000; WHO 2001). Arsenic released to the atmosphere is primarily in the form of soluble oxide particles, that are returned to land and water through wet and dry deposition (ATSDR 2000). The principal components of the biogeochemical cycle of arsenic are the redox transformations between arsenite and arsenate forms, the reduction and methylation of arsenic, and the biosynthesis of organoarsenic compounds (WHO 2001). In aquatic environments, arsenic exists primarily as As(V) and As(III), with As(V) being the dominant form under oxidizing conditions and As(III) under reducing conditions (ATSDR 2000). Arsenate (AsO_4^{-3}) predominates in surface waters, and arsenite (AsO_3^{-3}), arsines (As^{-3}), and arsenic sulfides (e.g. As_2S_3) can be found in low pH, anaerobic, or reducing environments (Garret 1988). Microorganisms are capable of converting inorganic arsenic to organic forms, including volatile arsines (ATSDR 2000). In the water column, arsenic adsorbs and co-precipitates with metal sulfides and oxides of iron and manganese. Arsenic in this form can be released under strongly reducing conditions (ATSDR 2000). Arsenic can also bind to suspended matter and to sediments under conditions of high organic content, low pH, low phosphorus, and low mineral content (Thanabalasingam and Pickering 1986). Inorganic As is the predominant form of As in sediment and water. In sediments, the fate and persistence of As are intricately connected with that of iron oxides, and are influenced by redox conditions, pH, and microbial activity in the sediments. For example, arsenic can be released as a result of changes to ambient environmental conditions such as sediment turbation, decrease in pH, and increase in redox potential (Pierce and Moore 1982; Thanabalasingam and Pickering 1986; Singh *et al.* 1988; DeVitre *et al.* 1991; Korte and Fernando 1991).

1.6 Bioaccumulation

Arsenic can accumulate in plants, invertebrates, and vertebrates, but does not biomagnify through the food chain (Eisler 1994; USEPA 1979; 1982; 1983; Mason *et al.* 2000). Laboratory bioconcentration factors (BCFs) measured in freshwater invertebrates and fish for several arsenic compounds ranged from 0 to 20, with values for fish all below 5 (USEPA 1980; WHO 2001). Reported BCFs from organisms collected in the field are up to two orders of magnitude higher (USEPA 2003). For example, in a Swedish study, the BCFs of bryophytes, invertebrates, and fish (livers) in lakes and brooks impacted by smelter emissions were 8700, 1900–2200, and 200–800, respectively (Lithner *et al.* 1995). The reason for this discrepancy is not completely understood, but it is proposed that the rates of biomethylation of inorganic arsenic species for aquatic organisms in the field may greatly exceed those for like organisms exposed to arsenic in a laboratory setting (USEPA 2003).

1.7 Effects on Aquatic Organisms

The toxicity of arsenic compounds depends on the chemical form of the compound, the route by which it enters the organism, the dose and duration of exposure, and the age and sex of the exposed individual. The most toxic form of arsenic in aquatic systems is As^{3+} , followed by As^{5+} , and the least toxic forms are organic complexes (USEPA 2000). Virtually all of the

mineralized forms of arsenic are relatively non-toxic, including arsenopyrite (FeAsS), realgar (AsS), orpiment (As₂S₃), niccolite (NiAs), and cobalite (CoAsS). In contrast to the mineralized and organic forms of arsenic, arsenic trioxide and arsine gas are highly toxic to aquatic and terrestrial organisms, including humans. This is important because arsenic trioxide (As₂O₃) and arsine gas (AsH₃) are the main forms of arsenic that are released into the atmosphere from gold roasting facilities (MacDonald 1997). More acidic aqueous conditions favour the formation of lower and often more toxic arsenic oxidation states (Ferguson and Gavis 1972). Increasing water temperature is known to promote greater arsenic uptake by fish and also to increase the intrinsic toxicity of a given amount of absorbed arsenic (Department of the Environment 1991). Conversely, increasing phosphorus levels reduce the toxicity of arsenic by competing with it for sorption sites (Reuther 1992).

The freshwater green alga *Scenedesmus obliquus* is quite sensitive to arsenic exposure. A 14-day EC50 demonstrated growth inhibition at a concentration of 50 µg/L (CCME 2001).

For freshwater and marine invertebrates the 48-h LC/EC50 values range from 0.68 to 73.5 mg/L for trivalent arsenic and from 3.6 to 49.6 mg/L for pentavalent arsenic. However, the lowest acute value was for the nauplius stage of the marine copepod *Tigriopus brevicornis*, with a 96-h LC50 of 10.9 µg As(V)/L (WHO 2001). No significant effect on survival of a natural assemblage of copepods was observed when organisms were exposed to arsenate at < 10 mg As(V)/L for 2 weeks; however, arsenite caused significant mortality at both 4 and 10 mg As(III)/L (Borgmann *et al.* 1980).

The World Health Organization (2001) reports acute toxicity 96-h LC50s for freshwater fish range from 10.8 to 91 mg/litre for trivalent arsenic and from 4.8 to > 360 mg/L for pentavalent arsenic. In marine fish 96-h LC50s ranged from 12.7 to 28.5 mg As(III)/L and from 21.4 to 157 mg As(V)/L. Other estimates of toxicity for fish ranged from a 28-day LC50 of 550 g/L for rainbow trout (*Oncorhynchus mykiss*; Birge *et al.* 1979), a 96-h LC50 of 14 900 g/L for the fourspine stickleback (*Apeltes quadracus*; USEPA 1980) and a 96-h LC50 of 230 g/L for Dungeness crabs (*Cancer magister*; Martin *et al.* 1981).

The majority of the data available to assess the effects of sediment-associated As are from studies on field-collected sediments that measured concentrations of As, along with concentrations of other chemicals, and associated biological effects. The results of spiked-sediment toxicity tests were not located in the literature. Adverse biological effects for As include decreased benthic invertebrate abundance, increased mortality, and behavioural changes (CCME 1999b). Chironomid abundance was low at locations in Toronto Harbour, Ontario where the mean concentration of As in sediments was 6.87 mg/kg, compared to sites with lower concentrations of As at 1.2 mg/kg (Jaagumagi 1988; Jaagumagi *et al.* 1989).

Very little information on the effects of arsenic on aquatic dependent wildlife was found. In tests where western grasshoppers (*Melanophus spp.*) poisoned by arsenic trioxide were fed to bird nestlings, the species tested that were most sensitive to various arsenicals included the brown-headed cowbird (*Molothrus ater*) with an LD50 (11-d) value of 99.8 mg of copper acetoarsenite/kg diet; California quail (*Callipepla californica*) with an LD50 single oral dose

value of 47.6 mg of sodium arsenite/kg body weight; and chicken and turkey at 33 and 17.4 mg/kg body weight respectively of 3-nitro-4-hydroxy phenylarsonic acid as a single oral dose (Hudson 1984; NAS 1977; Woolson 1975). Tissue samples collected near Yellowknife for the gray jay, *Perisoreus canadensis*, and the spruce grouse, *Dendragapus canadensis*, were found to have a high percentage (3-10% for jays and 23-36% for grouse) of total arsenic body burden as arsenobetaine, a relatively non-toxic form of arsenic (Koch *et al.* 2005). These results suggest that some species may be able to detoxify arsenic when exposed to high levels in the environment. This transformation may be a special adaptation developed in response to the elevated arsenic levels from gold mining in the area surrounding Yellowknife (Koch *et al.* 2005).

Acute or subacute arsenic exposure can lead to elevated tissue residues, appetite loss, reduced growth, loss of hearing, dermatitis, blindness, degenerative changes in the liver and kidneys, cancer, chromosomal damage, birth defects, and death (Eisler 1988). Death or malformations have been documented at single oral doses of 2.5 to 33 mg As/kg body weight, at chronic doses of 1 to 10 mg As/kg body weight, and at dietary levels >5 and <50 mg As/kg diet (Eisler 1988).

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2.0 An Overview of the Environmental Fate and Effects of Cadmium

Cadmium (Cd) is released to the environment from both natural and anthropogenic sources. Small amounts of Cd enter the environment from the natural weathering of minerals, forest fires, and volcanic emissions (ATSDR 1999). Mining and smelting operations, fuel combustion, disposal of metal-containing products, and application of phosphate fertilizer or sewage sludges are major anthropogenic sources (ATSDR 1999). In the marine environment, Cd tends to become associated with biological tissues or bottom sediments.

The toxicity of Cd to aquatic species is dependent on pH, salinity, and hardness (Voyer and McGovern 1991). Cd toxicity has been extensively investigated and found to cause toxicity in aquatic plants, invertebrates, and fish, causing effects on survival, growth, and reproduction. Cd has been shown to exhibit toxicity in avian receptors, causing renal pathological changes. Mammals may be more susceptible to Cd than birds, based on critical tissue concentrations. More information on the environmental fate and effects of Cd is provided in Outridge et al.(1992).

2.1 General Information

Cadmium (Cd) is a soft, silver-white, blue-tinged, lustrous metal, with an atomic number of 48 and a molar mass of 12.4 g (Budavari *et al.* 1989). Cadmium is found in the earth's crust at concentrations ranging from 0.1 to 1.0 mg/kg (ATSDR 1999). Cadmium is typically found in rocks as a minor constituent in mineral sulphides, particularly zinc sulphides such as sphalerite and wurtzite (Government of Canada 1994). Weathering of these primary minerals, particularly sphalerite, can result in surficial deposits of miteponite (CdO), otavite (CdCO₃), and greenockite and hawleyite (both sulfides, CdS).

There is no evidence that cadmium, a relatively rare heavy metal, is biologically essential or beneficial; on the contrary, cadmium is a known teratogen and carcinogen, a probable mutagen, and has been implicated as the cause of severe deleterious effects on fish and wildlife (Eisler 1985). The freshwater biota is the most sensitive group; concentrations of 0.8 to 9.9 µg Cd/L (ppb) in water were lethal to several species of aquatic insects, crustaceans, and teleosts, and concentrations of 0.7 to 570 ppb were associated with sublethal effects such as decreased growth, inhibited reproduction, and population alterations. These effects were most pronounced in waters of comparatively low alkalinity (Eisler 1985).

2.2 Uses

Cadmium has five main industrial applications: nickel cadmium batteries (50–55% of the world's cadmium consumption), pigments (18–20%), coatings (8–20%), stabilizers in plastics

and synthetic products (6–10%), and alloys (3–6%). Small amounts of cadmium compounds are also present in television picture tubes, telephone and trolley wires, the metal in automobile radiators, control rods and shields for nuclear reactors, motor oils, and in curing agents for rubber (CCME 1999a). In 1990, the domestic industrial consumption in Canada was 35.2 tonnes. Electroplating accounted for 61–77%, with soldering, alloys, chemicals, and pigments making up the remainder. Nickel cadmium batteries are not manufactured in Canada (Government of Canada 1994). Cadmium is mainly recovered as a byproduct from the smelting of zinc and other metal ores, and from precipitates obtained during the purification of zinc sulphate. The production of cadmium in Canada, therefore, is determined largely by the level of zinc production (CCME 1999a). Cadmium is produced in New Brunswick, Quebec, and Ontario, with total Canadian annual production (2004 estimate) of 698 tonnes (Natural Resources Canada 2005).

2.3 Sources

Cadmium is released to the environment from both natural and anthropogenic sources. Small amounts of cadmium enter the environment from the natural weathering of minerals, forest fires, and volcanic emissions (ATSDR 1999). Anthropogenic releases of cadmium are estimated to exceed natural inputs by a factor of ten (ATSDR 1999). In addition, until recently an unknown amount of cadmium had been applied through three cadmium-containing fungicides for turf grass production (ATSDR 1999; CCME 1999a). Mining and smelting operations, fuel combustion, disposal of metal-containing products, and application of phosphate fertilizer or sewage sludges are major sources (ATSDR 1999). In 1994, it was estimated that cadmium releases as a result of domestic anthropogenic activities contributed at least 147 t/yr to the atmosphere (predominantly as particulate cadmium oxide); 12 t/yr to aquatic environments (as hydrated cadmium ion or in ionic complexes) and 340 t/yr of cadmium slag, sludges, and solid wastes disposed of on land (Government of Canada 1994). Of the total released to the atmosphere, base metal smelting and refining operations contribute 82% (130 t) of total environmental releases (Government of Canada 1994). Of the common cadmium compounds found in air (cadmium oxide, cadmium chloride, and cadmium sulphate), cadmium oxide is insoluble and is removed by dry deposition, while cadmium chloride and cadmium sulphate, both readily soluble in water vapor, are removed by wet deposition (Government of Canada 1994). Most of the cadmium released into the atmosphere is deposited within four weeks and generally within 1000 km of the source. Major pathways for cadmium entering the aquatic environment are atmospheric fallout, effluents from smelting and refining industries, tailing pond overflow, and rainwater runoff from mine areas and natural weathering of minerals.

2.4 Physical and Chemical Properties

Elemental cadmium has a density of 8.65 g/cm³ at 20°C, a melting point of 321°C and a boiling point of 765°C (Budavari *et al.* 1989). Cadmium can occur in two oxidation states: metallic cadmium (Cd) and divalent cadmium (Cd²⁺). The metallic state is rarely encountered

in the environment (Government of Canada 1994). Metallic Cd is insoluble in water; cadmium chloride (CdCl₂), cadmium bromide (CdBr₂), cadmium iodide (CdI₂), cadmium nitrate [Cd(NO₃)₂], and cadmium sulphate (CdSO₄) are freely soluble in water; some water-insoluble compounds such as cadmium oxide (CdO), cadmium sulphide (CdS), cadmium carbonate (CdCO₃), cadmium ortho-phosphate [Cd₃(PO₄)₂], and cadmium fluoride (CdF₂) may be solubilized under strong oxidizing or acidic conditions (Government of Canada 1994). The most important factors determining the fate of cadmium in aquatic systems include pH, hardness, redox potential, and the type and relative abundance of organic ligands, hydroxides, and anions present, as cadmium has a high affinity for negatively charged particle surfaces (CCME 1999a).

2.5 Environmental Transport and Fate

Major pathways for cadmium entering the aquatic environment are atmospheric fallout and effluents from smelting and refining industries. In the marine environment, river runoff is another major pathway. Most cadmium entering water bodies eventually becomes associated with bottom sediments (CCME 1999a). Notwithstanding, Cd is more mobile in freshwater than other metals and is commonly found as a dissolved cation (Government of Canada 1994). The most important factors determining the fate of cadmium in aquatic systems include pH, hardness, redox potential, and the type and relative abundance of organic ligands, hydroxides, and anions present. In natural waters, most of the cadmium will exist as hydrated ions [Cd(H₂O)₆²⁺], with smaller amounts present as chloride salts, complexed with inorganic ligands, or chelated to form complexes with organic ligands (ATSDR 1999). Cadmium is not known to form volatile compounds in the aquatic environment, so partitioning from water to the atmosphere does not occur (ATSDR 1999). Cadmium has a high affinity for negatively charged particle surfaces and, consequently, cadmium tends to be removed rapidly from solution and accumulate in bottom sediments in both marine and freshwater systems. However, changes in environmental conditions, such as reduced pH, changes in redox status (e.g., due to spring and fall turnover), and biological and chemical oxidation of organic matter, may enable cadmium to be remobilized and transported to other compartments of the ecosystem (CCME 1999a). In anaerobic sediments, cadmium can be immobilized as cadmium sulphide (Government of Canada 1994).

2.6 Bioaccumulation

Cadmium bioconcentration factors (BCFs) in freshwater and marine biota range from 1 to 40 000, and from 1 to 19 500, respectively, with the highest values being in algae (CCME 1999a). Among rainbow trout (*Oncorhynchus mykiss*), for example, exposed for 2 weeks to 9 ppb Cd, BCFs were 260 for gill, 17 for liver, 26 for kidney, and zero for spleen and heart tissues (Roberts *et al.* 1979). At slightly higher ambient Cd levels of 10 ppm and exposure for 3 months, BCF values were substantially higher: 1,740 for gill, 4,900 for liver, 740 for kidney, 160 for spleen, and 100 for heart tissues (Roberts *et al.* 1979).

There is conflicting evidence as to whether cadmium can biomagnify in aquatic foodwebs. Biomagnification seems to be negligible or low in zooplankton or fish, but can be substantial in some marine invertebrates, waterfowl, and seabirds (CCME 1999a). The evidence for cadmium transfer through various trophic levels suggests that only the lower trophic levels exhibit biomagnification (Ferard *et al.* 1983). In the freshwater food chain extending from the alga *Chlorella vulgaris*, to the cladoceran *Daphnia magna*, to the teleost *Leucospius delineatus*, it was demonstrated that alga, after being exposed to water containing 10 pph Cd for 10 days, contained 30 ppm Cd dry weight, up from 4.5 ppm at the start (Ferard *et al.* 1983). Cladocerans feeding on cadmium-loaded algae for 20 days contained 32 ppm Cd dry weight, up from 1.4 ppm at the start. However, fish fed Cd-contaminated cladocerans for 4 days showed no change in body burdens (Ferard *et al.* 1983).

2.7 Effects on Aquatic Organisms

The water soluble salts, cadmium chloride and cadmium nitrate, are the most important compounds to consider when assessing the impact of cadmium on water-dwelling organisms. Both compounds readily disassociate in water to release Cd^{2+} , the most bioavailable and toxic of Cd species (Rainbow 1990). Cd is more toxic to aquatic species with water conditions of low pH (5 to 7), low salinity (<15 g/L) and in soft water (<100 mg/L calcium carbonate; Voyer and McGovern 1991).

Cadmium toxicity has been extensively investigated in aquatic plant, invertebrate, and vertebrate taxa. Among freshwater organisms, planktonic invertebrates appear to be sensitive to cadmium exposure. Acute toxicity for the water flea (*Simocephalus serrulatus*) was reported at 48-h LC50 of 7 $\mu\text{g/L}$. Other acutely sensitive invertebrates included the scud (*Gammarus fossarum*) and freshwater mussel (*Anodonta imbecilis*), which had 96-h LC50s of 7.6 and 9 $\mu\text{g/L}$ respectively (Musko *et al.* 1990; Keller and Zam 1991). *Lemna minor* (duckweed) in 14-day tests had a LC50 value of 14.8 mg/L (Outridge and Noller 1991). Cusimano *et al.* (1986) reported 96- and 168-h LC50s of <0.5 $\mu\text{g/L}$ for rainbow trout (*Oncorhynchus mykiss*) fry exposed to cadmium. In chronic toxicity studies, laboratory-derived lowest-observed-effect-level (LOELs; 16 % reproductive impairment; 21-d) of 0.17 $\mu\text{g Cd/L}$ (48.5 mg CaCO_3/L) for the zooplankton, *Daphnia magna* were reported (Biesinger and Christensen 1972). Salmonids were the most sensitive of eight fish families. In a 47-day test, 12% reduction in growth of *Salmo salar* alevins resulted from exposure to 0.47 $\mu\text{g Cd/L}$ in soft water ((CdCl_2) ; pH=7.3; Rombough and Garside 1982).

Cadmium is present in bed sediments associated with particulate matter, such as organic matter and iron and manganese hydroxides, and in precipitates of cadmium carbonate and cadmium sulphide (CCME 1999b). Acute effects including increased mortality, decreased reburial, and increased emergence were observed in the amphipod *Lepidactylus dytiscus* after exposure for a 10- and 20-d period to estuarine sediments that contained a mean concentration of Cd of 1.6 mg/kg (Hall *et al.* 1992). In this study, sediments containing <0.2 mg/kg Cd did not induce adverse biological effects in this species. No other studies on the effects of Cd on benthic organisms were located.

Cadmium has been shown to exhibit toxicity in a number of avian and mammalian receptors. Wood ducks (*Aix sponsa*) fed increasing doses of Cd in their diet for three months showed widespread renal pathological changes at an average renal concentration of 132 mg/kg fresh weight (FW), but none at 62 mg/kg. Similarly, captive mallard ducks (*Anas platyrhynchos*) exposed to Cd in their diet exhibited moderate to severe tubular degeneration over a renal Cd concentration range of 88 to 134 mg/kg (Outridge and Noller 1991). Mammals may be more susceptible to Cd than birds, based on critical tissue concentrations. The lowest renal concentration associated with tissue damage in a mammal (13 to 20 mg/kg FW) was reported in laboratory mice exhibiting mild to moderate degeneration of tubular epithelial cells. A four year experimental study showed that dogs with kidney Cd concentrations of 33 to 52 mg/kg FW, exhibited atrophied and inflamed tubules and other morphological alterations (Outridge and Noller 1991).

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3.0 An Overview of the Environmental Fate and Effects of Copper

3.1 Identity

Copper is a heavy metal that is widely distributed in the environment. Copper has an atomic number of 29 and an atomic weight of 63.546 g/mole. The divalent form of copper (i.e., Cu⁺⁺) can combine with chlorides, sulfates, or nitrates to form salts that are highly soluble in water (McNeely et al. 1979). Other copper salts, such as carbonates, hydroxides, and oxides, are not readily soluble in water (McNeely et al. 1979).

3.2 Uses

Metallic copper and copper compounds have been used by humans for thousands of years. Modern uses of copper include electrical wiring and electroplating, the production of alloys (e.g., bronze and brass), photography, utensils, antifouling paint, art designs, pesticide formulations, and textiles (CCREM 1987). Copper is also used in construction, in the production of roofing materials, and in the manufacturing of brass and copper plumbing (Demayo and Taylor 1981). United States is the third largest producer of copper worldwide, accounting for roughly 19% of the world production (CCREM 1987).

3.3 Sources

Copper is released into the environment from both natural and anthropogenic sources. Natural sources of copper include weathering of sulphide and carbonate ores under oxidizing conditions and from deposits of native copper. However, little of the copper found in water is of natural origin because copper minerals tend to be relatively insoluble. It is estimated that releases of copper into receiving water systems from anthropogenic sources represents 33 to 60% of the total global annual input (Demayo and Taylor 1981). These sources include corrosion of brass and copper pipe by acid waters, sewage treatment plant effluents, the use of copper compounds as aquatic algicides, runoff and groundwater contamination from agricultural uses of copper as fungicides and pesticides in the treatment of soils, and effluents and atmospheric fallout from industrial sources (CCREM 1987). Major industrial sources include mining, smelting and refining industries, copper wire mills, coal-burning industries, and iron- and steel-producing industries (USEPA 1980).

3.4 Physical and Chemical Properties

In nature, copper (Cu) can occur in four oxidation states (Cu, Cu⁺, Cu⁺⁺, and Cu⁺⁺⁺), with the cuprous (Cu⁺) and cupric (Cu⁺⁺) forms being the most common. As cuprous copper is

unstable in aqueous solutions, it is normally oxidized to the cupric form in water (CCREM 1987). The solubility of copper is influenced by both pH and alkalinity, with lower pHs and alkalinities favoring increased solubilities (Spear and Pierce 1979). Organically-complexed copper tends to be more soluble than inorganic copper complexes (Spear and Pierce 1979).

3.5 Environmental Transport and Fate

As copper is an element, it is neither created nor destroyed in the environment. Rather, the fate of this substance in the environment is determined by the processes that influence the cycling of copper. In aqueous media, copper ions coordinate with water molecules to form aquo ions [Cu(H₂O)₆⁺⁺; CCREM 1987]. The presence of other ligands [e.g., hydroxide (OH⁻) or sulfate (SO₄⁻⁻)], can result in formation of copper complexes by successively displacing water molecules [e.g., Cu(OH)⁺(H₂O)₅ and CuSO₄(H₂O)₅; Spear and Pierce 1979]. Such complexes tend to be relatively unstable and, hence, potent toxicants in the environment (i.e., the copper is readily available to aquatic organisms; CCREM 1987). Copper ions can also form associations with organic ligands (i.e., chelating agents), such as fulvic acid, tannic acid, and Ethylenediaminetetraacetic acid (EDTA; Spear and Pierce 1979). Such complexes tend to have much higher stability (Stumm and Morgan 1970) and lower toxicity. Sorption and precipitation also play major roles in determining the aquatic fate of copper; nevertheless, copper that becomes associated with suspended or bottom sediments can be remobilized under reducing acidic conditions (CCME 1999). Photolysis, volatilization, and biodegradation are minor fate processes for copper in aquatic ecosystems (CCREM 1987).

3.6 Bioaccumulation

As an essential trace nutrient, copper is readily accumulated by plants and animals, with bioconcentration factors of 100 to 26,000 reported for various aquatic species (Spear and Pierce 1979). However, whole body concentrations tend to decrease with increasing trophic level due to organ specific accumulation and metabolic regulation in higher organisms (CCREM 1987). There is little evidence that copper biomagnifies to any significant extent in aquatic or terrestrial food webs.

3.7 Effects on Aquatic and Terrestrial Organisms

The toxicity of water-borne copper to aquatic organisms varies depending on the form of copper under consideration and the physical and chemical characteristics of the water (e.g., dissolved oxygen, temperature, water hardness, turbidity, presence of chelating agents; Demayo and Taylor 1981). The results of laboratory studies indicate that copper salts are acutely toxic to aquatic plants, invertebrates, and fish, with LC50s (median lethal concentrations) as low as 6.5 µg/L reported in the literature (CCREM 1987). In long-term exposures, copper has been shown to adversely affect the behavior, growth, reproduction, and survival of aquatic organisms, with copper concentrations as low as 3.9 µg/L were found to

be toxic to fish (Spear and Pierce 1979; CCREM 1987; Sauter et al. 1976). Even lower concentrations of copper (i.e., 1 µg/L) inhibited the growth of plant species (USEPA 1980; 1985).

Sediment-associated copper can be acutely or chronically toxic to sediment-dwelling organisms. In freshwater sediments, 10 to 14-day LC50s of 380 to 1078 mg/kg dry weight (DW) have been reported for the amphipod, *Hyalella azteca* (Cairns et al. 1984; Milani et al. 1996). The midge, *Chironomus tentans*, appears to be less sensitive to the effects of this substance, with 10- to 14-day LC50s of 857 to 2296 mg/kg DW reported (Cairns et al. 1984; Milani et al. 1996). Adverse effects on the growth of these species have been noted at copper concentrations of 89.8 and 496 mg/kg DW, respectively (Milani et al. 1996). In marine sediments, long-term exposure (i.e., to 48-day) to copper-spiked sediments (13.6 to 38.2 mg/kg DW) resulted in delayed predator avoidance response (i.e., increased reburial time) and reduced survival rates in clams, *Protothaca staminea* and *Mya arenaria* (Phelps et al. 1983; 1985).

In birds and mammals, consumption of contaminated prey items represents the primary route of exposure to environmental copper. While no information is available on the toxicity of copper to avian wildlife species, laboratory studies have shown that the survival and growth were reduced when domestic turkeys were fed 50 mg Cu/kg food for three weeks (Eisler 1997). Adverse effects on the growth of chickens were observed at even lower levels of dietary exposure to copper. In mammals, long-term exposure to elevated levels of dietary copper can cause degeneration of liver, kidney, brain, and muscle tissues, anemia, impaired growth, and reduced survival rates.

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4.0 An Overview of the Environmental Fate and Effects of Chromium

4.1 Identity

Chromium, in the crystalline form, is a steel-gray, lustrous metal that is extremely resistant to most corrosive agents (Eisler 1986). Chromium has an atomic number of 24 and an atomic weight of 52.0 g/mole. Although chromium is the seventh most abundant element in the earth as a whole and more than 40 chromium-containing minerals have been identified, it is usually present in only trace amounts (i.e., < 1000 mg/kg in surface rocks and soils (Government of Canada 1994).

4.2 Uses

In the United States, chromium is used principally in the metallurgy and chemical industries. Ferrochromium, a chromium alloy, is used in the production of stainless steel and heat-resistant steels that are employed in petrochemical processing, in high-temperature environments (e.g., turbines and furnaces), and in consumer goods (e.g., cutlery and decorative trim (Phillips 1988). Copper-chromium alloys are used in electrical applications that require high strength and good conductivity, while copper-nickel-chromium alloys are used in marine equipment that require corrosion resistance (Government of Canada 1994). In the automotive industry, chromium alloys are used in stainless steel components, catalytic converters, chrome trim, and other applications. Chromium salts are used in paints, dyes, explosives, leather tanning, wood preservatives, copy machine toners, drilling muds, textiles, water treatment, magnetic tapes, ceramics, paper, and photography. Chromite ores and concentrates are used to make refractory products, such as bricks, mortars, and ramming mixtures for the production of iron and steel, portland cement, glass, and non-ferrous metals.

4.3 Sources

Chromium is released into the environment from both natural and anthropogenic sources. The weathering of chromium-bearing rocks, primarily chromium oxides, represents the principal natural source of chromium (Taylor et al. 1979). Weathering processes have been estimated to contribute 200,000 tonnes of chromium annually to the environment. By comparison, an estimated 77,700 tonnes of chromium are released worldwide as a result of human activities (CCREM 1987). The major sources of atmospheric chromium emissions are the chromium alloy and metal producing industries; coal combustion, municipal incinerators, cement production, and cooling towers represent less important sources (Eisler 1986). The major sources of chromium to aquatic ecosystems include atmospheric deposition, electroplating and metal finishing industries, and publicly-owned treatment plants. Locally, but less globally, important chromium sources to water include iron and steel

foundries, inorganic chemical plants, tanneries, textile manufacturing, and runoff from urban and residential areas (McNeely et al. 1979; CCREM 1987).

4.4 Physical and Chemical Properties

Data on the physical and chemical properties of chromium provides important information for evaluating the environmental fate of this substance. While elemental chromium tends to be a very stable substance, it is only rarely found in nature. It has a density of 7.14, melting point of 1900°C and a boiling point of 2642°C (Budavari et al. 1989). Of the nine possible oxidation states of chromium (i.e., ranging from -II to VI), only trivalent chromium [Cr (III)] and hexavalent [Cr (VI)] are commonly encountered in the environment (Government of Canada 1994). Chromium (II), (IV), and (V) are unstable and are rapidly converted to chromium (III). Both of the primary environmental forms of chromium form salts when released into water; however, the chromium (III) salts tend to be insoluble, whereas the chromium (VI) salts are readily soluble in water.

4.5 Environmental Transport and Fate

The fate of chromium that is discharged into the environment depends on the nature of the release and the chemical form of the chromium. Chromium released into the atmosphere tends to be chemically stable, with dry fallout and wet precipitation representing the most important fate processes. In water, dissolved trivalent chromium tends to form insoluble salts (e.g., oxides, hydroxides, phosphates), which adsorb to particulate matter and are rapidly removed from the water column by settling (Government of Canada 1994). However, chromium (III) can also form stable complexes with dissolved or colloidal ligands. This complexed chromium is relatively unaffected by adsorption and precipitation reactions and, thus, can remain for extended periods in the water column. Nevertheless, most of the chromium (III) that is discharged to surface water is ultimately transferred to sediments. By comparison, most hexavalent chromium salts are quite soluble in water and are not sorbed to any significant extent by sediment or other particulate matter; hence, this form of chromium tends to remain in the water column. Under anaerobic conditions, chromium (VI) can be reduced to chromium (III); however, the reverse reaction is more common in natural waters (CCREM 1987). Photolysis, volatilization, and biodegradation are minor fate processes for chromium in aquatic ecosystems (CCREM 1987).

4.6 Bioaccumulation

Chromium is readily accumulated by aquatic organisms, with bioconcentration factors of 100 to 1000 commonly reported in the literature (CCREM 1987). However, there is little evidence that chromium biomagnifies to any significant extent in aquatic or terrestrial food webs (Outridge and Scheuhammer 1993). Due to differences in their properties, chromium (VI) is absorbed more readily than chromium (III); however, the Cr(VI) species is reduced to the Cr(III) form in most organisms (Government of Canada 1994). Algae tends to

bioconcentrate chromium to a greater extent than other aquatic organisms, with BCFs (bioconcentration factors) of up to 8500 reported for these aquatic plants (CCREM 1987).

4.7 Effects on Aquatic and Terrestrial Organisms

Exposure to elevated levels of water-borne chromium is known to adversely affect aquatic organisms, with toxicity influenced by chromium species present, water hardness, and pH (CCREM 1987). Of the species tested, crustaceans (water fleas, *Daphnia magna* and *Ceriodaphnia dubia*) appear to be among the most sensitive to the effects of chromium, with acute toxicity thresholds (i.e., 96-hour LC50s (median lethal concentrations) as low as 15.3 µg/L reported for Cr(VI) and 2000 reported for Cr(III) (Eisler 1986). In long-term toxicity tests, exposure to concentrations as low as 2.5 µg/L of Cr(VI) resulted in impaired reproduction, growth, and/or survival of water fleas (Call et al. 1981). Chronic toxicity thresholds for Cr(III) were somewhat higher in these species, however (i.e., 66 to 445 µg/L; USEPA 1985). Algae appear to be nearly as sensitive to the effects of chromium as are water fleas (CCREM 1987).

Although the available data from spiked-sediment toxicity tests are limited, it is apparent that sediment-associated chromium is acutely toxic to sediment-dwelling organisms (CCME 1999). In freshwater sediments, 48-hour LC50s for water fleas of 195 and 167 mg/kg dry weight (DW) have been reported for trivalent and hexavalent chromium, respectively (Dave 1992). In marine sediments, 24 week exposure of blue mussels, *Mytilus edulis*, to 150 mg/kg DW of chromium caused reduced filtration rates. In the long-term, reduced filtration rates are likely to translate into reduced growth rates in bivalves.

Dietary exposure to chromium has the potential to adversely affect avian and mammalian wildlife species. In laboratory studies, short- and long-term consumption of chromium contaminated foods resulted in alterations in kidney and liver function, reduced spleen and liver weights, genotoxicity, and histological changes in the ovaries in mammals (Government of Canada 1994). Reduced egg production, growth and survival have been observed in birds in birds with elevated dietary exposure to chromium. (Eisler 1986). Insufficient data are available to evaluate the potential carcinogenicity of either species of chromium [i.e., Cr(III) or Cr(VI); Government of Canada 1994].

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5.0 An Overview of the Environmental Fate and Effects of Lead

5.1 Identity

Lead (Pb) is a heavy metal that is a constituent of over 200 minerals, most of which are very rare. Only three of these minerals, galena, anglesite, and cerussite, are sufficiently abundant to form mineral deposits (Eisler 1988). Galena (PbS), the most abundant lead-based mineral, is often found in association with sphalerite (ZnS), pyrite (FeS₂), chalcopyrite (CuFeS₂), and other sulfur salts. The main sources of lead-based minerals are igneous, metamorphic, and sedimentary rocks (CCREM 1987).

5.2 Uses

Lead is used in a variety of applications in the United States. The primary use of lead in the production of acid-storage batteries, while the second largest use is in the production of chemicals, such as tetramethyllead and tetraethyllead (Eisler 1988). Lead and its compounds are also used in electroplating, metallurgy, construction materials, coatings and dyes, electronic equipment, plastics, veterinary medicines, fuels, and radiation shielding (CCREM 1987). Other uses of lead include ammunition, corrosive-liquid containers, paints, glassware, storage tank lining, transporting radioactive materials, solder, piping, cable sheathing, roofing, and sound attenuators (CCREM 1987).

5.3 Sources

Lead is released into the environment from both natural and anthropogenic sources. The weathering of sulfide ores represents the principal natural pathway by which lead is released into the environment. There are a wide variety of anthropogenic sources of lead, with the relative importance of each changing over the past 20 years. In the early 1980's, for example, emissions of lead from gasoline-powered motor vehicles accounted for most of the total annual lead emissions. However, reductions in the use of leaded gasolines and improved emission controls in the automotive industry have dramatically reduced releases from this source. The major industrial sources of lead to the environment include emissions from copper, nickel, and lead smelters, from operations involved in the mining, milling, and concentrating of lead-bearing ores, and from iron and steel production facilities (McNeely et al. 1979). Discharges of liquid effluents from chemical manufacturing facilities, pulp and paper mills, and municipal wastewater treatment plants also result in the release of lead to aquatic ecosystems (Garrett 1985). Until recently, the use of lead shot in shotgun ammunition represented an important source of lead to aquatic systems that support hunting of waterfowl.

5.4 Physical and Chemical Properties

Elemental lead is a bluish-gray metal, with an atomic number of 82 and an atomic weight of 207.19 (Budavari et al. 1989). Lead can occur in four oxidation states, including elemental lead (Pb), monovalent lead (Pb⁺), divalent lead (Pb²⁺), and tetravalent lead (Pb⁴⁺), with the divalent form being the most stable and prevalent in the environment. While elemental lead is sparingly soluble in water (i.e., to 30 to 500 µg/L), certain lead salts are highly soluble in water (i.e., 443 g/L for lead acetate, 565 g/L for lead nitrate, and 9.9 g/L for lead chloride; Eisler 1988). Other lead salts, such as lead sulfate (42.5 mg/L) and lead oxide (17 mg/L), are only moderately soluble in water. Organoleads, such as tetraethyllead (0.18 mg/L) and tetramethyllead (18 mg/L), are relatively less soluble in water than many of the inorganic lead salts (Eisler 1988). The solubility of lead can be influenced by water pH and dissolved CO₂ levels (CCREM 1987).

5.5 Environmental Transport and Fate

Because lead is an element, its transport and fate in the environment is determined by the processes that influence the cycling of lead. Lead exists in three main forms in surface waters, including the dissolved labile form (e.g., Pb²⁺ and PbOH⁺), the dissolved bound form (i.e., colloids or strong complexes), and the particulate form (Benes et al. 1985). While photolysis (i.e., decomposition caused by light) is an important fate process for atmospheric lead (i.e., for converting lead halides into more soluble forms of the substance), there is no evidence that photolysis plays a significant role in the removal of lead from the water column. Rather, sorption is the dominant mechanism influencing the distribution of lead in aquatic ecosystems, with most of the lead entering natural waters forming associations with suspended particulates and, ultimately bottom sediments (CCREM 1987). Sediment-associated lead can be re-mobilized and released into the water column when pH decreases suddenly or when the ionic composition of the water changes (Demayo et al. 1982). Some of the lead in sediments can be transformed into organoleads.

5.6 Bioaccumulation

Exposure to elevated levels of lead can lead to bioaccumulation in the tissues of aquatic organisms. The accumulation of lead in aquatic organisms is influenced by water pH, with lower pHs favoring the accumulation of this substance (i.e., presumably due to increases in the abundance of divalent lead, Pb²⁺). For example, water-to-biota bioconcentration factors (BCF) of over 10⁶ have been observed in algae, while BCFs of 20 to 360 have been reported for aquatic invertebrates and fish (CCREM 1987). In one study conducted in Oklahoma, the levels of lead in water, surficial sediments, plankton, benthos, and mosquito fish were 0.013 mg/L, 529 mg/kg dry weight (DW), 281 mg/kg DW, 37 mg/kg DW, and 11 mg/kg DW, respectively (Demayo et al. 1982). Similarly, frog tadpoles, crayfish, and bluegills from a tailings pond in Missouri had 4139, 500, and 128 mg/kg DW of lead in their tissues (Gale 1976). Collectively, these results suggest that the concentrations of lead in biological tissues generally decreases at higher trophic levels in the food web (i.e., emphasizing that

bioconcentration, rather than biomagnification, is an important process in the accumulation of lead).

5.7 Effects on Aquatic and Terrestrial Organisms

Water-borne lead is highly toxic to aquatic organisms, with toxicity varying depending on the species and life stage tested, duration of exposure, the form of lead tested, and the physical and chemical characteristics of the water. Among the species tested, aquatic invertebrates, such as amphipods and water fleas, were the most sensitive to the effects of lead; species mean acute values ranged from 143 to 448 $\mu\text{g/L}$ for these taxa (USEPA 1985). Higher species mean acute values were reported for rainbow trout (2,448 $\mu\text{g/L}$) and brook trout (4,820 $\mu\text{g/L}$; USEPA 1985). Lead tends to be more toxic in longer-term exposures, with chronic toxicity thresholds for reproduction in water fleas ranging as low as 30 $\mu\text{g/L}$ reported (CCREM 1987). In general, organolead compounds are more toxic than inorganic lead compound, with tetraethyllead reported more toxic than tetramethyllead (Eisler 1988). Water hardness plays a key role in determining the toxicity of this substance, with the lowest toxicity thresholds reported in soft water exposure systems (CCREM 1987).

Exposures to sediment-associated lead can be toxic to sediment-dwelling organisms. In freshwater sediments, 48-hour exposure of water fleas to 7,000 mg/kg DW significantly reduced mobility, while exposure to 13,400 mg/kg DW for 24-hours produced the same effect (Dave 1992a; 1992b). Longer-term (i.e., 14-day) exposure of midges, *Chironomus tentans*, to sediments containing 31,900 mg/kg DW of lead resulted in 100% mortality. Field-derived toxicity thresholds (i.e., probable effect levels) were much lower than those that were derived from the results of spiked-sediment toxicity tests (CCME 1999).

In birds, consumption of lead shot probably represents a primary route of exposure to environmental lead. Lethality associated with the consumption of lead shot had been documented in a variety of bird species, including waterfowl, raptors, and others. In some cases, ingestion of a single lead shot pellet (i.e., 1 to 1.6 g of lead) resulted in increased mortality in mallard ducks (i.e., by 9 to 19%; Longcore et al. 1974). Sub-lethal effects associated with the ingestion of lead shot include damage to the nervous system, muscular paralysis, damage to liver and kidneys, impaired reproduction, and increased susceptibility to predation (Mudge 1983). Other forms of lead may be more toxic than lead shot, as single oral LD50s (i.e., the dose that causes 50% mortality in test organisms) as low as 107 mg/kg body weight (BW) have been reported for tetraethyllead (Eisler 1988).

Lead has been documented to be toxic to a variety of mammals. Acute oral LD50s of 5 to 108 mg Pb/kg BW have been reported in rats (Eisler 1988). Longer-term dietary exposure to this substance has been shown to cause headaches, fatigue, muscle atrophy, muscle paralysis, convulsions, coma, and death. Chronic oral lethality thresholds as low as 0.32 mg/kg BW/day have been reported in dogs; however, higher thresholds have been observed in several other species (Eisler 1988). As is the case for birds, the organolead compounds tend to be more toxic than the inorganic lead salts.

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6.0 An Overview of the Environmental Fate and Effects of Mercury

6.1 Identity

Mercury (Hg) is an elemental metal that belongs to group 2B (12) of the periodic table. It has a characteristic liquid form and silver-white color in its metallic state. Its atomic number is 80 with a molecular weight of 200.59. The water solubility of mercury is 0.28 $\mu\text{moles/L}$ at 25 C. It dissolves to some extent in lipids. Mercury has a melting point of -38 C, a boiling point of 357 C, and a vapor pressure of 0.002 mm Hg at 25 C (HSDB 2000).

6.2 Uses

Mercury is used in the chlor-alkali industry to produce chlorine, caustic soda (sodium hydroxide), and hydrogen. The metal is also used in the paint industry to produce paint pigments and preservatives (Hocking 1979; Health and Welfare Canada 1980). Other uses of mercury include production of thermometers, switches, batteries, fluorescent bulbs, dental amalgams, and pharmaceuticals. In the past, mercury was used to produce pesticides, but those were banned and subsequently phased out of production (McNeely et al. 1979; Reeder et al. 1979; Health and Welfare Canada 1980; USEPA 1980).

6.3 Sources

Mercury is a natural element and, thus, is subject to ordinary biogeological cycling. Natural mercury deposits occur in all types of rocks and minerals (Jonasson and Boyle 1979). Thus, terrestrial environments appear to be large sources of atmospheric mercury, with contributions from evapo-transpiration of leaves, decaying vegetation, and degassing of soils (Kothny 1973). Volcanic activity, weathering, and releases from the oceans (Beyer et al. 1996) contribute a steady stream of mercury into the environment. However, volcanic, fumarolic, and thermal spring activities probably make only small contributions on a global basis (Jonasson and Boyle 1979). Far greater amounts of mercury are released due to anthropogenic activities. Coal combustion, non-ferrous metal production, waste incineration, chemical production (e.g., chlorine and alkali production from chlor-alkali plants), and the dumping of sewage sludge (Beyer et al. 1996) are responsible for the majority of current contamination problems.

6.4 Physical and Chemical Properties

Chemically, mercury can exist in three oxidation states: Hg⁰ or elemental (metallic) mercury, Hg⁺ or mercurous ion (monovalent mercury), and Hg²⁺ or mercury II mercuric ion (divalent

mercury; USEPA 1997a). All three forms of mercury can be found in air, water, and sediments, albeit in different proportions. In air, mercury occurs mostly (95 to 99%) as Hg⁰. In water, mercury occurs mostly as Hg²⁺ in particulate and dissolved form. Methylmercury usually comprises less than 20% of total mercury. In sediments, Hg²⁺ forms complexes with particles that have a high organic or sulfur content. These complexes are stable and tend to immobilize mercury in the sediment layer (USEPA 1997a). In fact, Hg²⁺ sorption to sediments is probably the most important process for determining its abiotic fate in the aquatic environment (USEPA 1979).

6.5 Environmental Transport and Fate

Mercury can be transformed to mono- and dimethylmercury by microorganisms under aerobic and anaerobic conditions (Bisogni and Lawrence 1975; Wood 1976; McNeely et al. 1979). Bacteria that are common in most natural waters are capable of this action (Jensen and Jernelov 1969; Bisogni and Lawrence 1975). Both forms of methylmercury may also be demethylated by bacteria in sediments (Fagerstrom and Jernelov 1972; NAS 1977; McNeely et al. 1979; Ramamoorthy et al. 1982).

6.6 Bioaccumulation

Even though most of the mercury present in the water column is in the divalent inorganic form, methylated forms constitute most of the mercury residues in the tissues of aquatic organisms (Hattula et al. 1978). Bioconcentration factors for aquatic organisms are usually high (104) due to rapid uptake and slow depuration. The biological half-life for mercury in fish is estimated to be approximately 2 years (Lockhart et al. 1972; McKim et al. 1976).

6.7 Effects on Aquatic and Terrestrial Organisms

Mercury has no known biological function in vertebrate physiology (Beyer et al. 1996). However, it is a potent systemic toxin and acts primarily on the central nervous and reproductive systems of animals (USEPA 1997b). Although it has no teratogenic or carcinogenic activity, it may disrupt endocrine activity (Fynn-Aikins et al. 1998). Methylmercury is very toxic due to its high affinity for sulfur-containing organic compounds i.e. proteins. Methylmercury forms covalent bonds with sulfhydryl groups of proteins and other macromolecules. This allows methylmercury to migrate readily through biological membranes (USEPA 1997a). Thus, methylmercury can easily reach sensitive tissues such as the brain or migrate across the placenta to reach the sensitive fetus.

In aquatic animals, methylmercury rapidly diffuses across the gills (7 to 12% of MeHg) and enters the blood stream. Methylmercury is also rapidly accumulated through the gut (65 to 80%) and transferred to the blood stream. It is subsequently transported to all organs including the liver, kidney, and the brain. Methylmercury is ultimately deposited in the muscle tissue. Inorganic mercury is also absorbed through the gut and the fish gills, but at a much

lower efficiency. It is also excreted much more readily (Beyer et al. 1996). As mercury is a natural toxicant, fish and terrestrial mammals have developed depuration pathways, however, they are much slower than uptake.

Effects of mercury poisoning in fish include death, reduced reproduction, impaired growth and development, behavioral abnormalities, altered blood chemistry, impaired osmoregulation, reduced feeding rates and predatory success, and altered respiration (USEPA 1997a). USEPA's AQUIRE (Aquatic Toxicity Information Retrieval) database (USEPA 2001) indicates that total mercury concentrations as low as 20 µg/L causes median hatchability effects in fish (orangethroat darter). Median lethality concentrations to other fish, including bass, killifish and carp, range from 60 to 200 µg/L.

Mercury has also been observed to induce adverse effects in benthic organisms. The adverse effects include reduced fertilization, impaired development, and lethality. Jaagumagi (1988) and Jaagumagi et al. (1989) reported significant decreases in abundance of Gastropoda and Chironomidae at sites in Toronto Harbor compared to reference sites. Mercury concentrations at the test site were five times higher than interim sediment quality guidelines and twice as high as probable effect levels set out by Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME 1999).

Adverse effects reported for terrestrial species exposed to mercury include death, decreased reproduction, decreased growth, decreased immune response, inhibition of induction of enzymes, change in behavior, and change in respiration (USEPA 1997a). Toxicity data for mammals suggests that a mercury residue of 30 mg/kg WW (wet weight) in the liver or kidney is harmful and lethal to most mammals. Also, dietary methylmercury concentrations in the range of 2 to 6 mg/kg WW are sufficient to cause mercury poisoning.

The analysis of published data on mercury toxicity to birds reveals that mercury concentrations in the liver and the kidney higher than 30 mg/kg WW are lethal to several species. Mercury concentrations in eggs above 0.5 mg/kg WW (2.5 mg/kg dry weight (DW) at egg water content of 80%) begin to have detrimental effect on reproduction. Whereas dietary concentrations above 1 mg/kg WW begin to have detrimental effects on reproduction. Dietary mercury concentrations of 10 mg/kg WW are lethal to birds of prey, passerines, and pheasants.

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7.0 An Overview of the Environmental Fate and Effects of Nickel

7.1 Identity

Nickel (Ni) is the 24th most abundant element in the earth's crust, occurring at an average concentration of about 75 µg/g (Government of Canada 1994). Nickel is found in many minerals and ores, primarily in combination with sulfur, arsenic, and antimony (CCREM 1987). Some of the more common nickel-bearing minerals include niccolite (NiAs), pentlandite [(FeNi)₉S₈], and millerite (NiS; McNeely et al. 1979). The principal sources of nickel-based minerals are igneous and serpentine rocks.

7.2 Uses

Due to its resistance to corrosion, high strength, and favorable alloying properties, nickel has a wide range of uses. The production of stainless steel, nickel plating, and nickel alloys represent the principal uses of this substance (CCREM 1987). Nickel-containing stainless steel is used in the chemical manufacturing, food processing, and health care industries (CCREM 1987). It has been estimated that nickel is used in the production of over 3000 alloys that have more than 250,000 applications (Mining Association of Canada 1991). High-nickel alloys are used in electrical, chemical, marine, electronic, nuclear, and aerospace applications. Nickel is also used as a catalyst in industrial processes and oil refining, in colors and glazes for ceramics, and in electrolyte solutions, jewellery, batteries, and gas masks (Government of Canada 1994).

7.3 Sources

Nickel is released into the environment from both natural sources and human activities. The weathering and erosion of soils and bedrock, forest fires, and volcanoes represent the principal natural sources of nickel to the environment. The processing of nickel-bearing ores, metal plating, burning of fossil fuels, and waste incineration are the most important anthropogenic sources of nickel, with releases from the combustion of petroleum, coal, and coke accounting for the majority of total releases (CCREM 1987). In areas that have substantial nickel deposits, the mining of nickel-bearing ores and the smelting and refining of concentrates also represent important sources of nickel (Government of Canada 1994). The electroplating, alloy casting, and iron and steel processing industries are also major contributors of nickel to the environment (CCREM 1987). As the concentrations of nickel in crude oil are relatively high (i.e., 0.6 to >300 mg/kg; CCREM 1987), chemical manufacturing industries that utilize crude oil or petroleum products in their processes are likely to release nickel into the environment.

7.4 Physical and Chemical Properties

Elemental nickel is a silver-white metal, with an atomic number of 28 and an atomic weight of 58.71 (Budavari et al. 1989). Although nickel can occur in six oxidation states (i.e., -1, 0, +1, +2, +3, and +4), the divalent form (Ni²⁺) is the most common in the environment. While elemental nickel is relatively insoluble in water, certain nickel salts are highly soluble in water (e.g., nickel chloride hexahydrate - 2500 g/L; nickel sulfate hexahydrate - 660 g/L; nickel sulfate heptahydrate - 760 g/L; nickel nitrate hexahydrate - 2400 g/L; Lide 1992). Other nickel salts, such as hexaamine nickel nitrate (45 g/L), nickel hydroxide (0.13 g/L), and nickel carbonate (0.09 g/L) are only moderately soluble in water (Lide 1992). Nickel oxide and nickel subsulfide are considered to be insoluble in water (Government of Canada 1994).

7.5 Environmental Transport and Fate

Because nickel is an element, it is neither created nor destroyed. Rather, its transport and fate in the environment is determined by the processes that influence its cycling. The nickel that is released to the atmosphere is generally attached to small particles that are removed from the air by wet or dry precipitation. In aquatic systems, nickel occurs primarily in the form of hydroxide, carbonate, and sulfate salts, which may become associated with suspended organic or inorganic materials (Government of Canada 1994). While sorption to particulates and subsequent deposition can result in the enrichment of bottom sediments with this substance (particularly at higher pHs; i.e., > 9), microbial activity or changes in the physical and chemical characteristics of the receiving water body (e.g., decreasing pH, increasing dissolved organic carbon) can remobilize sediment-associated nickel (CCREM 1987). Hence, nickel is considered to be highly mobile in aqueous systems. There is no evidence that photolysis or volatilization play significant roles in the removal of nickel from the water column (Government of Canada 1994).

7.6 Bioaccumulation

While nickel is bioaccumulated in the tissues of aquatic organisms, there is no evidence that this substance is biomagnified in the food web. In aquatic plants, such as algae, lichens, mosses, and macrophytes, bioconcentration factors (BCFs) range between 100 and 10,000 (CCREM 1987). The range of BCFs is narrower for aquatic invertebrates, with BCFs of 200 to 1000 reported for clams, zooplankton, and benthos (Government of Canada 1994). Somewhat higher BCFs (i.e., 2,000 to 4,500) were observed in the water flea, *Daphnia* spp. (Cowgill 1976). Fish had the lowest BCFs, typically ranging from 220 to 330 (Hutchinson et al. 1976). Collectively, these results suggest that the concentrations of nickel in biological tissues generally decrease at higher trophic levels in the food web (i.e., emphasizing that bioconcentration, rather than biomagnification, is the dominant process influencing the bioaccumulation of nickel).

7.7 Effects on Aquatic and Terrestrial Organisms

The toxicity of water-borne nickel varies depending on the species and life stage tested, duration of exposure, and water hardness (USEPA 1980). Overall, acute and chronic toxicity thresholds for nickel ranged from 24 to 10,000 µg/L (Government of Canada 1994). In short-term toxicity tests (i.e., 96-hour) in soft waters, median lethal concentrations (i.e., median lethal concentrations; LC50s) of 102 µg/L and 190 µg/L were reported for the snail, *Juga plicifera*, and the mussel, *Anodonta imbecilis*, respectively (Government of Canada 1994). Exposure to water-borne nickel for longer periods of time caused an avoidance response in rainbow trout (*Oncorhynchus mykiss*; i.e., at 24 µg/L; Giattina et al. 1982), reduced longevity in water fleas (*Daphnia magna*; i.e., at 40 µg/L; Munzinger 1990), impaired growth in algae (*Scenedesmus acuminatus*; i.e., at 50 µg/L; Stokes 1981), and reduced embryo survival in rainbow trout, and toads (*Gastrophryne carolinensis*; i.e., at 50 µg/L; Birge 1978). Therefore, exposure to water-borne metal can adversely affect the survival, growth, and reproduction of aquatic organisms. The toxicity of nickel to aquatic organisms tends to increase with decreasing water hardness.

No data from spiked-sediment toxicity tests were available to assess the effects of sediment-associated nickel on benthic invertebrates (Long and Morgan 1991; Government of Canada 1994; CCME 1999).

Information from controlled laboratory experiments and epidemiological studies indicates that prolonged exposure to nickel has the potential to adversely affect mammalian and avian receptors. Based on the results of occupational health studies in humans, the respiratory system represents the critical target for adverse effects following exposure to nickel by inhalation (Government of Canada 1994). As ambient levels of nickel tend to be low in air, the dietary exposure route is likely to be more important in wildlife species. In mallard ducks, long-term dietary exposure (i.e., up to 90 days) to nickel caused tremors, ataxia, and death in newly-hatched ducklings (i.e., at dietary levels of 800 mg/kg dry weight (DW) or higher; Cain and Pafford 1981). Similarly, growth and survival were reduced in newly-hatched chickens maintained on nickel-contaminated diets (i.e., at dietary levels of 300 mg/kg DW or higher and 500 mg/kg DW or higher, respectively (Ling and Leach 1979). While dietary exposure to nickel (i.e., in drinking water) has been linked with bladder and lung cancer in mammalian studies; this linkage has not been conclusively demonstrated (Government of Canada 1994; Young 1995).

7.8 References

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8.0 An Overview of the Environmental Fate and Effects of Zinc

8.1 Identity

Zinc is a heavy metal that is a constituent of a variety of minerals. The most common ores of zinc are sulfides, such as sphalerite (cubic ZnS) and wurtzite (hexagonal ZnS), carbonates, such as smithsonite (or calamine; ZnCO₃), and silicates, such as willemite (Zn₂SiO₄). Zincite, franklinite [(ZnMnFe)O(FeMn₂)O₃], and gahnite (ZnAl₂O₄; McNeely et al. 1979; Budavari et al. 1989)). In sulfides, zinc usually occurs in combination with other elements, particularly iron, copper, and lead (CCREM 1987).

8.2 Uses

Zinc is used in a number of industrial and agricultural application. Worldwide, the production of galvanized metals and metal alloys represents the primary uses of zinc, accounting for roughly 75% of the global production (i.e., 35% is used to produce coatings for steel and iron, 25% is used in alloys for dye casting, and 20% is used to produce brass; CCREM 1987). In addition, zinc is used as a rubber vulcanization activator and accelerator, heat conductor, pigment, UV stabilizer, supplement in animal feeds, catalyst, chemical intermediate, and mildew inhibitor (Opresko 1992). Zinc-based compounds are also used in rayon manufacturing, wood preservatives, parchment paper, smoke bombs, cements for metals, artificial silk, deodorants, antiseptics, and pesticides (Opresko 1992).

8.3 Sources

Zinc is released into the environment from both natural and anthropogenic sources, with the weathering of zinc-bearing rock representing the principal natural pathway by which this substance is released into the environment. According to the CCREM (1987), discharges from primary zinc production facilities and municipal wastewater treatment plants represent the principal sources of zinc from human activities. Other sources of this substance include wood combustion, waste incineration, iron and steel production, and other releases to the atmosphere (CCREM 1987).

8.4 Physical and Chemical Properties

Elemental zinc is a bluish-white, lustrous metal, with an atomic number of 30 and an atomic weight of 65.38 (Budavari et al. 1989). Zinc can occur in two oxidation states, including elemental zinc (Zn) and divalent zinc (Zn²⁺). Elemental zinc is sparingly soluble in water; however, certain zinc salts are highly soluble in water (i.e., 435 g/L for zinc acetate, 4,320 g/L for zinc chloride, 1667 g/L for zinc sulfate, and 3,333 g/L for zinc iodide; Budavari et al.

1989). Other zinc salts, such as zinc phosphate, zinc sulfide, and zinc oxide, are virtually insoluble in water (Budavari et al. 1989).

8.5 Environmental Transport and Fate

The transport and fate of zinc in the environment is determined by the processes that influence its cycling. Zinc can exist in four main forms in surface waters, including the simple hydrated ion (i.e., Zn^{2+}), inorganic compounds (e.g., $ZnCO_3$), stable organic complexes (e.g., Zn-cysteinate), or adsorbed to organic (e.g., Zn^{2+} -humic acids) or inorganic (Zn^{2+} -clay) colloids (CCREM 1987). The fraction of the total zinc that is present in each of these forms depends on the pH of the water, the concentration of zinc, and the presence of other metal ions, with low pH, low alkalinity, and high ionic strength favoring the ionic form of the substance (Taylor and Demayo 1980). Sorption of zinc by hydrous metal oxides, clay minerals, and organic materials appears to be an important process influencing the distribution of zinc in aquatic ecosystems (USEPA 1987). Above pH 7.0, greater than 90% of the zinc is likely to be bound, subject to precipitation, and, ultimately, associated with bottom sediments (CCREM 1987). In contrast, little adsorption is likely to occur below pH 6.0 (CCREM 1987). Sediment-associated zinc can be re-mobilized and released into the water column under anaerobic conditions, when pH decreases suddenly, or when the ionic composition of the water increases (James and MacNaughton 1977).

8.6 Bioaccumulation

As zinc is an essential micronutrient, it is accumulated in the tissues of aquatic organisms. As many organisms have the capability to regulate the concentrations within relatively tight homeostatic limits, bioconcentration factors (BCFs) are influenced by the concentration of zinc in the water (i.e., high BCFs are observed when zinc concentrations are low and lower BCFs are reported at elevated levels of environmental zinc). As the ionic zinc is the most bioavailable form of the substance, BCFs are also influenced by the factors that influence chemical equilibrium among its four primary forms. In general, BCFs in the order of 1,000 have been reported for freshwater invertebrates, while higher BCFs (i.e., in the order of 10,000) have been observed in fish and aquatic plants. While zinc does bioconcentrate in aquatic organisms, there is no evidence that it biomagnifies in aquatic food webs.

8.7 Effects on Aquatic and Terrestrial Organisms

Water-borne zinc is highly toxic to aquatic organisms, with the respiratory organs being the primary site of toxic action (Eisler 1993). The toxicity of water-borne zinc varies depending on the species and life stage tested, duration of exposure, and the physical and chemical characteristics of the water. According to Eisler (1993), freshwater fish tend to be more sensitive than marine species and embryos and larvae are the most sensitive development stages. For fish and aquatic invertebrates, acute toxicity thresholds ranged from 90 to 58,100 $\mu\text{g/L}$ (CCREM 1987). While acute toxicity to zinc is modified by water hardness (i.e., zinc

is more toxic in soft water than in hard water), chronic toxicity is not (USEPA 1980). Zinc is also more toxic at low dissolved oxygen concentrations, high sodium levels, low levels of organic complexing agents, and low pH. The results on long-term toxicity tests indicate that zinc toxicity increases with duration of exposure. Adverse effects on the survival, growth, and reproduction of aquatic organisms start at roughly 30 µg/L to 70 µg/L, depending on the life stage and species tested.

Exposures to sediment-associated zinc can be toxic to sediment-dwelling organisms. In freshwater sediments, an LC25 of 3531 mg/kg dry weight (DW) was reported for the amphipod, *Hyalella azteca* (Borgmann and Norwood 1997). By comparison, Oakden et al. (1984) reported >50% mortality in amphipods, *Rhepoxynius abronius*, exposed to 613 mg/kg DW of zinc for 72-hours in marine sediments. Swartz et al. (1988) reported a 10-day LC50 (median lethal concentration) of 276 mg/kg DW for the same species of amphipod. Collectively, these data suggest the toxicity of zinc may vary depending on the species tested, duration of exposure, and the physical-chemical characteristics of the receiving water.

Zinc is an essential micronutrient in birds and mammals. For this reason, the balance between excess and insufficient zinc is important (Eisler 1993). Zinc deficiency can occur in many wildlife species and is associated with severe effects on the growth, development, reproduction, and survival. The diets of birds and mammals should contain > 25 and > 30 mg Zn/kg DW of ration, respectively, to prevent zinc deficiency (Eisler 1993).

Exposure to elevated levels of dietary zinc can be toxic to birds and mammals, with effects including impaired survival, growth, and health. For example, survival was reduced in ducks fed single oral doses of > 742 mg Zn/kg body weight (BW) or diets containing 2,500-3,000 mg Zn/kg ratio for 30 days (NAS 1979). While adult chickens appear to be less sensitive than ducks, dietary exposure of chicks to 100 and 178 mg Zn/kg ration (i.e., 5 to 9 mg Zn/kg BW/day) caused increased pancreas histopathology and immunosuppression, respectively (Eisler 1993). Mammals appear to be as sensitive as birds to zinc, with acute oral LD50s (median lethal dose) of 350 to 800 mg Zn/kg BW reported for rats (Eisler 1993). Sub-lethal effects, such as weight loss, pancreas histopathology, digestive problems, and immunosuppression, were observed in various mammalian species fed 80 to 300 mg Zn/kg ration (i.e., 4 to 15 mg Zn/kg BW/day) for extended periods of time (i.e., several months; Eisler 1993).

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9.0 An Overview of the Environmental Fate and Effects of Polycyclic Aromatic Hydrocarbons

9.1 Identity

Polycyclic aromatic hydrocarbons (PAHs) are a diverse class of organic compounds that includes about one hundred individual compounds containing two or more fused benzene, or aromatic, rings (McElroy et al. 1989). The term low molecular weight (LMW) PAHs is applied to the group of PAHs with fewer than four rings, while high molecular weight (HMW) PAHs have four or more rings. The LMW PAHs are considered to include acenaphthene, acenaphthylene, anthracene, fluorene, naphthalene, 2-methylnaphthalene, and phenanthrene. The HMW PAHs are considered to include benz[a]anthracene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene, and pyrene. While these 13 parent PAHs are composed entirely of carbon and hydrogen atoms, nitrogen, sulphur, and oxygen atoms may be substituted on one or more of the benzene rings to form a variety of heterocyclic aromatic compounds (HACs; McElroy et al. 1989; Wilson and Jones 1993).

9.2 Uses

While many PAHs do not have any significant commercial applications, several are important in various industrial processes. For example, acenaphthene, anthracene, and pyrene are used as intermediates in the chemical (i.e., soap, pesticide, and dye production), photographic and pharmaceutical industries (Fidler et al. 1991). Certain PAHs, such as anthracene and phenanthrene, are also used in the production of explosives, including pyrotechnic materials, and in the processing of certain foods. Importantly, naphthalene is used extensively in the production of phthalic anhydride, which is a precursor in the production of dyes, plasticisers, resins, and insect repellents (Government of Canada 1994).

9.3 Sources

A variety of natural and anthropogenic activities result in the production of PAHs. Most commonly, PAHs are produced as a result of the incomplete combustion of wood and fossil fuels. However, pyrolysis of organic materials (e.g., coal tar, creosote, anthracene oil, coal tar pitch, and carbon black) and diagenesis of sedimentary organic materials (e.g., which form fossil fuels) can also result in the formation of PAHs (LGL 1993). Other sources of these substances include biosynthesis by microbes and plants, tire wear, cigarette smoke, asphalt production, and wood preservatives (Slooff et al. 1989). Oil spills represent an important source of the PAHs that are released into marine and estuarine waters.

9.4 Physical and Chemical Properties

As might be expected based on the differences in their structures, the physical and chemical properties of the substances within these groups are highly variable. In general, PAHs tend to have high melting points, high boiling points, low water solubilities, and low vapour pressures. The LMW PAHs are generally more soluble in water (45 to 31 700 g L⁻¹ at 25°C) than the HMW PAHs (0.5 to 140 g L⁻¹ at 25°C; Southworth 1979; NRCC 1983). The solubility of PAHs tends to increase with increasing water temperature and to decrease with increasing salinity (NRCC 1983). The octanol/water (K_{ow}) and organic carbon (K_{oc}) partition coefficients of all PAHs are relatively high; however, those of HMW PAHs (5.32 - 6.04 and 5.23 - 5.94, respectively) exceed those of LMW PAHs (3.37 - 4.46 and 3.32 - 4.39, respectively). As a result, these compounds tend to be lipophilic (i.e., they have an affinity for fatty organic substances) and readily adsorb to both organic and inorganic particulate matter (Government of Canada 1994)

9.5 Environmental Transport and Fate

The behavior of PAHs in surface waters depends on a variety of chemical-specific and site-specific factors, with physicochemical properties playing an important role in determining their fate in aquatic systems. While PAHs with high solubilities (such as naphthalene) may remain dissolved in surface waters, those with lower solubilities are likely to form associations with colloidal material (Wijayarante and Means 1984) or suspended particulates (Varanasi 1989). Hence, PAHs are commonly associated with suspended particulates in aquatic systems (Harrison et al. 1975; Germain and Langlois 1988). While PAHs associated with suspended particulates may be photochemically degraded (David and Boule 1993), biodegraded (Hall et al. 1986), transported to other areas (Murphy et al. 1988), and incorporated into aquatic biota (Baker et al. 1991), deposition and consolidation with bedded sediments (often within several hundred meters of the source) probably represents the most important environmental fate process (Murphy et al. 1988; Herrmann and Thomas 1984). Hence, sediments represent the major environmental sink for these compounds (Government of Canada 1994).

9.6 Bioaccumulation

Bioaccumulation may occur as a result of exposures to PAHs in water, through contact with suspended and bedded sediments, and through consumption of contaminated food organisms (Ringuette et al. 1993). Bioaccumulation of PAHs is generally evaluated by calculating the ratio of the concentration of a chemical in the organisms tissues (expressed on a wet weight basis) to its concentration in the exposure medium. When water represents the exposure medium, this ration is termed a bioconcentration factor (BCF); the comparable ratio for sediment exposures is the biota-sediment bioaccumulation factor (BSAF).

Information from laboratory studies suggest that water-to-tissue BCFs are directly correlated with the K_{ow} (octanol/water partition coefficient) of the PAH under investigation. For example, BCFs in the cladoceran, *Daphnia pulex*, after one hour of exposure ranged from 131

for naphthalene to 10,100 for benz[a]anthracene (Southworth et al. 1978). Similar results (i.e., Kow -dependent bioaccumulation) have been observed when benthic invertebrates were exposed to PAH-contaminated sediments (Eadie et al. 1982). In addition to an array of physical and chemical factors, the bioaccumulation of sediment-associated PAHs may be influenced by the physiology and feeding strategy of the species under consideration. Fish, for example, have well developed mixed function oxidase (MFO) systems which rapidly transform PAHs into substances that are more readily excreted (Stegeman 1981; Varanasi et al. 1989). In contrast, certain benthic invertebrates (e.g., bivalve mollusks) have much less efficient MFO systems and, therefore, accumulate higher concentrations of PAHs in their tissues (Naf et al. 1993; Germain et al. 1993). Invertebrate species and tissues with high lipid contents tend to accumulate higher levels PAHs than those with lower lipid contents (Neff 1985). Furthermore, lipid-associated PAHs may be mobilized, transferred to lipid-rich eggs, and released during spawning activities (Rossi and Anderson 1977; NAS 1985). Therefore, overall condition and reproductive state are important considerations when assessing bioaccumulation.

9.7 Effects on Aquatic and Terrestrial Organisms

The acute toxicity of PAHs is primarily associated with their action as non-polar narcotics (i.e., narcosis; Eisler 1987). That is, PAHs tend to enter the organisms and bind irreversibly to lipophilic sites within the cell. Binding to sites on cell membranes tends to disrupt surface membrane processes, inhibit ion and gas exchange, and increase osmosis across the membrane (Van Overbeek and Blondeau 1954). In fish and other organisms that rely on gills for respiration, hypoxia and osmotic imbalances may result from impaired membrane function (Sims and Overcash 1983). In the tissues, changes in membrane permeability may disrupt neurological and muscular function (Neff 1985).

While non-polar narcosis is the primary mode of toxicity for PAH with three or fewer aromatic rings, certain HMW-PAHs may also be associated with mutagenic, carcinogenic, and teratogenic effects (Eisler 1987). In particular, methyl-substituted PAHs tend to be much more mutagenic than the parent compound (Government of Canada 1994). Interestingly, however, PAHs with longer alkyl-substitution tend to be less toxic due to their decreased ability to cross cell membranes (NRCC 1983). In addition, the metabolic degradation products of HMW-PAHs, particularly epoxide derivatives, tend to be highly mutagenic (NRCC 1983). These metabolites tend to be much more electrophilic and reactive than the parent compound, which increases the likelihood that they will bind covalently to DNA (deoxyribonucleic acid), RNA (ribonucleic acid), and other cellular proteins (Varanasi 1989). In turn, these complexes may be associated with alterations in normal cellular processes (e.g., cell division, protein synthesis). Such alterations may be expressed by tumour formation, developmental abnormalities, and/or other related effects in aquatic animals (Heidelberger 1976; Larson et al. 1976; 1977). In plants, PAH metabolites may bind with various components of the chloroplast and, thereby, inhibit photosynthesis (Neff 1979).

Exposure to PAHs has been associated with a wide range of adverse effects in aquatic organisms, including effects on survival, growth, reproduction, metabolism, and health (Eisler

1987). The responses of aquatic biota vary significantly among taxonomic groups and depend, at least in part, on their ability to metabolize and excrete PAHs (Fidler et al. 1991). In addition, biotic responses may be affected by the duration of exposure to PAHs, by the substance or group of substances under consideration, and by ambient environmental conditions. Among the various PAHs, the lowest observed effect levels of PAHs ranged from 5 µg/L for benzo[a]pyrene (96-hour LC50 (median lethal concentration) for the water flea, *Daphnia pulex*) to 125 µg/L for fluorene (which resulted in reduced fecundity in the water flea, *Daphnia magna* in a 14-day test; Government of Canada 1994)

In the field, PAHs always occur as complex mixtures of the individual PAHs, commonly in association with other contaminants. Toxic effects on sediment-dwelling organisms are likely to result from the cumulative effects of these mixtures of contaminants. For this reason, it is important to evaluate the interactive effects of the individual PAHs using a toxic units model (Swartz 1999). Such models provide a basis for determining the overall toxicity of the contaminant mixture by summing the toxic units (i.e., TU = measured concentration/toxicity reference value) for the substances that have a similar mode of toxicity (i.e., the individual PAHs). Acute and chronic toxicity thresholds (i.e., for narcosis) of 50.2 and 9.9 mg/kg dry weight (DW) @ 1%OC, respectively, have been determined for total PAHs using equilibrium partitioning (DiToro and McGrath 2000). By comparison, a 10-day LC50 of 23.9 mg tPAH/kg DW @ 1%OC has been reported for the amphipod, *Rhepoxynius abronius* (Swartz et al. 1997).

A variety of adverse effects have been observed in birds and mammals exposed to PAHs, including non-neoplastic effects and carcinogenicity (Eisler 1987). While metabolic dysfunction, immobility, and death have been reported in birds and mammals fed PAH-contaminated diets, the doses that cause such effects tend to be much higher than those that induce neoplasms (i.e., up to an order or magnitude higher; ATSDR 1990). In mice, ingestion of diets containing 50 to 250 mg/kg benzo[a]pyrene (i.e., 6.5 to 32.5 mg/kg body weight; BW/day) for 70 to 197 days resulted in a > 70% incidence of stomach tumors (ATSDR 1990). Long-term dietary to benz[b]fluoranthene, benz[j]fluoranthene, benz[k]fluoranthene, and indeno[1,2,3-cd]pyrene have also been shown to induce tumors in mice when exposed via other exposure routes (IARC 1983).

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10.0 An Overview of the Environmental Fate and Effects of Polychlorinated Biphenyls

10.1 Identity

Polychlorinated biphenyls (PCBs) is the generic term applied to a group of 209 chlorinated organic compounds that have similar molecular structures and properties. PCBs are synthetic chemicals that were produced commercially in the United States between 1929 and 1977, at which time their production was banned. The principal manufacturer of PCBs in the United States was the Monsanto Chemical Company; the PCBs sold by Monsanto were marketed under the trade name of Aroclor.

10.2 Uses

As a class of compounds, PCBs are fire-resistant and chemically stable. In addition, PCBs conduct electricity poorly. These and other properties made PCBs useful in a range of industrial and consumer applications. The vast majority of the PCBs used in North America were employed as cooling and insulating fluids in industrial transformers and capacitors. However, PCBs have also been used in several other applications, including as hydraulic fluids, heat transfer fluids, and plasticizers. As a result of their widespread use, PCBs have been released into the environment worldwide. The results of various monitoring programs indicate that PCBs are ubiquitous environmental contaminants and are commonly detected in air, precipitation, soil, surface water, groundwater, sediment, and living organisms.

10.3 Sources

PCBs are synthetic substances and, as such, they are released into the environment solely as a result of human activities. In recent years, restrictions on the use and disposal of PCBs has greatly reduced the magnitude and extent of PCB inputs into the environment. Nonetheless, a variety of activities resulted in significant losses of these substances prior to the implementation of those regulations, including uncontrolled past use, past disposal practices, illegal disposal, and accidental releases.

10.4 Physical and Chemical Properties

The majority of PCB congeners tend to have low solubilities, low vapour pressures, high dielectric constants (i.e., low conductivity), low flammability, and high resistance to chemical breakdown. Commercial PCB formulations are usually light coloured, viscous liquids that have a slippery or oily appearance. The density of all PCB formulations is greater than that of water (WHO 1993) and increases with increasing chlorine content. As a group, PCBs are

sparingly soluble in water. However, aqueous solubilities vary substantially among the various PCB mixtures and congeners. In contrast to water, PCBs are readily soluble in oils and other organic solvents (WHO 1993). The vapour pressure of PCBs is variable, spanning two orders of magnitude for PCB mixtures and eight orders of magnitude for PCB congeners. As is the case for solubility, vapour pressures tend to decrease with the addition of each chlorine atom (Mackay et al. 1983). The available data indicate that PCBs are highly lipophilic (Mackay et al. 1992).

10.5 Environmental Transport and Fate

Many of the same physical and chemical properties that made PCBs useful in commercial and industrial applications dictate their fate upon release into the environment. Due to the density of PCBs, once released to aquatic systems they tend to sink to the bottom of the water body. As a result of their hydrophobicity, as well as their generally low water solubilities, PCBs tend to accumulate in sediments and soils that contain organic carbon. Together, these properties give PCBs a high potential for uptake by aquatic and terrestrial organisms, including fish, birds, mammals, and other wildlife. Due to chemical stability, PCBs are highly persistent in the environment. Hence, cycling, rather than degradation, represents the most important process affecting PCBs once they have been released into the environment.

10.6 Bioaccumulation

Information from both field and laboratory studies indicates that PCBs bioaccumulate in the tissue of benthic invertebrate species (van der Oost et al. 1988; Lester and McIntosh 1994). For total PCBs, laboratory-derived sediment-to-biota bioaccumulation factors (BSAF = [tissue] ÷ [sediment]; Ferraro et al. 1990) for clams, shrimp, and sandworms ranged from 0.02 to 1.89 (Pruell et al. 1990; Boese et al. 1995; Lester and McIntosh 1994). PCBs are also known to accumulate to elevated levels in the tissues of freshwater fish species (Schwartz et al. 1987; van der Oost et al. 1988; Macdonald et al. 1993; Lores et al. 1993), with the partitioning of PCBs depending on fish lipid content, the trophic level of the fish species, and the trophic structure of the food web (Rowan and Rasmussen 1992). As a result, calculated BSAFs and bioavailability indices (BI = [tissue] ÷ lipid content x TOC (total organic carbon) content ÷ [sediment]; Carey et al. 1990; Foster et al. 1987) vary substantially between species and between lake systems (Macdonald et al. 1993). For example, BIs ranged from 0.72 to 259 for chinook salmon in the Great Lakes basin (Rowan and Rasmussen 1992). Intermediate BSAFs and BIs were calculated for the fish in Lake Ontario, Lake St. Clair, and Lake Superior (Evans et al. 1991; Rowan and Rasmussen 1992). Fish-eating birds (e.g., bald eagles) and mammals (e.g., dolphins) at the highest trophic levels in the food web tend to accumulate PCBs to the highest levels in their tissues (Eisler 1986).

10.7 Effects on Aquatic and Terrestrial Organisms

Exposure to PCBs is known to cause a broad range of adverse effects in aquatic organisms. In controlled laboratory studies, both short- (i.e., 96 hrs) and longer- (i.e., > 96 hrs) term exposure of aquatic organisms (plants, invertebrates, fish, and amphibians) to water-borne PCBs has been shown to cause a variety of adverse effects, including increased mortality, reduced metabolic rates, reduced growth rates, and impaired reproduction (CCREM 1987; Moore and Walker 1991; CCME 1999). In aquatic invertebrates, acute toxicity thresholds range from 10 µg/L for amphipods (*Gammarus fasciatus*) to 400 µg/L for damselflies (*Ischnura verticalis*; CREM 1987). Freshwater fish appear to be more sensitive than invertebrates to the effects of PCBs, with 96-hour LC50s (median lethal concentrations) of 2.0 and 2.3 µg/L reported for rainbow trout and largemouth bass, respectively (Birge et al. 1979). In long-term tests, chronic toxicity thresholds for fish and invertebrates ranged from 0.2 to 15 µg/L (USEPA 1980). Exposure to relatively low levels of PCBs (i.e., 1 µg/L) inhibited photosynthesis in phytoplankton (CCREM 1987).

Exposure to sediment-associated PCBs can adversely affect sediment-dwelling organisms. For example, Swartz et al. (1988) demonstrated that PCBs (Aroclor 1254) were acutely toxic to amphipods (*Rhepoxynius abronius*), with a 10-day LC50 of 8.8 mg/kg dry weight (DW) reported. Impaired reproduction in copepods (*Microarthridion littorale*) was observed at PCB concentrations as low as 4 mg/kg DW (DiPinto et al. 1993). Because acute-to-chronic ratios tend to be large for PCBs (i.e., 11 to 58; DiPinto et al. 1993; MacDonald et al. 2000), sublethal effects on sensitive species and life stages are likely to occur at concentrations below 1 mg/kg DW.

In aquatic-dependent avian and mammalian wildlife, consumption of contaminated prey items (i.e., fish and invertebrates) represents the primary source of exposure to PCBs (Moore et al. 1999). The Ah-receptor mechanism is considered to be the primary mode of action for PCBs (Coulston and Kolbye 1994; Metcalfe and Haffner 1995). The biological effects associated with the induction of enzyme systems by PCBs arise because these enzymes are critical to the homeostasis of the organism. Induction of MFO (mixed function oxidase) enzyme systems, including the aryl hydrocarbon hydroxylase (AHH) and ethoxyresorufin O-deethylase (EROD) systems, can result in altered activity of gonadal (e.g., estrogens), pituitary (growth hormone), thyroid (e.g., thyroxine), and adrenocortical (e.g., cortisol) hormones. As many bodily functions are regulated by hormonal (or endocrine) systems, alteration of these systems can lead to adverse effects on the physiology of the organism. For example, suppression of various gonadal hormones is likely to result in direct effects on reproduction, such as reduced fertility. Similarly, reduction in the production of hormones from the pituitary gland can result in adverse effects on growth. Carcinogenic, mutagenic, and teratogenic effects have also been observed in terrestrial organisms exposed to sub-lethal levels of certain PCBs in field and laboratory studies (Eisler 1986). Consumption of higher doses of PCBs has been shown to be lethal in many wildlife species, with mink being among the most sensitive species tested (MESL 1996). In this species, long-term dietary exposure to daily doses as low as 1.5 mg/kg body weight (BW) resulted in > 50% mortality, while reduced growth was observed at much lower doses of PCBs (i.e., 0.17 mg/kg BW/day; Bleavens 1980).

The results of mammalian toxicity tests suggest that a relatively small group of congeners are highly toxic and may account for most of the toxicity (Safe et al. 1985). The non-ortho-, mono-ortho-, and di-ortho-PCBs are considered to have a similar receptor-mediated mechanism of action as the polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (Safe 1990; 1994). For this reason, a method has been developed to facilitate assessments of the cumulative effects of dioxins, furans, PCBs, and other related halogenated aromatic compounds that occur in complex mixtures. This method is based on the determination of the relative toxicities of dioxin-like substances in relation to 2,3,7,8-TCDD. Specifically, toxic equivalency factors (TEFs) are assigned to each chemical based on the results of both in vivo and in vitro studies. The most recent TEFs that have been established for co-planar PCBs using mammalian data are presented in Table 9.1 (van den Berg *et al.* 1998).

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11.0 An Overview of the Environmental Fate and Effects of Organochlorine Pesticides: Aldrin and Dieldrin

11.1 Aldrin

11.1.1 Identity

Aldrin (309-00-2) is an organochlorine pesticide whose pure form is a white powder with a mild chemical odor. The technical compound is light tan to brown solid or powder. It has a molecular weight of 364.9. The technical grade aldrin contains 95% active ingredient (Ashworth et al. 1970). Aldrin is also known as Alarite, Aldrec, Aldrex, Aldrine, Aldrosor, Algran, Compound 118, Aldrite, Drinox, HHDN [(1R,4S,4aS,5S,8R,8aR)-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene], Octalene, Seedrin Liquid, and Soildrin (McNeely et al. 1979).

11.1.2 Uses

Aldrin has been used as a soil insecticide to control root worms, beetles, and termites. Its original use included control of soil, fruit, and vegetable pests. Specific targets included grasshoppers, locusts, and termites. Aldrin's current use in the United States is restricted to those situations in which there is no effluent discharge, e.g. in ground injection for termite control (USEPA 1980).

In 1974, the USEPA banned most of the uses of aldrin due to its suspected carcinogenicity. Ultimately, all uses on food crops were banned. The use of aldrin as a subterranean termiticide continued after 1974, but the sole importer ceased importation in 1985 and cancelled its registration in 1987. All other termiticide registrations of aldrin have been either cancelled or suspended. Two minor uses that were still allowed, mothproofing in manufacturing processes and dipping roots and tops of non-food plants, have been voluntarily cancelled by industry. In 1981, a labeling improvement program (LIP) was initiated by the USEPA to attempt to avoid errors of misapplication to buildings for termite control. In accordance with an agreement with the United States Department of Agriculture (USDA) and the Food and Drug Administration (FDA), the USEPA is currently reevaluating recommended tolerances for unavoidable residue levels of aldrin or dieldrin in food products.

11.1.3 Sources

Since aldrin is not currently produced or imported in the United States, its use and release into the environment is minimal. Possible new releases may come from the use of old stockpiles for the underground control of termites. Aldrin is applied to soil and vegetation by injection or aerial spraying. Leaching of aldrin is thought to be minimal, with soil erosion

and sediment transport the major pathways for entering the aquatic environment (USEPA 1980).

11.1.4 Physical and Chemical Properties

Aldrin has a water solubility of 27 µg/L at 25°C (Park and Bruce 1968). Its log K_{ow} (octanol/water partition coefficient) is quite high at 6.9 (Hansch et al. 1995). Aldrin's vapor pressure is 3.1 mPa at 25°C (Martin 1972).

11.1.5 Environmental Transport and Fate

Aldrin is rapidly transformed to dieldrin in the environment (USEPA 1979, 1980). One study reported that 60% of aldrin added to river water has dissipated after four weeks of incubation (Eichelberger and Lichtenberg 1971). Trace concentrations of 1 to 2 ng/L were found in rain and snow (Strachan and Huneault 1979). Some studies report concentrations of aldrin in surface waters ranging from 0.1 to 85 ng/L (Lichtenberg et al. 1970; USEPA 1976; USEPA 1982).

Biotransformation, volatilization, bioaccumulation, and indirect photolysis play significant roles in the removal of aldrin from the water column (USEPA 1979). Sunlight and bacteria change aldrin to dieldrin. As a consequence, one mostly finds dieldrin in environmental samples. Aldrin binds tightly to soil and slowly evaporates into the air. Plants take up aldrin from soil and store it in their tissues, where it is rapidly transformed to dieldrin.

Hydrolysis is not expected to be an important process in the aquatic environment. Although very few data are available, it is expected that sorption processes play a relatively minor role (USEPA 1979). In general, soil sorption coefficients are small (400; Kenaga and Goring 1978).

The half-life of aldrin in a sample of natural water in the presence of sunlight is about 24 h (Singmaster 1975). Studies with non-aqueous systems showed that aldrin is converted to photoaldrin (Rosen and Carey 1968; Ivie and Casida 1971). The photolysis of aldrin in sterile paddy water yielded 25% dieldrin in 36 h (Ross and Crosby 1975).

Laboratory measures of volatilization under simulated wind and temperature conditions have yielded volatilization half-lives ranging from as short as 0.4 h (Singmaster 1975) to a maximum of 7.7 days (Mackay and Wolkoff 1973; Mackay and Leinonen 1975).

11.1.6 Bioaccumulation

In terms of exposure potential, some of the released aldrin will be available for direct uptake from the aquatic environment, but given its affinity for sediment adsorption, most will partition to sediments. Thus, the principal route of exposure to aldrin would be through a

direct contact with, and ingestion of, sediment, soil, and through trophic transfer of the contaminant through consumption of benthic and soil organisms.

Short term bioconcentration factors measured in terrestrial-aquatic microcosm studies range from 103 to 104 (Metcalf et al. 1973). Biomagnification is not considered to be important because aldrin is rapidly converted to dieldrin in aquatic biota (USEPA 1979). Biotransformation appears to be the most important process governing the fate of aldrin in the aquatic environment (USEPA 1979). The transformation process occurs in virtually all organisms, from microbes, algae, invertebrates, fish to birds and mammals (Rosenblatt et al. 1975; Sanborn et al. 1977). A biological half-life of 7 days has been reported for aldrin in the Atlantic salmon (*Salmo salar*; Addison et al. 1976).

11.1.7 Effects on Aquatic and Terrestrial Organisms

Aldrin is highly toxic to aquatic organisms. Acute exposures to a variety of fish species (salmon, trout, minnow, catfish, bass, and bluegill) have resulted in lethal concentrations in the range of 2 to 50 µg/L. Invertebrates, such as *Daphnia magna* have experienced adverse effects (EC50; median effect concentration) at concentration ranges of 20 to 30 µg/L (HSDB 2000a). As aldrin rapidly transforms to dieldrin in the environment, aquatic and sediment toxicity for dieldrin may be considered for this substance. See the dieldrin portion of this appendix for more information.

Aldrin is moderately to highly toxic to mammals. Acute oral LD50 (median lethal dose) ranges from 38 to 67 mg/kg (HSDB 2000a). Studies with animals fed aldrin have shown that the liver can be damaged and the ability of the immune system to protect against infections can be suppressed. It is thought to exert its hepatotoxicity by increasing the activity of microsomal biotransformation enzymes. This appears to be associated with the occurrence of reversible hypertrophy of centrilobular hepatocytes with cytoplasmic changes and hepatomegaly in the liver of rodents (IPCS 1989). Goats administered 50 mg aldrin/kg body weight showed mild degenerative changes, congestion, and petechial hemorrhages in various organs. In the kidneys, degenerative changes of the proximal convoluted tubules were found (IPCS 1989). Cats fed aldrin at 1 mg/kg/day or made to inhale 0.1 µg/L of air had marked lowering of conditioned reflexes and of unconditioned food and orientation reflexes, which required up to 8 days to return to normal (NRC 1977). Acute symptoms were observed in ducks, pheasants, and bobwhite quail following oral exposure, including ataxia, low carriage, nictitating membrane closed for long periods, fluffed feathers, tremors, phonation, violent wing-beat convulsions, seizures, and opisthotonos. Death occurred ½ hours to 10 days post-treatment. Weight losses occurred among survivors of higher levels. Gross autopsies revealed occasional liver adhesions to parietal peritoneum (USFWS 1970)

For chronic exposures, groups of male and female Osborne-Mendel rats were fed diets containing 0, 0.5, 2, 10, 50, 100, or 150 ppm recrystallized aldrin for 2 years. Considering together the groups given 0.5, 2, or 10 ppm (i.e., the groups showing survival rates at 2 yr comparable to those of controls), number of tumor-bearing animals was 25/60 compared with 3/17 controls. Among those treated, 12 developed lymphomas (9 located in lungs), 13 had

mammary tumors (malignant in 4 rats), 2 had fibrosarcomas and 3 had tumors at other sites (IARC 1974). Microscopic exam of costochondral junction of goats after chronic aldrin intoxication revealed drastic reduction in width of proliferating, maturing and degenerating cartilage cells (Singh and Jha 1982). Administered in single, 50 mg/kg doses to hamsters during the period of organogenesis, high incidence of fetal deaths, congenital abnormalities, and growth retardation were observed (ACGIH 1991).

The Environmental Protection Agency (EPA) considers aldrin a probable carcinogen, as a result of animal testing. Further, aldrin is classified as a probable human carcinogen. This is based on the observations where orally-administered aldrin produced significant increases in tumor responses in three different strains of mice in both males and females. Tumor induction has been observed for structurally related chemicals, including dieldrin, a metabolite of aldrin (USEPA 2000).

11.2 Dieldrin

11.2.1 Identity

Dieldrin (CAS; Chemical Abstracts Service Number 60-57-1) is an organochlorine insecticide that is closely related structurally and chemically to aldrin. Pure dieldrin is a white powder with a mild chemical odor. The less pure commercial powders have a tan color. Dieldrin is also known as HEOD (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-1,4-exo-5,8-dimethanonaphthalene), Compound 497, Octalox, Insecticide no.497, ENT 16225, Alvit, Dieldrex, Dieldrite, and Panoram D31 (USEPA 1979; McNeely et al. 1979; Windholtz et al. 1983; Agriculture Canada 1984). Its toxicity does not differ significantly from that of aldrin.

11.2.2 Uses

Dieldrin has been used in agriculture for soil and seed treatment and in public health to control disease vectors such as mosquitoes and tsetse flies. Dieldrin has also had veterinary use as a sheep dip and has been used in treatment of wood and mothproofing of woolen products (Marth 1965).

Dieldrin used to be one of the most widely used domestic pesticides (Lykken 1971; Waldbott 1978; USEPA 1980). The original uses of dieldrin were as a pesticide for control of soil, fruit, and vegetable pests, as well as for control of grasshoppers, locusts and termites. However, its use was restricted in the United States in 1974 to those situations in which there is no effluent discharge (USEPA 1980). The United States no longer manufactures dieldrin as a result of a ban in 1974, but instead imports the insecticide from the Shell Chemical Company which manufactures it in Holland (USEPA 1980).

11.2.3 Sources

The pathways for environmental contamination by dieldrin include atmospheric dispersion, wind and water erosion of soil, and transport while sorbed onto soil particles in the silt of streams and lakes. Dieldrin can also move through the environment as residues in plants and animals, especially in fish and wildfowl (Lykken 1971).

Dieldrin is everywhere in the environment, but at very low levels. Since its use was banned, most foods contain very little, if any, dieldrin. Air, surface water, or soil near waste sites may contain higher levels.

11.2.4 Physical and Chemical Properties

Dieldrin has a melting point of 175 to 176°C and a vapor pressure of 400 μ Pa at 20°C (Worthing 1983). The pesticide does not dissolve in water to a great extent (0.186 mg/L at 20°C; Park and Bruce 1968). Also, it tends to be hydrophobic (log Kow of 4.55; Brooke et al. 1986).

11.2.5 Environmental Transport and Fate

Dieldrin is considered to be persistent in the environment. Sorption volatilization and bioaccumulation are the important processes determining its fate (USEPA 1979). Dieldrin binds to soil particles and slowly evaporates into the air. Although dieldrin is persistent in soil, environmental background levels are known to be decreasing slowly. Plants take up dieldrin from the soil and store it in their tissues. When animals take up dieldrin, it is stored in the fat and leaves the body very slowly.

The hydrolysis of dieldrin in the aquatic environment is very slow (Eichelberger and Lichtenberg 1971). However, sorption to sediments containing organic matter is appreciable. An organic carbon partition coefficient (Koc) of approximately 104 at 15°C has been reported (Weil et al. 1973). Experimental studies suggest that direct photolysis of dieldrin does occur; its photolytic half-life is approximately 2 months (Henderson and Crosby 1968). Volatilization of dieldrin from aquatic systems is also an important removal process. Half-lives in the order of a few hours to a few days have been determined from laboratory experiments (Singmaster 1975).

Sorption, volatilization, and bioaccumulation are the important processes determining its fate (USEPA 1979). Dieldrin binds to soil particles and slowly evaporate into the air. Although dieldrin is persistent in soil, environmental background levels are known to be decreasing slowly. Plants take up dieldrin from the soil and store it in their tissues. When animals take up dieldrin, it is stored in the fat and leaves the body very slowly.

11.2.6 Bioaccumulation

Some of the released dieldrin will be available for direct uptake from the aquatic environment, but given its affinity for sediment adsorption, most dieldrin will partition to sediments. The principal route of exposure to dieldrin would be through direct contact with, and ingestion of, soils and sediments, and through trophic transfer of the contaminant through consumption of benthic and soil organisms. Thus, the most likely route of exposure to dieldrin is through the consumption of contaminated food and drinking water.

Dieldrin may be bioaccumulated by various organisms in the aquatic environment. Bioconcentration factors ranging from 10² to 10⁴ for bacteria (Grimes and Morrison 1975) and averaging 10⁴ for freshwater algae (Neudorf and Khan 1975) have been reported. Data from microcosm experiments also suggest significant bioaccumulation (Sanborn and Vu 1973; Metcalf et al. 1973). Bioconcentration factors of 10² to 10³ for algae, 10⁴ to 10⁵ for snails, and 10³ for fish were reported. Biological half-lives in fish vary from 7 days in bluegill sunfish (*Lepomis macrochirus*; Gakstatter and Weiss 1967) to 40 days in rainbow trout (*Salmo gairdneri*; Macek et al. 1970). Very little microbial biotransformation of dieldrin occurs in the aquatic environment (Bohonos and Francis 1975; Sanborn et al. 1977).

11.2.7 Effects on Aquatic and Terrestrial Organisms

Dieldrin has also shown to be highly toxic to aquatic organisms. Acute exposures to a variety of fish species (salmon, trout, minnow, catfish, bass, bluegill) have resulted in lethal concentrations in the range of 1 to 20 µg/L (USEPA 2001). Dieldrin has also been observed to illicit adverse effects to benthic organisms, such as reduced populations and species richness. Jaagumagi (1988) and Jaagumagi et al. (1989) reported significant decreases in abundance of benthic organisms at sites in Humber Bay, Lake Huron compared to reference sites. Toxicity to the marine amphipod, *Rhepoxynius abronius* was observed at a concentration of 1.17 µg/g from sediments from Puget Sound, WA (Pastorok and Becker 1990). The USEPA (Ingersoll 1995) published proposed freshwater quality criterion of 0.00625 µg/L and sediment quality criterion (at 1% OC; organic carbon) of 0.166 µg/g.

Dieldrin is moderately to highly toxic to mammals. Acute oral LD₅₀ for rats has been reported in the range of 24 to 87 mg/kg, and in rhesus monkeys, as low as 3 mg/kg (HSDB 2000b). Studies with animals fed dieldrin have shown that the liver can be damaged and the ability of the immune system to protect against infections can be suppressed. An oral exposure study fed 1,500 CF1 mice at concentrations of 0.1 to 10 ppm dieldrin. Fifty percent of the mice fed dieldrin at 10 ppm were dead at 15 months and 50% in the other groups were at 20 months. Statistically-significant and dose-related increases in liver tumors occurred in dieldrin-exposed mice in both sexes. Incidences of pulmonary adenomas and pulmonary carcinomas in males and females exposed to dieldrin at 0.1 and 1 ppm were increased above those in controls (Walker et al. 1972). Dieldrin at 1, 2, or 4 mg/kg/day produced hyperplastic goiters in the thyroids of pigeons. Visual exam indicated that the thyroids were significantly enlarged and microscopic exam revealed small follicles with decreased amount of colloid, epithelial hyperplasia, and vascular congestion (NIOSH 1978). Dieldrin affects the central

nervous system. It inhibits gamma amino butyric acid-induced chloride ion uptake into skeletal muscles and the binding of tritiated dihydropicrotoxinin (anion channel probe) to the membrane. This results in central nervous system excitation and convulsions due to the blocking of gamma amino butyric acid transmitter (IPCS 1989). Ingesting moderate levels of dieldrin over a longer period may also cause convulsions as dieldrin builds up in tissues. Dieldrin also caused immunosuppression in mice. Levels of 1 or 5 mg dieldrin/kg diet were fed to BALB/c mice for 3.5 or 10 weeks, this resulted in decreased antibody formation to PVP, a T-independent antigen (IPCS 1989).

Lifetime feeding studies were conducted with Syrian golden hamsters. Groups of nearly equal size (i.e. 32 to 41 per group) of male and female hamsters were fed a diet containing 0, 20, 60, or 80 mg/kg for up to 120 weeks at which time the remaining survivors were killed. While there was no decrease in survival at 50 weeks, the numbers of females remaining at 70 weeks was one-half or less than that of the males. At 90 weeks the survival rate was about 10% for all groups except the males of the 180 mg/kg level which had 32% survivors. Both males and females at the low and high doses demonstrated a marked retardation of growth and it was also noted that there was a dose-related increase in the incidence of hepatic cell hypertrophy in the dieldrin-treated hamsters (USEPA 1980). Purified dieldrin was administered at concentrations between 0.08 and 40 ppm in the diet to Wistar rats for up to 2 years. Nonspecific neural lesions, cranial edema, convulsions, and dieldrin residues in the brain were reported in most exposed rats (NIOSH 1978).

In a reproductive toxicity study, 39 to 140 day old female Wistar rats were fed dieldrin at 2.5 to 10.0 ppm in the diet. Parental mortality and reduced fecundity was noted at 10 ppm. Convulsions in pups was observed at 2.5 ppm (NIOSH 1978). In a teratogenic study, dieldrin was administered in doses of 1.5, 3.0, and 6.0 mg/kg/day on days 7 to 16 of gestation, to DCI mice and CD rats. In mice, the highest dose produced an increased percentage of supernumerary ribs and a decrease in the number of caudal ossification centers (Clayton and Clayton 1994).

Oral doses of dieldrin have caused liver cancer in mice, but not in rats. The Environmental Protection Agency (EPA) considers dieldrin a probable carcinogen based on experiments with animals. A series of experiments on mice involving continuous feeding of recrystallized (>99% pure) dieldrin was found to produce liver-cell tumors, while the incidence of tumors at other sites was either unaffected or decreased in relation to the shorter life span of animals with liver tumors (IARC 1974).

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**A p p e n d i x 3 -
Site-Specific Relation-
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Appendix 3 Site-Specific Relationships Between the Concentrations of Selected Metals in Various Sediment Particle Size Classes for the Tri-State Mining District

1.0 Introduction

A substantial number of studies have been conducted to evaluate sediment quality conditions within the Tri-State Mining District (TSMD; see Appendix 5 for a complete listing of the studies that provided relevant data for assessing risks to ecological receptors in the study area). While the analytical methods that have been used to generate the associated sediment chemistry data are generally comparable, different methods have been used to prepare the sediments for chemical analysis. In some cases, whole-sediment samples were collected and submitted for analysis (sediment that had not been sieved to remove larger particles). In other cases, sediments were sieved before submitting samples to the analytical laboratories, resulting in data that are applicable to the < 63 μm , < 250 μm , and/or < 2000 μm (< 2.00 mm) size classes. Because fine-grained sediments can contain lower or higher concentrations of metals and/or other chemicals of potential concern (COPCs) than do coarse-grained sediments (Ackermann 1980; de Groot and Zschuppe 1981; de Groot *et al.* 1982), these differences in sample preparation procedures have the potential to influence the uses of the resultant data and potentially, the results of the ecological risk assessments.

Chapter 3 and 4 present the results of the screening-level ecological risk assessment (SLERA) that was conducted for the TSMD. For the purposes of screening, the metal concentration data for all of the sediment size classes were considered to be roughly equivalent and were used directly in the SLERA (i.e., all of the COPC concentration data were compared directly to the selected toxicity screening values; TSV). Because the selected TSVs are considered to be conservative, this simplifying assumption was thought to have little influence on the results of the SLERA. While this approach was considered to be appropriate and reasonable for the purposes of screening, further evaluation of the impact of this assumption is warranted to support the detailed ecological risk assessment (DERA). For this reason, the site-specific relationships between the concentrations of selected metals (i.e., cadmium, lead, and zinc, the principal COPCs in the TSMD) in the various particle size fractions were evaluated. This appendix presents the results of these evaluations.

1.1 Methods

A step-wise approach was used to evaluate the relationships between the concentrations of cadmium, lead, and zinc in various particle sizes of sediment samples from the TSMD. These metals were selected for further evaluation because they have been identified as primary COPCs in the TSMD and because site-specific toxicity thresholds have been established for these metals (MacDonald *et al.* 2009). As a first step, data that provided matching chemical concentrations for two or more particle sizes were identified and compiled in the project database. Next, the relevant data were extracted from the project database and imported into SigmaPlot to facilitate data analysis. For each metal, the following relationships were evaluated:

- Concentration in < 63 μm fraction vs. concentration in < 2000 μm fraction;
- Concentration in < 250 μm fraction vs. concentration in < 2000 μm fraction; and,
- Concentration in whole sediment vs. concentration in < 2000 μm fraction.

These relationships were explored because MacDonald *et al.* (2009) developed site-specific toxicity thresholds for benthic invertebrates that were directly applicable to the < 2000 μm fraction. Normalization of all sediment chemistry to the < 2000 μm fraction was used because this is the size fraction of sediment that was used to conduct the TSMD toxicity or bioaccumulation tests with amphipods, midge or oligochaetes. Larger size fractions of sediment may also contain COPCs that are not highly bioavailable to sediment-dwelling organisms. Accordingly, procedures for expressing whole-sediment, < 250 μm , and < 63 μm chemistry data as < 2000 μm equivalents were needed to support the DERA. Subsequently, the preliminary plots were reviewed to identify outliers in the underlying data. Finally, definitive plots were prepared by removing outliers (e.g., samples with very high concentrations of zinc, cadmium, or lead in a particular size fraction) and re-plotting the relationships for each particle-size fraction pair for each of the three metals. Simple linear regressions were fitted to the underlying data in SigmaPlot and the resultant equations, coefficients of determination (r^2), and p-values were reported.

1.2 Results and Discussion

The relationships between the concentrations of cadmium, lead, and zinc in the < 63 μm fraction and the concentrations in < 2000 μm fraction are presented in Figures A3.1, A3.2 and A3.3. Both the regression lines and the unity lines are shown on these plots. Evaluation of these relationships suggests that the concentrations of cadmium, lead, and zinc tend to be similar for these two particle size fractions. For cadmium, the measured concentration in the < 2000 μm fraction explained about 78% of the variability in the data for the < 63 μm fraction (Figure A3.1; $r^2 = 0.78$; $p < 0.0001$). The results for lead were similar, but the regression was not significant at the $p < 0.05$ level (Figure A3.2; $r^2 = 0.17$; $p = 0.054$). While the underlying data were more variable for zinc, the regression was significant (Figure A3.3; $r^2 = 0.68$; $p <$

0.0001). For cadmium and zinc, the slope of the regression line was close to unity, indicating that the concentration of these metals in the < 63 μm fraction provides a reasonable estimate of the concentrations in the < 2000 μm fraction.

The relationships between the concentrations of cadmium, lead, and zinc in the < 250 μm fraction and the concentrations in < 2000 μm fraction are presented in Figures A3.4, A3.5 and A3.6. Both the regression lines and the unity lines are shown on these plots. Evaluation of these graphs suggests that the concentrations of cadmium, lead, and zinc tend to be similar for these two particle size fractions. More specifically, the measured concentrations of cadmium in the < 2000 μm fraction explained about 59% of the variability in the concentration data for the < 250 μm fraction (Figure A3.4; $r^2 = 0.59$; $p < 0.0001$). Concentrations in the < 250 μm and < 2000 μm size fractions were also well correlated for lead (Figure A3.5; $r^2 = 0.54$; $p < 0.0001$). Similarly, the concentrations of zinc in the < 250 μm and < 2000 μm size fractions were high correlated, as evidenced by the r^2 (0.84) and p -values (< 0.0001 ; Figure A3.6). For all three metals, the slope of the regression line was close to one. As such, the concentrations of these metals in the < 250 μm fraction provide reasonable estimates of the concentrations in the < 2000 μm fraction.

The relationships between the concentrations of cadmium, lead, and zinc in whole sediment in the < 2000 μm fraction are presented in Figures A3.7, A3.8 and A3.9. Both the regression lines and the unity lines are shown on these plots. Evaluation of these results indicates that the concentrations of cadmium, lead, and zinc tend to be higher in the < 2000 μm fraction than they are in whole sediment. While the underlying data were variable, the measured concentration of cadmium in the < 2000 μm fraction explained about 50% of the variability in the data for whole sediment (Figure A3.7; $r^2 = 0.51$; $p = 0.0004$). The results for lead showed that the concentrations in the whole sediment and < 2000 μm fractions were strongly correlated (Figure A3.8; $r^2 = 0.87$; $p = 0.0001$). While the underlying data were more variable for zinc, the resultant regression was significant (Figure A3.9; $r^2 = 0.49$; $p = 0.0006$). The slope of the regression lines were not close to unity for any of the three metals, however; indicating that the concentration of these metals in whole sediment would not provide a reasonable estimates of the concentrations in the < 2000 μm fraction. As the slopes of all three regression lines were similar (0.612, 0.488, and 0.607; mean = 0.569, standard deviation = 0.070), the slopes were averaged to obtain a multiplier that could be used for all three chemicals (i.e., 1.76); calculated as the inverse of the average slope).

1.3 Conclusions

Relationships between the concentrations of metals (cadmium, lead, and zinc) in various particle size classes were evaluated. The results of these evaluations showed that the concentrations of these metals in the < 63 μm , < 250 μm , and < 2000 μm size fractions were similar. Accordingly, it is concluded that the measured concentrations of cadmium, lead, and zinc in the < 63 μm or < 250 μm can be treated as roughly equivalent to the concentrations

of these metals in the < 2000 μm size fraction (i.e., no multiplier is needed to convert the data for the < 63 μm or < 250 μm fractions to facilitate comparison to the site-specific toxicity thresholds that apply to the < 2000 μm size fraction). In contrast, the concentrations of these metals were substantially lower in whole sediment than they are in the < 2000 μm size fraction. For this reason, a multiplier of 1.76 was developed to estimate concentrations in the < 2000 μm size fraction from the whole-sediment chemistry data for these metals.

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Figure A3.4. Relationship between the concentration of cadmium in < 250 μm samples and < 2000 μm sediment samples from the Tri-State Mining District.

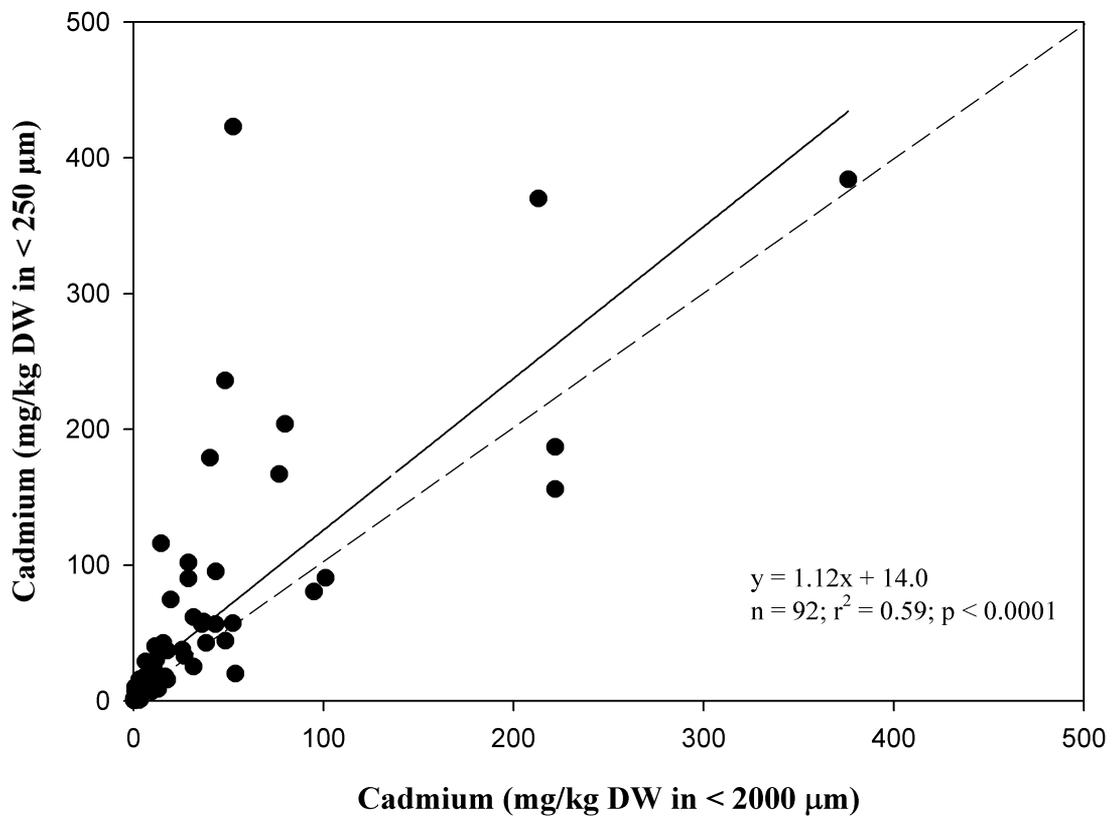


Figure A3.5. Relationship between the concentration of lead in < 250 μm samples and < 2000 μm sediment samples from the Tri-State Mining District.

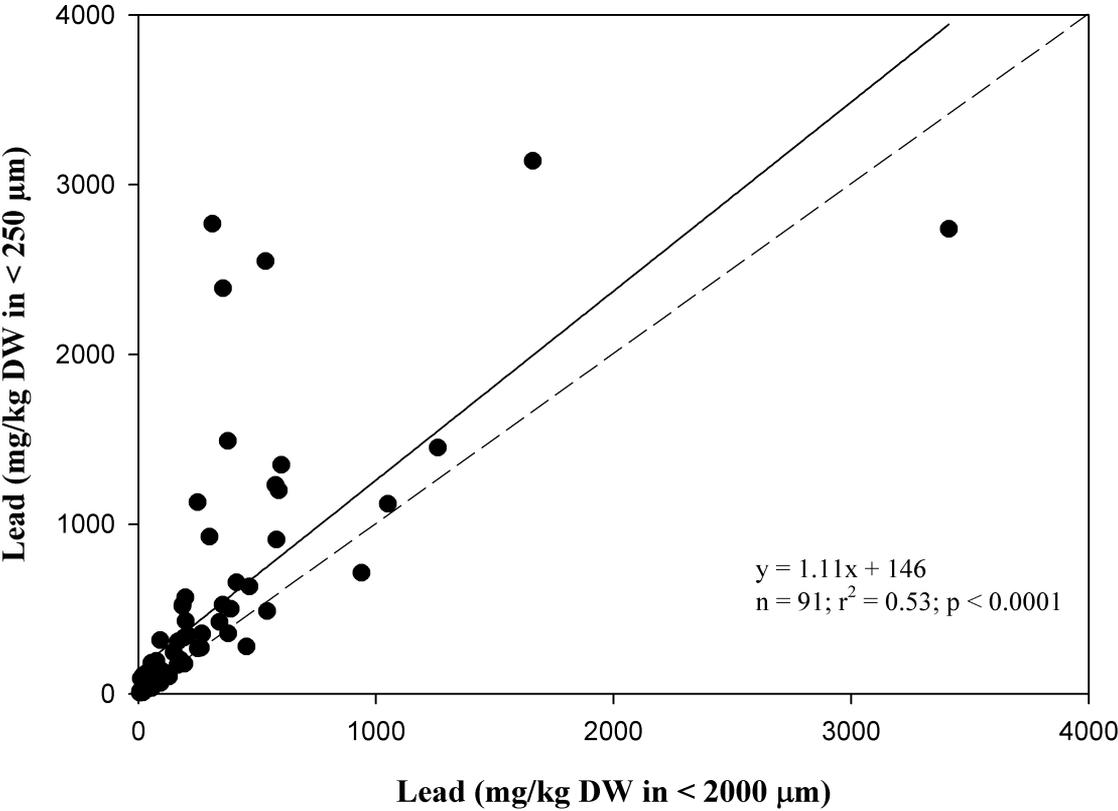


Figure A3.6. Relationship between the concentration of zinc in < 250 μm samples and < 2000 μm sediment samples from the Tri-State Mining District.

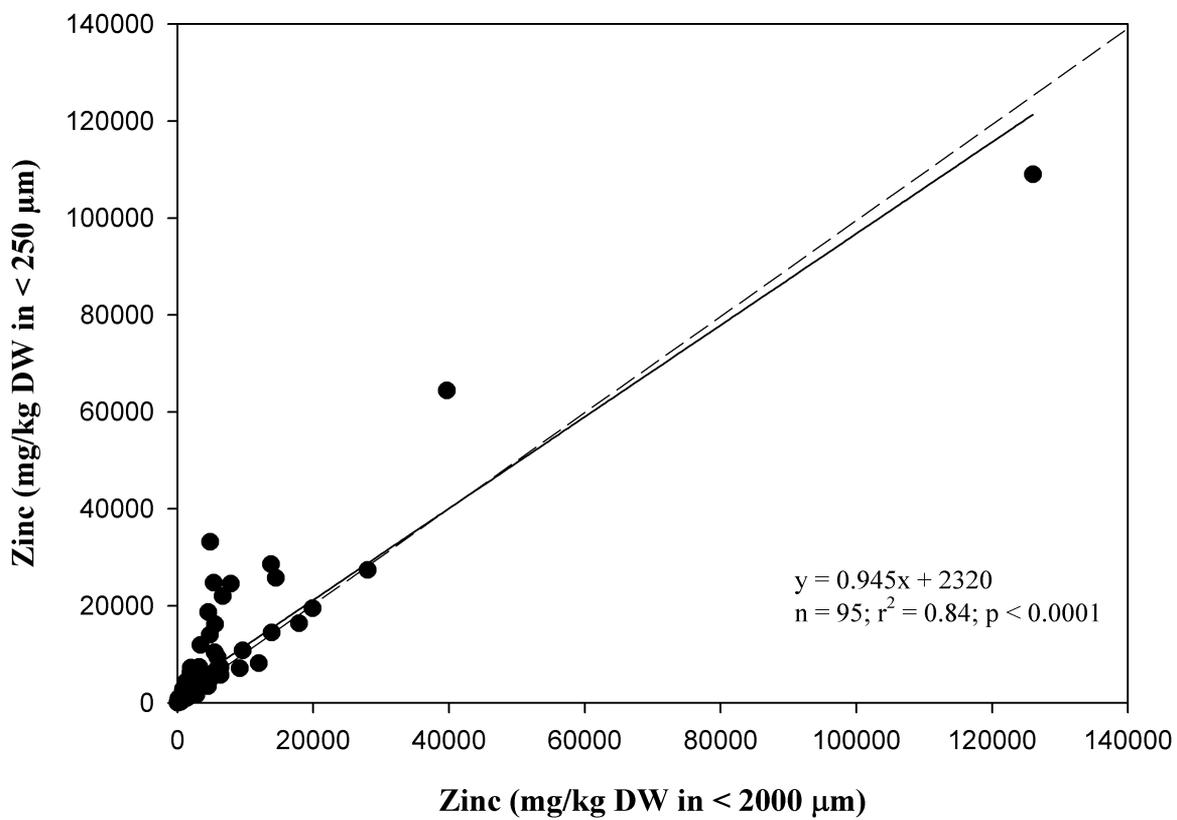


Figure A3.7. Relationship between the concentration of cadmium in whole-sediment samples and < 2000 μm sediment samples from the Tri-State Mining District.

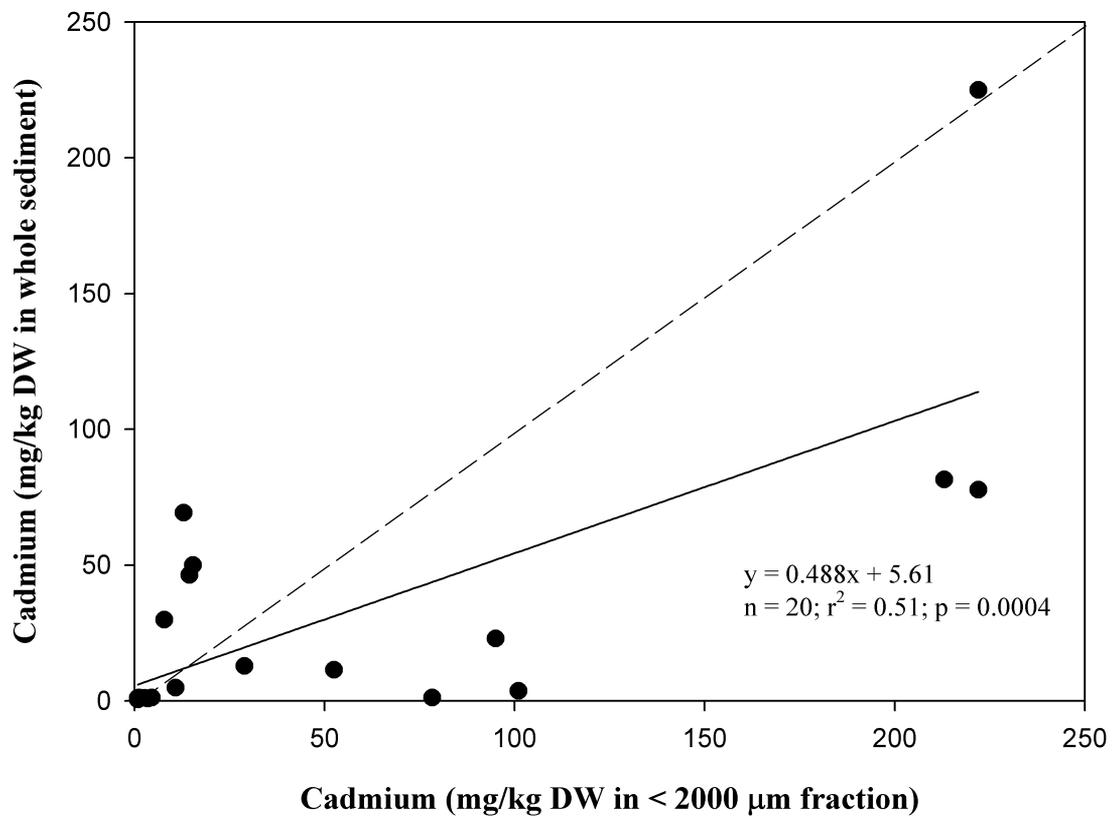
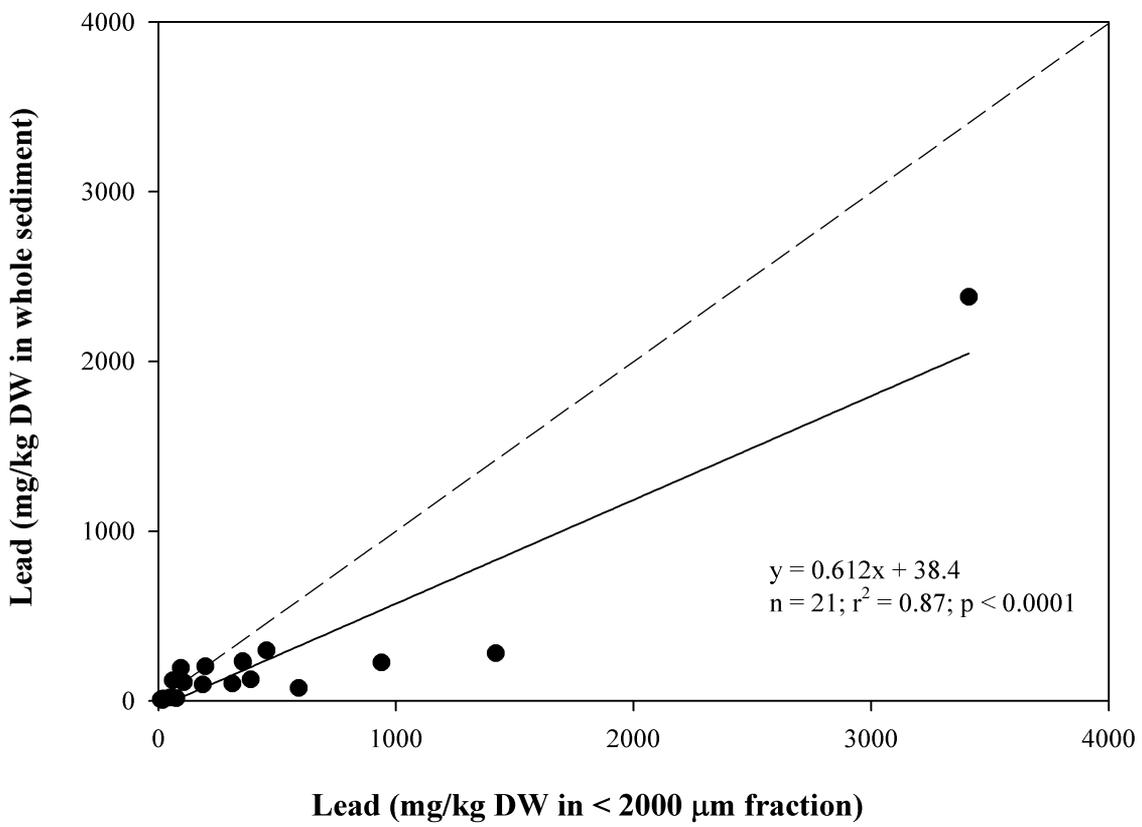


Figure A3.8. Relationship between the concentration of lead in whole-sediment samples and < 2000 μm sediment samples from the Tri-State Mining District.



Appendix 4 - Procedures for Interpreting the Results of Sediment Toxicity Tests

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Appendix 4 Procedures for Interpreting the Results of Sediment Toxicity Tests

1.0 Introduction

A number of sediment toxicity tests have been conducted to evaluate the effects on benthic invertebrates associated with exposure to contaminated sediments in the Tri-State Mining District (TSMD). More specifically, 10-d sediment toxicity tests with the midge, *Chironomus dilutus*, 28-d sediment toxicity tests with the amphipod, *Hyaella azteca*, and 28-d sediment toxicity tests with the freshwater mussel, *Lampsilis siliquoidea*, have been conducted on up to 76 sediment samples from the study area (Endpoints: survival, growth, and biomass for all of the tests). Interpretation of the results of these toxicity tests requires a procedure for designating the samples as toxic or not toxic to benthic invertebrates. This appendix describes the procedures that were used to interpret the results of the toxicity tests that were conducted in the TSMD to evaluate risks to the benthic invertebrate community

1.1 Approaches for Interpreting the Results of Sediment Toxicity Tests

A number of approaches can be used to interpret the results of whole-sediment toxicity tests with benthic invertebrates. These approaches can be classified into four general categories, including control comparison approach, minimum significant difference approach, reference envelope approach, and the multiple category approach. Each of these approaches are briefly described below:

- **Control Comparison Approach** - Application of the control comparison approach involves statistical comparison of the responses of test organisms exposed to site sediments to the responses of test organisms exposed to control sediments. Treatment(s) that have responses that are significantly different from those observed in the control treatment(s) are designated as toxic.
- **Minimum Significant Difference Approach** - Application of the minimum significant difference approach is dependent on the completion of power analyses with data from multiple studies for a specific toxicity test. These results are used to identify the minimum significant difference (MSD or minimum detectable difference; MDD) from the control treatment. Treatments with response levels

greater than the MSD are designated as toxic (Thursby *et al.* 1997; Phillips *et al.* 2001).

- **Reference Envelope Approach** - Application of the reference envelope approach involves collection and testing of sediment samples from a number of reference sites within or nearby the study area. In this context, a reference sediment sample is considered to be a whole-sediment sample obtained near an area of concern used to assess sediment conditions exclusive of the materials of interest [i.e., chemicals of potential concern (COPCs); ASTM 2009]. The results of the toxicity testing conducted on these samples can be used to develop a reference envelope (i.e., normal range of responses of test organisms exposed to reference sediments, as defined by ASTM 2009). Sediment samples with response levels that fall outside the normal range of responses (e.g., survival below the 5th percentile for the reference samples) are designated as toxic.
- **Multiple Category Approach** - Application of the multiple category approach involves classifying sediment samples into various groups (e.g., not toxic, low toxicity, moderate toxicity, or high toxicity), based on the magnitude of the observed response. The results of statistical comparisons to the negative control results are also used to classify sediment samples into the various categories.

In 2007, the Sustainable Fisheries Foundation (SFF) convened an experts workshop in Victoria on behalf of the Ministry of the Environment of British Columbia to explore the question of how to interpret the results of sediment toxicity tests (SFF 2007). At this workshop, participants agreed that site-wide ecological risk assessments represent the most important applications of whole-sediment toxicity data. More specifically, it was agreed that the results of the toxicity-testing program that is implemented at a site should support the development of site-specific toxicity thresholds (i.e., to support development of preliminary remediation goals and/or clean-up goals). In this context, the magnitude of effect data can be used directly in the development of concentration-response relationships for COPCs at the site. The magnitude of effect data can also be used to classify sediment samples into risk categories, without having to designate individual sediment samples groups as toxic or not toxic. This approach to the interpretation of whole-sediment toxicity data was considered to be desirable because no information is lost during the interpretation process.

1.2 Interpretation of the Results of Toxicity Tests Using the Reference Envelope Approach

Workshop participants also recognized that interpretation of toxicity test results may necessitate designation of individual sediment samples as toxic or not toxic (e.g., hot spot

identification, evaluation of the incidence or spatial extent of toxicity; SSF 2007). In these cases, workshop participants agreed that a step-wise approach should be used to interpret the results of individual toxicity tests. The approach suggested by workshop participants was adapted to support toxicity designation for the sediment samples collected within the TSMD, as follows:

- Conduct whole-sediment toxicity tests in accordance with standardized protocols, as described in the project Quality Assurance Project Plan (QAPP);
- Evaluate the validity of each whole-sediment toxicity test. The project data quality objectives, which are documented in the QAPP, should define the performance criteria for measurement data that will be used to evaluate toxicity test acceptability. At minimum, such performance criteria should define the acceptable range of negative control and positive control (i.e., reference toxicant) results. Evaluation of potential test interferences should also be conducted during this step in the process (e.g., comparison of ammonia and hydrogen sulfide levels to lowest observed effect concentrations for the test species);
- Conduct analysis of variance to determine if responses are significantly different between two or more samples within a batch of samples. Proceed with reference envelope calculations only if significantly different response rates are observed for two or more samples;
- Compare the toxicity test results obtained for each sediment sample to the reference envelope developed for the corresponding toxicity test endpoint. Sediment samples would be designated as toxic if the measured control-adjusted response is below the lower limit of responses for reference sediment samples (e.g., if the reference envelope for amphipod control-adjusted survival in a 28-d whole-sediment toxicity test is 77 to 98%, then sediment samples for which amphipod survival is less than 77% would be designated as toxic). Control-adjusted response rates for reference sediment samples should be used to develop the reference envelope because the negative control results for multiple batches of samples may be different; and,
- Sediment samples for which the control-adjusted response of the test organism falls within the reference envelope should not be designated as toxic and should be considered to pose the lowest risks to the benthic invertebrate community.

1.3 Development of Reference Envelopes for Interpreting the Results of Sediment Toxicity Tests

In general, application of the reference envelope approach necessitates identification of candidate reference sites as part of the overall sampling program design. The following procedure was used for developing reference envelopes for the toxicity test endpoints that have been used to characterize sediment quality conditions in the TSMD:

- Sediment samples from the study area that are representative of reference conditions were identified. Candidate reference sediment samples were identified on an *a posteriori* basis by applying a series of criteria for sediment chemistry and sediment toxicity.
- The following criteria for sediment chemistry were used for identifying candidate reference sample (USEPA 2003; 2005; MacDonald *et al.* 2007):
 - Mean PEC-Q < 0.1;
 - Mean PEC-Q_{metals(1% OC)} < 0.1;
 - $(\sum \text{SEM-AVS})/f_{\text{oc}} < 130$;
 - $\sum \text{ESB-TU}_{\text{PAHs}} < 0.1$;
 - PEC-Q_{tPAHs} < 0.1; and,
 - PEC-Q_{tPCBs} < 0.1.

(PEC-Q = probable effect concentration quotient; $\sum \text{SEM-AVS}$ = sum simultaneously extracted metals minus acid volatile sulfides; $\sum \text{ESB-TU}$ = sum equilibrium partitioning-based sediment benchmarks toxic unit; f_{oc} = fraction organic carbon; tPAH = total polycyclic aromatic hydrocarbons; tPCB = total polychlorinated biphenyl)

- Candidate reference samples that met the criteria for whole-sediment chemistry, were further evaluated to confirm that they were not toxic to sediment-dwelling organisms. More specifically, reference sediment samples were required to meet the criteria for an acceptable negative control treatment. These biological criteria were applied to ensure that samples for which the biological response may have been adversely affected due to the presence of unmeasured COPCs (or COPCs for which sediment quality guidelines are not available) were not used in the reference envelope calculation.
- Sediment samples that meet both the chemical and biological criteria were selected as reference samples for the study area.
- The normal range of toxicological responses for each toxicity test conducted and endpoint measured was then determined for the reference samples. The reference

envelope is commonly calculated in a manner such that it encompasses 95% of the variability in the response data for the reference samples. While several procedures could have been used to calculate the reference envelope, the lower limit of the reference envelope was calculated as the minimum of the control-adjusted response data for each toxicity test endpoint for the reference samples. The normal range of reference responses was considered to span the range from the minimum value to the maximum value in the data set.

- Sediment samples with effect values lower than the lower limit of the normal range of control-adjusted responses in reference samples (i.e., lower than the 5th percentile) were designated as toxic for the endpoint under consideration (see Appendix E2 of the MacDonald *et al.* 2002 for a more detailed description of these procedures).

It is important to note that application of this approach results in the designation of toxicity on an endpoint-by-endpoint basis. Therefore, a single sample can be designated as toxic for certain endpoints and not toxic for other endpoints. This reflects differences in species sensitivities and responses to different mechanisms of toxic action, as represented by the mixture of contaminants in the sediments.

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**Appendix 5 -
Summary of Candidate
Data Sets Available to
Support the SLERA of
the Tri-State Mining
District.**

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Appendix 5. Summary of candidate data sets compiled to support the screening level ecological risk assessment of the Tri-State Mining District.

Source/ Description	Sampling Dates	Media Type	Number of Samples	Particle Size Fraction	Analytes Measured							
					Metals (ICP-MS)	Dissolved Metals (ICAP)	Conventionals	Metals (XRF)	SEM/ AVS	Organics	TOC	Grain Size
<u>Angelo et al. (2007; unpublished data)</u>												
Water quality samples collected in the Kansas portion of the TSMD												
	2002-06	Sediment	114	<250 µm; <63 µm	x							
	2002-06	Tissue	218	NA	x							
<u>Eastern Shawnee Tribe of Oklahoma (2005; unpublished data)</u>												
Eastern Shawnee Tribe of Oklahoma; Samps collected in 2003-2005												
EPA STORET DB	2003-05	Water	25	NA	x			x				
<u>Kirschner (2008; unpublished data)</u>												
Sediment samples collected by the Quapaw tribe in 2005												
	June, 2005	Sediment	117	<63 um	x			x				
<u>HSPH (2007; unpublished data)</u>												
HSPH Tar Creek Data (2005-2007)												
	2005-06	Water	38	NA	x	x		x				
	2006	Sediment (cores)	59	WS				x	x			
	2006-07	Floodplain soils	104	<2 mm				x	x			
<u>Juracek (2006)</u>												
Sediment samples collected from Empire Lake in 2005												
	2005	Sediment	68	<63 um	x			x				x
<u>ODEQ (2005; unpublished data)</u>												
ODEQ/USGS (2004-2005), Surface-Water Quality in the Grand-Neosho River Basin, NE Oklahoma												
	2004-05	Water	666	NA	x	x		x				
	2004-05	Sediment	114	WS	x	x		x				

Appendix 5. Summary of candidate data sets compiled to support the screening level ecological risk assessment of the Tri-State Mining District.

Source/ Description	Sampling Dates	Media Type	Number of Samples	Particle Size Fraction	Analytes Measured							
					Metals (ICP-MS)	Dissolved Metals (ICAP)	Conventionals	Metals (XRF)	SEM/ AVS	Organics	TOC	Grain Size
<u>ODEQ (2008)</u>												
Fish tissue samples collected by ODEQ in 2006												
	2006	Fish	95	NA	x			x				
Water, sediment and fish tissue samples collected concurrently by ODEQ in 2002 (includes river and pond samples).												
	2002	Fish	69	NA	x			x				
	2005	Water	6	NA	x	x		x				
	2005	Sediment	6	WS	x							
<u>Pope (2005)</u>												
Sediment samples collected from the Kansas portion of the TSMD in 2004												
	2004	Sediment	101	<63 um	x			x				x
<u>Quapaw Tribe of Oklahoma (2005; unpublished data)</u>												
Quapaw Tribe of Oklahoma; Samples collected in 2003-2005												
EPA STORET DB	2003-05	Water	89	NA	x	x		x				
<u>USEPA (2006; unpublished data)</u>												
USEPA sediment samples collected in 2006												
	2006	Sediment	310	WS	x				x		x	x
	2006	Surface Water	240	NA	x			x			x	
	2006	Porewater	26	NA		x		x				
<u>USEPA (2007; unpublished data)</u>												
USEPA sediment samples collected in 2007												
	2007	Sediment	70	<2 mm	x				x	x	x	x
		Sediment	70	<250 µm	x						x	
		Porewater	70	NA		x		x				
		Tissue	21	NA	x							

Appendix 5. Summary of candidate data sets compiled to support the screening level ecological risk assessment of the Tri-State Mining District.

Source/ Description	Sampling Dates	Media Type	Number of Samples	Particle Size Fraction	Analytes Measured							
					Metals (ICP-MS)	Dissolved Metals (ICAP)	Conventionals	Metals (XRF)	SEM/ AVS	Organics	TOC	Grain Size
<u>USEPA (2009; unpublished data)</u>												
<u>Tar Creek OU5 Transect Data from CH2MHill</u>												
	2009	Sediment	75		x							
		Seep Sediment	16		x							
		Seep Water	22		x		x					
		Surface Water	163		x		x					
<u>USFWS (2007; unpublished data)</u>												
<u>Sediment samples collected by USFWS in 2007; samples collected along 7 transects in the upper 1/3 of Grand Lake.</u>												
	March, 2007	Sediment	6	WS	x			x	x		x	x
<u>USFWS (2006; unpublished data)</u>												
<u>Splits of USEPA sediment samples collected in 2006 for chemical analysis of various grainsizes</u>												
	2006	Sediment	172		x							
<u>USGS (2004; unpublished data)</u>												
<u>USGS KS, Sediment samples collected by USGS in 2004 for select locations</u>												
	2004	Sediment	53	<63 um	x		x					
<u>USGS (2006; unpublished data)</u>												
<u>Matching sediment chemistry and toxicity data for sediment samples collected by USGS in 2006</u>												
	2006	Sediment (chem and tox)	6	<2 mm				x			x	x

NA = not available; SEM/AVS = simultaneously extracted metals/acid volatile sulfides; ICAP = inductively coupled argon plasma; ICP-MS = inductively-coupled plasma - mass spectrometry; XRF = X-Ray Fluorescence.

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**Appendix 6 - Overview
of the Quality of the Data
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Appendix 6 Overview of the Quality of the Data Collected During the 2007 Sediment Sampling Program (as excerpted from Ingersoll *et al.* 2008)

A. Sediment toxicity and sediment bioaccumulation testing data

Appendix A of Ingersoll *et al.* (2008) provides a summary of the data for the toxicity tests and bioaccumulation tests conducted with samples from the TSMD (n=76 sediment toxicity samples for amphipods and midges, n=48 sediment toxicity samples for mussels, and n=21 sediment bioaccumulation samples for oligochaetes across the three sediment sampling events; Table 1, of Ingersoll *et al.* 2008). Table A1 of Ingersoll *et al.* (2008) summarizes the water quality characteristics of the pore-water samples isolated by centrifugation at the start of the sediment toxicity and sediment bioaccumulation tests. Table A2 of Ingersoll *et al.* (2008) summarizes the mean water quality characteristics of the overlying water sampled during the sediment toxicity and sediment bioaccumulation tests. Table A3 of Ingersoll *et al.* (2008) summarizes the mean treatment responses of test organisms in each sediment toxicity treatment. Table A4 of Ingersoll *et al.* (2008) summarizes the treatment responses of test organisms in each replicate beaker within each sediment toxicity treatment. Table A5 of Ingersoll *et al.* (2008) summarizes the body length measurements of individual amphipods (and the associated estimated weight of individual amphipods) and shell length measurements of individual mussels within each beaker within each sediment treatment. Appendix B of Ingersoll *et al.* (2008) provides a summary of the bioaccumulation of metals by oligochaetes within each replicate beaker and as treatment mean responses. Table 6 of Ingersoll *et al.* (2008) provides a summary of the response of test organisms in the control sediment and a summary of the size or age of test organisms at the start of the sediment toxicity and sediment bioaccumulation tests. Table 6 of Ingersoll *et al.* (2008) also provides a summary of the response of test organisms in 48- to 96-hour water-only NaCl reference toxicant tests conducted in conjunction with the sediment toxicity and sediment bioaccumulation tests.

The Quality Assurance Project Plan (of I) for the project established acceptable levels of precision, accuracy, completeness and sensitivity for the chemical, physical, or biological data measured in the sediment toxicity and sediment bioaccumulation tests (Table 5 in the QAPP, Ingersoll 2007). Precision in the sediment toxicity and sediment bioaccumulation tests was established based on analyses of laboratory duplicates of pore-water samples (Table A1 of Ingersoll *et al.* 2008). Relative percent deviation between duplicate measures of water quality characteristics of pore water were typically less than 20%; however, wider ranges were observed for ammonia for some duplicate samples (e.g., sample CERC-19; Table A1 of Ingersoll *et al.* 2008).

For biological data measured in sediment toxicity or sediment bioaccumulation tests, no true accuracy estimates are possible because of the lack of available standard sediment(s) (Ingersoll 2007). Instead, accuracy was established for sediment toxicity testing based on test

acceptability for test organisms in the negative control sediment [without the addition of the test chemical; American Society for Testing and Materials (ASTM) 2008a, USEPA 2000].

Completeness was established as the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Target completeness was established as 90% for chemical analyses of pore water, overlying water, toxicity tests, and bioaccumulation tests (Ingersoll 2007). Sensitivity of toxicity test organisms was evaluated using 48- to 96-hour reference toxicant water-only exposures with NaCl (Table 6 of Ingersoll *et al.* 2008, described below).

Amphipod toxicity tests: Mean 28-d survival of amphipods in control sediment ranged from 90 to 100% across the three sets of sediment tests (Set 1, 2, and 3; Table 6 of Ingersoll *et al.* 2008). Mean 28-d body length of amphipods in control sediment ranged from 3.41 to 4.35 mm, with increases ranging from 2.2 to 3.6X (Table 6 of Ingersoll *et al.* 2008). Both control mean survival and growth exceeded the test acceptability criteria (ASTM 2008a, USEPA 2000; Table 6 of Ingersoll *et al.* 2008). Hence, the data quality objectives (DQOs) were met for all of the amphipod toxicity tests (as identified in Table A1.1 of the QAPP, Ingersoll 2007). Specifically, completeness was 100% for the 76 sediment samples evaluated in sediment toxicity tests conducted with amphipods (based on performance of amphipods in control sediment; Table 6 of Ingersoll *et al.* 2008). More than 11 test organisms were recovered from CERC-41, replicate 2 (Table A4 of Ingersoll *et al.* 2008), so this replicate was not included in the calculation of the mean response of test organisms in this treatment (Table A3 of Ingersoll *et al.* 2008).

Mean starting lengths of amphipods (range from 1.21 to 1.54 mm) were consistent with the starting length of about 7-d-old amphipods historically used to start sediment toxicity tests at the USGS laboratory in Columbia, MO (Table 6 of Ingersoll *et al.* 2008). Because of the difference in mean length of amphipods in the control sediment on Day 28 (3.41 mm for Set 2 to 4.35 mm for Set 1; Table 6 of Ingersoll *et al.* 2008) amphipod lengths in the test sediment were normalized to the percent of control response (Table A3 of Ingersoll *et al.* 2008). Estimated mean weight of amphipods in the control sediment at Day 28 ranged from 0.20 to 0.41 mg/individual and estimated mean biomass of amphipods in control sediment at Day 28 ranged from 1.7 to 3.9 mg/treatment (Table 6 of Ingersoll *et al.* 2008). No guidance is provided in USEPA (2000) or in ASTM (2008a) regarding acceptable growth of control organisms (other than the statement that amphipods in the control sediment should grow during the 28-d exposure). The response of amphipods in the two 48-hour water-only NaCl reference toxicant tests (LC50s) was 5.7 and 6.1 g/L (Table 6 of Ingersoll *et al.* 2008) and is representative of historic reference toxicant tests for amphipods conducted at the CERC laboratory in ASTM hard water (ASTM 2008d). No reference toxicant tests were conducted with amphipods associated with the Set 3 samples conducted in 2006.

Midge toxicity tests: For the Set 1 and Set 2 sediment samples tested in 2007, mean survival of midges in the control sediment was 83% in Set 1 to 95% in Set 2 (Table 6 of Ingersoll *et al.* 2008) and exceeded the test acceptability criterion (ASTM 2008a, USEPA 2000, Table

6 of Ingersoll *et al.* 2008). For the Set 3 sediment samples tested in 2006, mean 10-d survival of midges in the control sediment was 53% (n=6 TSMD samples; Table 6 of Ingersoll *et al.* 2008) which was less than the test acceptability criterion of 70% mean control survival (USEPA 2000, ASTM 2008a).

Before the start of the sediment toxicity tests conducted with the Set 1 and Set 2 samples evaluated in 2007, personnel at the USEPA laboratory in Duluth, Minnesota (MN) were contacted to discuss the poor control performance of the midge associated with the Set 3 samples (and in other studies conducted at the CERC laboratory). Two changes to the ASTM (2008a) and USEPA (2000) method were suggested for conducting 10-d sediment toxicity tests with *C. dilutus* to improve performance of midges in control sediment. The changes included: (1) starting toxicity tests with larvae less than 10-d old (to reduce the possibility of larvae emerging by the end of a 10-d sediment exposure) and (2) starting the exposures with larvae isolated from cultures still in their surrounding tubes rather than with larvae that have left (or have been removed from) their culture tubes (Dave Mount, USEPA, Duluth MN; personal communication). Larvae outside of their culture tubes may not be as healthy as larvae still inside their culture tubes. Once in the sediment exposures, larvae will typically rebuild their tubes with material in the beakers within 24 hours (Dave Mount, personal communication).

In 2007, the CERC laboratory implemented these two revisions to the ASTM (2008a) and USEPA (2000) method for conducting 10-d sediment toxicity tests with *C. dilutus* and improved control survival of midges was observed in the Set 1 and Set 2 sediments evaluated in 2007 and improved control survival has been observed in other subsequent midge sediment toxicity tests conducted at the CERC laboratory (>80% and typically >90% survival of midges in control sediment).

Mean 10-d ash-free-dry weight of midges in the control sediment was 1.51 mg/individual in Set 1, 1.33 mg/individual in Set 2, and 1.41 mg/individual in Set 3 (Table 6 of Ingersoll *et al.* 2008). Mean weight of midges in controls at Day 10 for all three sets of sediment tests met the test acceptability criterion of 0.48 mg/individual (Table 6 of Ingersoll *et al.* 2008; ASTM 2008a, USEPA 2000). Mean biomass of midges in control sediment at Day 10 ranged from 9.71 to 12.7 mg/treatment (Table 6 of Ingersoll *et al.* 2008). No guidance is provided in USEPA (2000) or in ASTM (2008a) regarding acceptable mean biomass of control organisms at Day 10. The DQOs were met for all of the sediments evaluated with midges in 2007; however, the 6 samples evaluated with midges in 2006 did not meet test acceptability requirements (as identified in Table A1.1 of the QAPP, Ingersoll 2007). Specifically, completeness was 92% (70 of the 76 sediment samples) in the sediment toxicity tests conducted with midges (the six Set 3 midge samples did not meet acceptability requirements based on poor control survival in this test; Table 6 of Ingersoll *et al.* 2008). An error was made in weighing two replicate chambers of midges at the end of the exposure to CERC-55 sediment (negative weight for these two replicates, Table A4 of Ingersoll *et al.* 2008), so these two replicates were not included in the calculation of the mean response of midges in Table A3. If more than 11 test organisms were recovered from a replicate, this replicate was

not included in the calculation of the mean test organism response for that treatment in Table A3 (i.e., [CERC-4, replicate 3]; [CERC-25, replicate 4]; [CERC-27, replicate 2]; [CERC-41, replicate 2]; [CERC-S6, replicate 3]; [CERC-WB, Set 1, replicate 3]; and [CERC-WB, Set 3, replicate 4]; Table A4 of Ingersoll *et al.* 2008). Extra midge larvae in these treatments may have resulted from inadvertently transferring two midge larvae at a time with some of the individual tubes from the cultures.

Average ash-free-dry weight of midge larvae at the start of the tests was 0.08 mg/individual in Set 1, 0.31 mg/individual in Set 2, and 0.25 mg/individual in Set 3 (Table 6 of Ingersoll *et al.* 2008). This wide range may have resulted from only weighing two replicates of 10 organisms each at the start of the sediment exposures. The proportional increase in mean weight of midges at Day 10 in the control sediment ranged from 4.3 to 19X (which may reflect high variance in the two replicate weight measurements at the start of the exposures). The CERC laboratory is now measuring at least 4 replicates of 10 organisms each at the start of midge exposures, with lower variance observed in starting weight of midge larvae. Control survival of midges in the 96-hour water only reference toxicant test conducted in conjunction with the first set of sediment samples was 85%, which is below the acceptability criterion of 90% (Table 6 of Ingersoll *et al.* 2008; ASTM 2008a, USEPA 2000). Even with the low control survival, the response of midges in the two water-only NaCl reference toxicant tests (LC50s) was 7.0 and 9.1 g/L, and is representative of historic reference toxicant tests for midges conducted at the CERC laboratory in ASTM hard water (ASTM 2008d; no reference toxicant tests were conducted with midges associated with the Set 3 samples).

Mussel toxicity tests: Mean 28-d survival of mussels in control sediment ranged from 88 to 100% across the three sets of sediment tests (Table 6 of Ingersoll *et al.* 2008). Mean survival of mussels in the control sediment exceeded a test acceptability criterion of 80% established for this study based the test acceptability criterion for water-only 28-d mussel toxicity tests (ASTM 2008b; Table 6 of Ingersoll *et al.* 2008). Mean shell length of mussels in control sediment on Day 28 was 2.56 mm/individual in Set 1, 3.18 mm/individual in Set 2, and 1.66 mm/individual in Set 3 with increases from Day 0 shell lengths ranging from 1.4 to 1.7X (Table 6 of Ingersoll *et al.* 2008). Mean weight of mussels in the control sediment at Day 28 ranged from 0.29 to 2.2 mg/individual and mean biomass of mussels in control sediment at Day 28 ranged from 2.5 to 21 mg/treatment (Table 6 of Ingersoll *et al.* 2008). The wide range in mean length, mean weight and mean biomass reflects the wide range in age and size of the mussels at the start of the exposures (Set 1: 3-months old, Set 2: about 4-months old, and Set 3: about 2 months old at the start of the exposures). No guidance is provided by ASTM (2008b) regarding acceptability of mussel growth in 28-d water-only or sediment exposures. The DQOs were met for all of the mussel toxicity tests (as identified in Table A1.1 of the QAPP, Ingersoll 2007) and specifically, completeness was 100% for the 48 sediment samples evaluated in sediment toxicity tests conducted with mussels (based on performance of mussels in control sediment; Table 6 of Ingersoll *et al.* 2008). The response of mussels in the two 96-hour water-only NaCl reference toxicant tests (LC50s) was 3.1 and 3.3 g/L (Table 6 of Ingersoll *et al.* 2008) and is representative of historic reference toxicant tests for juvenile

mussels conducted at the CERC laboratory in ASTM hard water (ASTM 2008d; no reference toxicant tests were conducted with mussels associated with the Set 3 samples).

Oligochaete sediment bioaccumulation tests: About 2 g of oligochaetes tissue was obtained from each replicate beaker at the end of the 28-d sediment exposures. No overt mortality or avoidance of sediment was observed in any of the sediment exposures. Appendix B of Ingersoll *et al.* (2008) provides a summary of the metal analyses of oligochaetes that were isolated from sediment on Day 28. Despite the 6-hour depuration period recommended by USEPA (2000) and by ASTM (2008c), some sediment was visible in some of the oligochaetes samples after digestion, which likely contributed to increased variability and greater than anticipated concentrations of some metals (additional discussion follows). The DQOs were met for all of the oligochaete sediment bioaccumulation tests (as identified in Table A1.1 of the QAPP, Ingersoll 2007) and specifically, completeness was 100% for the 21 sediment samples evaluated in sediment bioaccumulation tests conducted with oligochaetes. The response of oligochaetes in the two 96-hour water-only NaCl reference toxicant tests (LC50s) were 6.0 and 11 g/L (Table 6 of Ingersoll *et al.* 2008); however, the CERC laboratory does not have historic reference toxicant tests for oligochaetes, given that reference toxicant tests are not typically conducted for test organisms used in bioaccumulation exposures.

In summary, the response of amphipods, mussels, and oligochaetes in the sediment exposures for all three sets of samples met the DQOs identified in Table A1.1 of the QAPP (Ingersoll 2007). The response of the midges in the sediment exposures for the Set 1 and Set 2 samples also met the DQOs identified in Table A1.1 of the QAPP (Ingersoll 2007). While the lower control survival of midges in the reference toxicant test conducted in conjunction with the Set 1 samples was 85%, this deviation should not compromise the subsequent use of the data for this set of samples. However, control survival of midges in the Set 3 samples (n=6) did not meet the DQOs identified in Table A1.1 of the QAPP, so these data should be used with caution.

B. Metals data for oligochaetes used in sediment bioaccumulation tests

The concentrations of metals in oligochaetes used in bioaccumulation testing are presented in Appendix B-1 of Ingersoll *et al.* (2008). A sample of each of the four oligochaete replicates was analyzed for nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), and lead (Pb) using a quantitative method, and the first replicate sample for each treatment also was analyzed for a total of 52 elements using a semi-quantitative method. Only results for 14 of those 52 elements are reported, because concentrations of the remaining elements (excluding the 5 elements run by quantitative analysis) were at or less than the reporting limits for all samples. Individual recoveries of Ni, Cu, Zn, Cd, and Pb obtained from analysis of 3 replicates of each of two certified mussel reference tissues were between 100 and 114% of certified ranges, with the exception of one Cu result (132%). Recoveries of all 13 certified elements analyzed by semi-quantitative method were between 79 and 140% of certified ranges (Appendix B-2 of

Ingersoll *et al.* 2008), indicating that the selected analytical methods provided acceptable levels of accuracy.

Six oligochaete samples were prepared in duplicate for analysis of Ni, Cu, Zn, Cd, and Pb by the quantitative method. The mean relative percent differences (RPDs) between the duplicates ranged from 12.3 to 18.4% for Ni, Cu, Zn, and Pb, which were within the target of $\pm 20\%$, but the mean RPD for Cd was 41.6% (Appendix B-3 of Ingersoll *et al.* 2008). Although the oligochaetes were depurated in clean water for 6 hours before sampling so as to allow them to eliminate ingested sediment particles (as is recommended by USEPA 2000 and by ASTM 2008c), sediment was still evident in most of the digested samples, and this probably contributed to greater than expected variability between duplicates. Aluminum, which is usually present at percent levels in sediments or soils, but only at a few parts per million in biological tissues, can be used to qualitatively indicate the presence sediment particles in the guts of the oligochaetes. In this study, the aluminum concentration in replicate-1 of the oligochaetes at the start of the exposures (not yet placed into sediments) was only 18 $\mu\text{g/g}$, whereas concentrations in oligochaetes following the sediment exposures ranged in the hundreds to thousands of $\mu\text{g/g}$ for all other samples analyzed (Appendix B-1 of Ingersoll *et al.* 2008). Oligochaete tissues were assumed to be reasonably homogeneous, and therefore were not physically homogenized before sub-sampling for digestion. Coupled with the fact that only 0.05-g subsamples were used for each analysis, sediment particles (which could be enriched with metals relative to the oligochaete tissue) that were non-uniformly distributed in the tissues could account for the large differences measured between some of the duplicates for Cd and other elements.

Six oligochaete samples were spiked with Ni, Cu, Zn, Cd, and Pb before digestion and analysis by the quantitative method. Mean recoveries of these spikes ranged from 97.3% (Cu) to 102.5% (Zn); only one individual result (for Zn) exceeded the target recovery of $100 \pm 20\%$ (Appendix B-4 of Ingersoll *et al.* 2008). Overall, recoveries of pre-digestion spikes were considered acceptable. Blank equivalent concentrations and method detection limits for the 3 sample preparation sets are presented in Appendix B-5. Mean blank equivalent concentrations were less than the corresponding method detection limits for all but 1 instance each for Cu (0.08 $\mu\text{g/g}$), Pb (0.05 $\mu\text{g/g}$), and Zn (0.38 $\mu\text{g/g}$); however, each of those values was many-fold less than the corresponding concentrations of all oligochaete samples except for Pb in 2 of the 4 replicates of oligochaetes at the start of the exposures (Appendix B-1 of Ingersoll *et al.* 2008). Therefore, laboratory-induced contamination was not considered to be a significant source of error in the measurement of metals in any of the oligochaete samples.

C. Water quality data for centrifuged pore water

Results of selected water quality parameters in filtered samples of centrifuged pore water are presented in Appendix C of Ingersoll *et al.* (2008). These measurements were performed by USGS contractors who conducted internal quality control checks during the analyses, but did

not provide summaries of those results. Consequently, only results for 8 “field” duplicates and 2 filtration blanks (Appendix C-2 of Ingersoll *et al.* 2008) are discussed herein. For DOC, RPDs between duplicates averaged 10.4%. The RPDs for sulfide averaged 85%, but all duplicate sample results were near method detection limits, so variation this large was not unusual. For anions, mean RPDs ranged from 7.0% (chloride) to 20.9% (sulfate); however, the mean RPD for sulfate was affected by one result for sample duplicates of pore water isolated from the control sediment (WB-1 and WB-2). Excluding aluminum (78%) and iron (77.7%), the mean RPDs for major cations ranged from 1.8% (sodium) to 13.6% (manganese). In many of the duplicate samples, aluminum and iron concentrations were near detection limits, which probably was a reason why the mean variation was large for those elements. In addition, iron was probably present as ferrous ion in most of the digested samples, which might have been partly lost in some samples as a result of oxidation and precipitation during sample processing. Overall, the variation between duplicate samples was not considered unusual for these measurements.

D. Simultaneously extracted metals and acid-volatile sulfide data

Concentrations of acid-volatile sulfide and simultaneously extracted metals (1N HCl) in sediments are presented in Appendix D-1 (Sets 1 and 2, collected in 2007, Ingersoll *et al.* 2008) and in Appendix D-1A (Set 3, collected in August 2006, Ingersoll *et al.* 2008). A single subsample, obtained at the start of toxicity testing, was analyzed for each of the 2006 sediments. For 2007 sediments, subsamples were obtained for analysis from simulated toxicity test beakers on Day 7 and Day 28 of the tests (from additional replicate chemistry beakers containing amphipods that were fed during the exposures). Calculations of the difference between SEM and AVS, and the difference divided by the fraction of organic carbon (USEPA 2005) are presented for each of the two samples individually, and for the mean of the two (Appendix D-1 and Appendix D-1A of Ingersoll *et al.* 2008). Results for 1N HCl extractable elements and AVS obtained from NIST 1645 river sediment are presented in Appendix D-2 of Ingersoll *et al.* (2008). Results are shown in chart form, and include CERC historical results because reference sediments having certified concentrations of AVS or extractable metals do not exist. Results obtained during analyses of TSMD sediments are indicated by open symbols, all which fell within the usual range for each respective analyte (Appendix D-2 of Ingersoll *et al.* 2008). Compared to the certified total metal concentrations, the percentage of each metal recovered by the 1N HCl procedure was about 40% for Ni, 50% for Cu, 78% for Zn, 66% for Cd, and 72% for Pb. Duplicate preparations of eight 2007 sediment samples produced mean RPDs of 9.6% for AVS (Appendix D-3 of Ingersoll *et al.* 2008) and between 2.6% and 15.8% for simultaneously extracted metals (Appendix D-4 of Ingersoll *et al.* 2008). Similarly, RPDs were between 4.6% and 18% for duplicate preparation of a 2006 sample (Appendix D-8 of Ingersoll *et al.* 2008). The mean recovery of AVS for pre-extraction blank spikes (as sodium sulfide) was 96% (Appendix D-5 of Ingersoll *et al.* 2008), and was between 99% and 111% for metals (Appendix D-6 of Ingersoll *et al.* 2008). Recoveries of pre-extraction spikes prepared with the 2006 samples were between 93% and 107% (Appendix D-9 of Ingersoll *et al.* 2008). Blank equivalent concentrations (BECs), method detection

limits (MDLs), and method quantitation limits (MQLs) are presented in Appendix D-7 and in Appendix D-10 of Ingersoll *et al.* (2008). There were some instances in which BECs were greater than the corresponding MDLs, particularly for Cd, Zn, and Pb in the first sample set prepared on August 7, 2007. Consequently, all of the samples prepared in the first set were re-prepared on December 4, 2007 and re-analyzed for those 3 elements (12/04/07 BECs; Appendix D-7 of Ingersoll *et al.* 2008). All of the results from the re-analysis were in close agreement with those obtained from the first preparation and analysis (data not shown), indicating that the metal levels detected in the first blank were largely absent during subsequent preparations. Based on results from the re-preparation of the first set combined with the other preparation sets, none of the BECs were significant compared to the sample concentrations. Overall, QC results indicated acceptable precision and accuracy for these measurements and generally met targeted values.

E. Metals data for pore water sampled by peepers

Results for metals in peeper samples are indicated in Appendices E-1 (quantitative analyses of Ingersoll *et al.* 2008) and E-2 (semi-quantitative analyses of Ingersoll *et al.* 2008). Recoveries of various elements from reference water solutions analyzed with peeper samples are indicated in Appendix E-3 of Ingersoll *et al.* (2008). Recoveries of Ni, Cu, Zn, Cd, and Pb ranged from 88 to 102% using the quantitative analysis mode and, with the exception of potassium (158%), ranged from 79 to 125% for 26 elements determined in the semi-quantitative mode. Duplicate analyses of selected diluted and spiked peeper samples using the quantitative analysis mode for Ni, Cu, Zn, Cd, and Pb produced relative percent differences ranging from 0.0 to 2.7%, and averaged less than 1% for Ni, Cu, Zn, Cd, and Pb (Appendix E-4 of Ingersoll *et al.* 2008). Recoveries of analysis spikes added to 12 different peeper solutions ranged from 96.4% to 106.4% for Ni, Cu, Zn, Cd, and Pb (Appendix E-5 of Ingersoll *et al.* 2008). Blank equivalent concentrations for peepers were at or below method detection limits in most instances except for Zn, which ranged from 8 to 22 µg/L in the first set of peeper samples (Set 1 samples; Appendix E-6 of Ingersoll *et al.* 2008). Overall, QC results indicated acceptable precision and accuracy for peeper measurements.

F. Grain size, total organic carbon (TOC), and total solids data AND

G. Polycyclic aromatic hydrocarbon (PAH) data and Semi-Volatile Organic Compounds (SVOC) in whole sediment

Results for analyses of grain size, TOC, and water, are presented in Appendix F of Ingersoll *et al.* (2008). Results for PAH and SVOC analyses are presented in Appendix G of Ingersoll *et al.* (2008). Data quality review of these data by USEPA Region 6 is provided in Appendix L of Ingersoll *et al.* (2008). Based on the USEPA Region 6 Laboratory's review, the overall quality of the analytical data was found to satisfy the QC requirements established by the

analytical methods and the USEPA Region 6 Laboratory (Appendix L of Ingersoll *et al.* 2008). Concentrations of hexachlorocyclopentadiene was not recovered in one laboratory control sample and well below acceptance criteria in spiked samples which resulted in the rejection of the hexachlorocyclopentadiene results for six samples (indicated by the letter “R” in Appendix G of Ingersoll *et al.* 2008). No TOC results were rejected; however, multiple recovery failures resulted in several TOC results being qualified as estimated. A total of 73 of the TOC samples were analyzed outside holding time with some analyzed as late as six months past the holding time expiration. Quality control issues were encountered with grain size determinations for nine sediment samples. More specifically, clay or silt settled out with the sand which resulted in underestimating the fine fractions and overestimating the sand fraction. This resulted in negative results for clay in some instances. In the SLERA, these data will be adjusted by setting negative values to 0 and apportioning the amount of the negative value to the other grain-size fractions.

H. Organochlorine pesticides and polychlorinated biphenyl data AND

I. Total recoverable metals data in whole sediment

Results for analyses of pesticides and PCBs are presented in Appendix H of Ingersoll *et al.* (2008). Results for analyses of total recoverable metals are presented in Appendix I-1 of Ingersoll *et al.* (2008; <2-mm sediment samples) and in Appendix I-2 of Ingersoll *et al.* (2008; <0.25-mm sediment samples). Data quality review of these data by USEPA Region 7 is provided in Appendix M of Ingersoll *et al.* (2008). Based on the USEPA Region 7 Laboratory’s review, the overall quality of the analytical data was found to satisfy the QC requirements established by the analytical methods and the USEPA Region 7 Laboratory. All of the pesticide and PCB samples were analyzed after the required holding time and all results were qualified in Appendix M of Ingersoll *et al.* (2008). All analytical results, with the exception of 14 rejected results for barium (indicated by the letter “R”) and the poor precision of mercury in samples CERC-42 and -42_9 (values followed by the letter “J”) may be used to support project decisions.

J. Comparison of sampling methods (shovel versus scoop)

Results from comparisons between shovel and scoop sampling performed at 3 locations are presented in Appendix J-1 (grain size comparison, see Ingersoll *et al.* 2008) and in Appendix J-2 (metal concentrations in equipment rinses, see Ingersoll *et al.* 2008). No QC results are presently included with these data because the analyses were performed by USEPA (grain size) or a contract laboratory (metals in equipment rinseates). Based on these data, there were minimal and insignificant differences between the two sampling methods with respect to grain size sampled or to metals contamination from use of a shovel to collect some of the Set 1 sediment samples (iron and sodium were slightly elevated in samples collected with a shovel compared to samples collected with the PVC sediment scoop; Appendix J-2 of Ingersoll *et al.* 2008).

K. Comparison of methods for metals in pore water (peepers versus centrifugation)

Six samples of centrifuged pore water isolated on Day -7 (before the start of the exposures) were subsampled for ICPMS analyses so that comparisons could be made to peeper samples isolated on Day 7 of the exposures which were also measured by ICPMS. In addition, all of the centrifuged pore-water samples were analyzed for “major cations and metals” using ICPAES (which has marginal sensitivity for some of the metals of interest), but never-the-less, these six samples could also be used to compare analysis methods directly. Results for Cu, Ni, Zn, Cd, and Pb obtained by the ICPMS and ICPAES methods are compared in Appendix K-1 of Ingersoll *et al.* (2008). Trace metal results obtained by the ICP-AES method for all centrifuged pore-water samples are indicated in Appendix K-2 of Ingersoll *et al.* (2008). Also included in Appendix K-1 of Ingersoll *et al.* (2008) are pore-water results for 12 sediments in which pore-water Zn concentrations were >500 µg/L, obtained either by ICPAES for centrifuged pore waters prepared 7 days before the addition of test animals to sediment samples (Day -7), or by ICPMS for peepers retrieved 7 days after the addition of test organisms (Day 7). Results from these 12 samples were selected for comparing pore-water preparation methods because the Zn concentrations were well above the method quantitation limit for ICPAES, thereby avoiding large analytical variability which is expected at concentrations near the detection limit. For comparison of the first six samples, there was close agreement between ICPMS and ICPAES results (considering that many of the results were near detection limits for the ICPAES method), except for Zn in sample CERC-35 (148 µg/L versus 65 µg/L). Concentrations obtained by peeper sampling on Day 7 of the test tended to be lower than those obtained by centrifugation (on Day -7), except for Zn in samples CERC-53, -67, and -69. A similar trend, in which most peeper samples had lower concentrations, was apparent for the 12 additional samples which contained high concentrations of Zn. Lower concentrations obtained by peeper sampling was not unexpected because dissolved metals are prone to partial losses over time caused by co-precipitation with iron as pore waters become more oxidic, or by diffusion into overlying water which is periodically renewed during toxicity testing. Moreover, centrifugation may result in the release of insoluble metals from sediment particles compared to the measurement of dissolved metal concentrations in the peeper samples. Overall, the agreement between sampling and analysis methods was quite reasonable, indicating that sampling and analysis precision was acceptable.

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**Appendix 7 - Data
Evaluation and
Treatment**

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Appendix 7 Data Evaluation and Treatment

1.0 Introduction

A step-wise approach was used to compile, evaluate, and analyze the surface-water chemistry, sediment chemistry, pore-water chemistry, invertebrate tissue chemistry, sediment toxicity, and mussel taxa richness data that were used to support the Advanced Screening Level Risk Assessment (SLERA) of the Tri-State Mining District (TSMD). These steps included:

- Development of a list of contacts for candidate data sets;
- Identification of candidate data sets;
- Acquisition and screening of candidate data sets;
- Compilation of data into a relational database;
- Verification and auditing of the project database; and
- Data treatment procedures.

Each of these steps is described in the following sections of this Appendix.

1.1 Contacts List for Candidate Data Sets

A list of candidate data sets is presented in Table 18 of the advanced SLERA technical report. The key sources of the candidate data sets included:

- Quapaw Tribe of Oklahoma;
- Eastern Shawnee Tribe of Oklahoma;
- State Agencies [Kansas Department of Health and Environment (KDHE), Oklahoma Department of Environmental Quality (ODEQ)];
- Federal Agencies [United States Geological Survey (USGS), US Environmental Protection Agency (USEPA), US Fish and Wildlife Service (USFWS)]; and,
- Harvard School of Public Health (HSPH).

All of the data sets received from these sources were considered for inclusion into the project database.

All members of the TSMD Watershed Partnership were invited to identify candidate data sets that should be considered for inclusion into the project database. As a result, a substantial list of candidate data sets was developed. The key contacts for receiving these data sets were as follows:

- CH2M Hill, Rick Dobbins
- HSPH, Jim Shine, Lauel Schaidler

- IEC, Kara Lanahan
- KDEH, Bob Angelo
- ODEQ, Dennis Datin, Jay Wright
- Quapaw Tribe of Oklahoma, Fred Kirschner
- USEPA, Dane Pehrman, Dave Mosby
- USFWS, Suzanne Dudding, Dave Moseby
- USGS, Chris Ingersoll, Bill Brumbaugh, Nile Kemble, Robert Gale, John Besser, Kyle Juracek

1.2 Identification of Candidate Data Sets

The project database was developed by integrating the data sets that were compiled by the Natural Resources Trustees and by USEPA. First, IEC supported the Natural Resources Trustees by compiling data and information on environmental quality conditions throughout the TSMD, including the Tar Creek Superfund Site. MacDonald Environmental Sciences Ltd. (MESL) and CH2M Hill supported USEPA by compiling the most relevant information on surface-water chemistry, pore-water chemistry, sediment chemistry, sediment toxicity, fish-tissue chemistry, mussel abundance, and other data to support the advanced screening level ecological risk assessment of the TSMD.

1.3 Acquisition and Screening of Candidate Data Sets

A substantial quantity of data and information has been generated on the condition of aquatic habitats within the TSMD. To support the current assessment, the available data on surface-water, pore-water, and sediment quality conditions in the study area were assembled in the project database. A description of each of the studies that were used in this evaluation is provided in Appendix 5.

To ensure that the most relevant data sets were compiled into the project database, selection criteria were formulated to guide the database development process. The following list describes the data set selection criteria:

- Include data generated between 2002 and 2009 to provide a basis for evaluating current conditions in the TSMD;
- Preferentially include data sets for the Ottawa County and Newton County portions of the TSMD (i.e., because baseline ecological risk assessments had been completed previously for the Jasper County and Cherokee County portions of the site; Dames and Moore 1993; Black and Veatch Special Projects Corp. 1998).

Compile data from elsewhere in the watershed when provided in electronic format; and,

- Primarily focus on compilation of surface-water chemistry, sediment chemistry (for surficial sediment samples; i.e., the top 15 cm of sediment), sediment toxicity, and benthic invertebrate community data (i.e., to support assessment of risks to benthic invertebrates). Compile other data types (soil chemistry data, invertebrate-tissue chemistry data, or fish-tissue chemistry data) when provided in electronic format.

All of the data sets that were retrieved during the course of the study were critically reviewed according to these criteria to determine their applicability to the assessment of environmental quality conditions in the study area.

1.4 Compilation of Data into a Relational Database

Development of a project database represents an essential element of the SLERA process. As the project database is likely to represent a useful tool for all of the partners in the remedial investigation/feasibility study process and for the natural resources trustees, USEPA Region VI agreed to play a lead role in the development of a database for the TSMD watershed.

The data sets that contained information on the study area and met the selection criteria were incorporated into a relational database in MS Access format. The data sets were typically received in either Excel or Access formats. From these formats, they were translated into one master database. This translation process included ensuring the vital information from the multiple data sets was collected, captured and organized in the same order so that the data from all data sets would be comparable within a single database. The compiled data sets are listed in Table of the advanced SLERA technical report.

To support the compilation and subsequent analysis of the information on environmental quality conditions, a geographic information system (GIS)-compatible, relational project database was developed in MS Access format. All of the data compiled in the database were georeferenced to facilitate mapping and spatial analysis using GIS-based applications [i.e., Environmental Systems Research Institute (ESRI's) ArcMap and Spatial Analyst programs]. The database structure made it possible to retrieve data in several ways, including by data type (i.e., chemistry vs. toxicity), by sediment horizon (i.e., surficial vs. sub-surface sediments), by AoI (i.e., Center Creek vs. Tar Creek), and by date. As such, the database facilitated a variety of data analyses to support the SLERA (and detailed ecological risk assessment).

1.5 Verification and Auditing of the Project Database

Database auditing of the MS Access database was conducted to ensure that the underlying data were accurate and complete for use in the assessment. Following translation into database format, the data were verified to ensure that any potential translation errors had not occurred. Data verification involved an initial confirmation of data in the database against data in the translated MS Excel sheets as well as in the original Access database or Excel workbooks. Data auditing involved 10% number-for-number checks against the primary data source initially, increasing to 100% number-for-number checks if significant errors were detected in the initial auditing step. For the 10% check, the data for a randomly selected ten out of a hundred analytes were verified against the original data. All data for ten out of a hundred samples were verified against the original source. Additional steps were taken in verifying that the database included cross-checking the complete list and number of samples in the database against the originally supplied data sets, checking unit consistencies (i.e., all sediment measurements in dry weight basis), ensuring geo-coordinates were all expressed in same coordinate system, and standardizing chemical names.

Subsequently, data auditing was conducted to assure data quality. The auditing process involved analyses of outliers (i.e., to identify inconsistencies with units) and completeness (i.e., to identify missing samples or missing data), examination of data qualifier fields (i.e., to assure internal consistency in the project database), and, checking of sample identification numbers (i.e., to ensure that data were not duplicated or missing). Anomalous data points that appeared to fall out from the trend of the majority of the data were identified based on reviews of summary tables (i.e., maximum and minimum values per analyte, hazard quotients). If the identified issue was not resolved at that stage of the process, the data were checked against the original data. In some cases, this process necessitated communication with the original contributors of the data in order to resolve data quality issues. Statistical analyses of resultant data were conducted to evaluate data distributions, identify the appropriate summary statistics to generate, and evaluate the variability in the observations. This ongoing iterative process throughout the data analysis phase helped to ensure overall completeness and accuracy of the database. The results of the data verification and auditing procedures indicated that the compiled information represents a reliable basis for conducting a SLERA.

1.6 Data Treatment Procedures

Analysis of the data compiled on the TSMD necessitated a number of decisions on the treatment of various types of information. These data treatment procedures are described in the following sections of this appendix.

1.6.1 Treatment of Replicate Samples/Duplicate Samples

In this report, field replicate samples were treated as unique samples in the data analyses (i.e., by providing information on the small scale spatial variability in sediment quality conditions). By comparison, laboratory split samples were treated as duplicates and averaged to support subsequent data analysis. Duplicate samples prepared in the field were also averaged to support data analysis.

1.6.2 Calculation of Total Concentrations by Chemical Class

To support subsequent interpretation of the water and sediment chemistry data, totals were calculated for certain chemical classes [i.e; total polycyclic aromatic hydrocarbons (PAHs), total polychlorinated biphenyls (PCBs), total dichlorodiphenyl-trichloroethane (DDTs)] when available for samples in the database.

The concentration of total PAHs was calculated by summing the concentrations of up to 13 individual PAHs (MacDonald *et al.* 1996). At minimum, data on the following 10 individual PAHs were required for a sample before total PAHs were calculated: acenaphthene, anthracene, fluorene, naphthalene, phenanthrene, benz(a)anthracene, benzo(a)pyrene, chrysene, fluoranthene, and pyrene. Additionally, acenaphthylene, 2-methylnaphthalene, or dibenz(a,h)anthracene were included in the total PAH calculation, if their concentrations were reported.

For PCBs, the concentrations of total PCBs were determined using various procedures, depending on how the data were reported in the original study. If only the concentrations of total PCBs were reported in the study, then those values were used directly. If the concentrations of various Aroclors (e.g., Aroclor 1242, Aroclor 1248) were reported, then the concentrations of the various Aroclors were summed to determine the concentration of total PCBs. If congener data was available for PCBs then the concentrations of total PCBs were also estimated by summing the concentrations of measured congeners and multiplying by 2.01 (Lauenstein and Cantillo 1993). This procedure has been shown to provide a reliable basis for estimating the sum of 209 PCB congeners when only a selected group of congeners was measured. If homolog data were report, then these report values were also summed (e.g., hexachlorobiphenyls, octachlorobiphenyls) to calculate the total PCB concentration. If PCBs were reported in two or more different ways for a given sample (e.g., congeners and Aroclors), two or more different sums were calculated using the different methods described above. The lowest of all the sums was then selected as the total PCB concentration for that sample in the database.

For DDTs, the concentrations of p,p'-DDD and o,p'-DDD (dichlorodiphenyldichloro-ethane), p,p'-DDE and o,p'-DDE (dichlorodiphenyldichloroethylene), and p,p'-DDT and o,p'-DDT (dichlorodiphenyltrichloroethane) were summed to calculate the concentrations of sum DDD, sum DDE, and, sum DDT, respectively. Total DDTs was calculated by summing the concentrations of sum DDD, sum DDE, and, sum DDT.

Microsoft Excel was used to generate the following summary statistics for each analyte by station and media type (sediment, surface water, pore water): sample size, 5th, 10th, 25th, 50th, 75th, 90th, 95th percentiles, mean, standard deviation, geometric mean, minimum and maximum value, and number and percent of samples reported as less than detection limit.

Consistent with the guidance developed by USACE (1995), one-half of the detection limit was substituted for concentrations that were report as less than detection limit.

1.6.3 Calculation of Hazard Quotients/Hazard Indices

Equilibrium partitioning sediment benchmark toxic units (\sum ESB-TUs) were calculated for PAHs. At minimum, the following 10 individual PAHs must have been reported to calculate a \sum ESB-TU_{PAH}: acenaphthene, anthracene, benz(a)anthracene, benz(a)pyrene, chrysene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene. Additionally, any or all of acenaphthylene, benzo(b)fluoranthene, or benzo(k)fluoranthene, if reported, were included in the \sum ESB-TU_{PAH} calculation. Total organic carbon must also have been reported in order for a \sum ESB-TU_{PAH} to be calculated for a sample. An organic carbon-normalized concentration is calculated for each PAH by dividing the chemical concentration by the fraction organic carbon. A substance-specific ESB-TU was then calculated by dividing the organic carbon normalized concentration by the final chronic value (a toxicity threshold) for that substance. Summing up all the 10 to 13 substance-specific ESB-TUs for a sample gives the \sum ESB-TU_{PAH} for a sample. No uncertainty factor was applied to this sum. Accordingly, the calculated \sum ESB-TU_{PAH} may have underestimated the actual \sum ESB-TU_{PAH} for a sample if alkylated PAHs were present at elevated levels. \sum ESB-TUs could not be calculated for semi-volatile organic compounds, as no single sample had all 29 of the required individuals SVOCs required for the \sum ESB-TU_{VOC} calculation.

Hazard quotients (HQs) were calculated to evaluate potential risks to ecological receptors posed by the different analytes. More specifically, the exposure estimates were used in conjunction with the toxicity screening values (TSVs) to estimate potential risks to ecological receptors associated with exposure to surface water, sediment, pore water, or soil within the TSMD, using the following equation:

$$HQ = EPC / TSV$$

Where: HQ = Hazard Quotient;
 EPC = Exposure Point Concentration (i.e; maximum concentration);
 and,
 TSV = Toxicity Screening Value (No observed adverse effect level were selected preferentially; units must match units for EPC).

For all calculations, values that were reported as less than detection limit were assigned a value of one-half of the detection limit, except when the detection limit was greater than the

selected toxicity reference value (TRV). In this latter case, the less than detection limit result was not used in the calculation of the total concentration of the substance. Additionally, in the event that all constituents being used in the summation were reported as less than detection limit, but the detection limit was less than or equal to the selected TRV, the final sum was reported as less than the sum of all the full detection limits. A value of one-half the detection limit was also plotted for all less-than-detection-limit results in the figures. In the frequency of exceedence analysis, less-than-detection-limit results that exceeded selected TRVs were excluded from that analysis. Full detection limits were presented in the summary statistics tables.

1.6.4 Identification of Contaminants of Concern

The process of determining contaminants of concern (COC) for the TSMD area involved a multiple-step screening process. The first step identified all of the chemicals of interest (COIs). Table 1 of the advanced SLERA technical report lists these COIs for surface and pore water, sediment, and tissue. The second step eliminated negligible-risk combinations of COIs and exposure pathways from further consideration by evaluating the calculated hazard quotients for the COIs (Tables 11 to 13 of the advanced SLERA technical report). If the COI had a hazard quotient of greater than or equal to 1.0 it was retained for further analysis as a chemical of potential concern (COPC). If there was no TSV available for a COI (and therefore no hazard quotient could be calculated), the COI was also retained, and brought forward as an uncertain COPC. The third step further evaluated the COPCs by comparing the 95th percentile of the TSMD to the 95th percentile of the reference samples (Tables 14 to 16 of the advanced SLERA technical report). If this ratio was greater than or equal to 2, the COPC was retained as a COPC. If the ratio was less than 2, it was dropped from the evaluation. Retained COPCs were further evaluated in a fourth and final step of the process (Tables 37 to 39 of the advanced SLERA technical report), in which COPC concentrations were compared against probable effect concentrations (PECs) or equivalent values (see Table 42 of the advanced SLERA technical report). In addition, the 95th percentile of the TSMD was compared to the 95th percentile of the reference samples. If the COPC concentration exceeded both of those values then it was retained as a COC. If it exceeded only one or none of these values, then the COPC was not identified as a COC. The results of the complete four-step COC identification process are summarized for individual Areas of Interest (AoIs) in Tables 37 to 39 of the advanced SLERA technical report. Table 43 of the advanced SLERA technical report summarizes COCs retained for each of the three sub-basins: Upper/Middle Spring River, Lower Spring River, and Neosho River.

1.6.5 Spatial Evaluation of Data

In this report, the spatial extent of risk to benthic invertebrates was evaluated by linking the chemistry and biological response data contained in the project database with GIS-based applications (ESRI's ArcView software). To facilitate spatial analyses of these data, the assessment area was first divided into three sub-basins (Upper/Middle Spring River, Lower

Spring River, and Neosho River sub-basins). Next, each sub-basin was divided into several AoIs using readily identifiable physiographic features (e.g., confluence of two streams). In this way, it was possible to evaluate and isolate the sediment chemistry, surface- and pore-water chemistry, tissue chemistry, pore-water toxicity, and benthic invertebrate community structure data in individual AoIs, as well as group the data for individual sub-basins.

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