Guidelines for Designing and Implementing Aquatic Effects Monitoring Programs for Development Projects in the Northwest Territories

Recommended Procedures for Problem Formulation to Support the Design of Aquatic Effects Monitoring Programs

AEMP Technical Guidance Document
Volume 2

Indian and Northern Affairs Canada
Yellowknife, Northwest Territories

June 2009 Version

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List of Acronyms

AEMP	-	Aquatic Effects Monitoring Program
CCME	-	Canadian Council of Ministers of the Environment
CEAA	-	Canadian Environmental Assessment Act
DQO	-	data quality objective
EEM	-	Environmental Effects Monitoring
EQG	-	environmental quality guideline
EQO	-	environmental quality objective
FSP	-	field sampling plan
GIS	-	geographic information system
GLWB	-	Gwich'in Land and Water Board
HSP	-	health and safety plan
INAC	-	Indian and Northern Affairs Canada
K_{oc}	-	organic carbon partition coefficient
K_{ow}	-	octanol water partition coefficient
LWB	-	the Land and Water Board
MRP	-	Management Response Plan
MVEIRB	-	Mackenzie Valley Environmental Impact Review Board
MVLWB	-	Mackenzie Valley Land and Water Board
MVRMA	-	Mackenzie Valley Resource Management Act
NWTWA	-	Northwest Territories Water Act
NWTWB	-	Northwest Territories Water Board
NWT	-	Northwest Territories
QAPP	-	quality assurance project plan
QA/QC	-	quality assurance/quality control
SLWB	-	Sahtu Land and Water Board
TK	-	Traditional Knowledge
USEPA	-	U.S. Environmental Protection Agency
VEC	-	valued ecosystem component
WLWB	-	We'eezhii Land and Water Board
WQG	-	water quality guideline
WQO	-	water quality objective

1.0 Introduction

The process of defining the questions that will be addressed by an Aquatic Effects Monitoring Program (AEMP) is termed problem formulation. Problem formulation is a systematic planning process that identifies the factors to be addressed in an AEMP and consists of eight key activities, including:

1. Refinement of the preliminary list of stressors of potential concern;
2. Evaluation of the potential effects of physical, chemical, and biological stressors on human health and on ecological receptors;
3. Evaluation of the transport and fate of chemicals of potential concern;
4. Characterization of potential exposure pathways;
5. Identification of receptors potentially at risk;
6. Development of a conceptual site model that links stressors and receptors at the site;
7. Selection of assessment and measurement endpoints; and,
8. Development of a preliminary AEMP Analysis Plan.

At the conclusion of the problem formulation, there should be agreement among the members of the AEMP Working Group on four items: 1) the assessment endpoints; 2) the exposure pathways; 3) the monitoring or risk questions that need to be answered; and, 4) the conceptual model that integrates these components. In addition, measurement endpoints should have been identified and an AEMP Analysis Plan should have been established at the end of the problem formulation step (see AEMP Guidelines Overview Report for more information on the recommended use of an AEMP Working Group).

This Technical Guidance Document describes the steps that ought to be used to formulate the problem for a single development project. This process was selected to support AEMP development because it provides a logical and transparent procedure for evaluating the potential effects of project activities on the physical, chemical, and biological characteristics of aquatic ecosystems (Environment Canada 1996; Golder Associates 2008). As a result the assessment and measurement endpoints that are selected for inclusion in the AEMP are likely to provide effective tools for evaluating project-related effects. It is important to note that multiple disturbance activities can result in cumulative effects on the aquatic ecosystem, including aquatic-dependent wildlife and human health. For areas that are potentially affected by multiple disturbance activities, the problem formulation process should be used to:

- Predict the effects of the development project on the aquatic ecosystem and its uses (i.e., consumption of fish and water by residents or visitors to the area); and,
- Predict the cumulative effects of multiple disturbance activities on the aquatic ecosystem and its uses.

In this way, the resultant AEMP can be used to evaluate project-related effects, both alone and in combination with other developmental activities. Monitoring to evaluate cumulative effects should be coordinated with regional cumulative effects assessment initiatives (e.g., the Mackenzie Valley Cumulative Impact Monitoring Program).

2.0 Refinement of the Preliminary Stressors of Potential Concern

The first activity in the problem formulation process involves the refinement of the preliminary stressors of potential concern (including chemical, biological, and physical stressors) that were identified during Step 1 in the AEMP development framework. In the context of aquatic effects assessment, chemicals of potential concern are defined as the toxic and/or bioaccumulative substances that are released into aquatic ecosystems at levels that have the potential to adversely affect human health or the environment. The chemicals of potential concern that need to be considered in an assessment of aquatic effects can be identified by conducting a systematic evaluation of the sources of toxic and bioaccumulative substances that occur within the area under investigation (i.e., study area). In addition, the physical and/or biological stressors that are associated with the development project need to be identified and/or refined at this time. Aboriginal governments/organizations and other interested parties can play an important role in refining this list.

There are a number of natural and project-related sources of toxic and bioaccumulative substances to surface waters and groundwater. Under natural conditions, a variety of organic (e.g., organic carbon, organic nitrogen) and inorganic (e.g., metals, minerals, nutrients) substances are released into surface water or groundwater due to weathering of native rocks and soils, biological processes, and atmospheric deposition (i.e., forest fires, volcanoes). Environmental contaminants released to surface waters from developments include 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. Environmental contaminants released to groundwater can come from spills and other releases to soils from industrial sites, leaching from landfills and municipal sludge disposal sites, application of agricultural chemicals, and others. Evaluation of land and water use activities provides a basis for determining the sources of environmental contaminants in the study area and, hence, a preliminary list of stressors of potential concern (BCE 1997; Thomson *et al.* 2007).

For new projects, stressors of potential concern must be identified based on an detailed understanding of the nature and scope of activities that are associated with the development. Such an understanding provides a basis for determining the types of contaminants that could be released into aquatic ecosystems and identifying the likely locations of those releases. In addition, information on the sources and releases of chemicals of potential concern associated with similar projects that have been constructed in other areas provides a means of expanding the preliminary list of stressors of potential concern. In conducting this review and evaluation of prospective activities and relevant information on existing projects, it is important to consider the potential for non-contaminant related effects on aquatic ecosystems (e.g., effects on hydrology, direct effects on fish populations due to increased fishing pressure, introductions of exotic species). In this way, most or all of the potential physical, chemical, and biological stressors associated with the proposed project can be identified early in the AEMP development process.

3.0 Evaluation of the Potential Effects of Physical, Chemical, and Biological Stressors

A stressor is any physical, chemical, or biological entity that has the potential to cause a change in the ecological condition of the environment (CCME 1996; USEPA 1997; 2000; Suter *et al*. 2000; 2007). Accurate identification of the stressor(s) that are associated with a development project is essential for predicting project-related effects, identifying mitigation strategies that will minimize effects on human health and the environment, and designing an AEMP that will effectively identify the nature, magnitude and extent of such effects.

The procedures for identifying physical, chemical, and/or biological stressors that are associated with a development project were described in AEMP Technical Guidance Document Volume 1. To facilitate prediction of the potential effects of these stressors on human health or ecological receptors, a literature search should be conducted during this stage of the problem formulation process. The literature search should focus on identification of no observed adverse effect levels, lowest observed adverse effect levels, exposure-response functions, the mechanisms of toxic responses to chemicals of potential concern, and the potential effects of physical/biological stressors on receptors (USEPA 1997; Suter *et al.* 2007; Solomon *et al.* 2008).

4.0 Determination of the Environment Fate and Partitioning of Chemicals of Potential Concern

Upon release into aquatic ecosystems, the chemicals of potential concern 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 chemicals of potential concern can occur in surface water (including the surface microlayer), bottom sediments, and/or the tissues of aquatic organisms. Information on physical and chemical properties, such as aqueous solubility, vapour pressure, Henry's Law constant, and octanol-water partition coefficient, can be used to determine how each substance is likely to partition into environmental media. In addition, information on degradation (e.g., by hydrolysis, photolysis, oxidation, and biodegradation) and/or relocation (e.g., by scouring or dredging for sediment) rates can be used to evaluate their persistence in each environmental medium. Subsequent integration of the information on partitioning and persistence provides a means of assessing the potential environmental fate of the chemicals of potential concern that are identified. In turn, this information can be used to classify the chemicals of potential concern into four groups based on their likely fate upon release into aquatic ecosystems, including:

- Bioaccumulative substances (i.e., substances that accumulate in the tissues of aquatic organisms);
- Toxic substances that partition into sediments;
- Toxic substances that partition into water (i.e., surface water or groundwater); and,
- Toxic substances that partition into the surface microlayer (i.e., the immediate surface of the water, important because it often has the highest concentrations of certain chemicals of potential concern; MacDonald *et al.* 2000).

The results of this analysis can then be used to identify the media types that need to be included in AEMPs and the chemicals of potential concern that should be targeted for analysis in each media type (i.e., water, sediment, and biota). For other stressors, information on their potential effects is useful for identifying the media types that should be targeted in the AEMP.

5.0 Characterization of Potentially Complete Exposure Pathways

Identification of potentially complete exposure pathways represents the next activity in the problem formulation process. 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 and humans, ingestion of contaminated water represents the principal route of exposure to toxic substances that partition into surface water. For humans, this exposure route can also be important for contaminated groundwater. However, direct contact during recreational activities may represent an important exposure route for certain classes of chemicals of potential concern (e.g., microbiological variables).

For toxic substances that partition into the surface microlayer (the interface for atmosphere/water equilibria processes), 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 and, to a lesser extent, humans 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 when slicks are present on the water surface. Ingestion during drinking can also represent an important exposure route for aquatic-dependent wildlife when elevated levels of chemicals of potential concern are present in the surface microlayer.

In establishing exposure pathways, it is also important to consider that chemicals of potential concern that partition into sediments can be released into the water column under various conditions (e.g., during period of pH depression). In addition, certain water-borne and sediment-associated chemicals of potential concern can accumulate in the tissues of aquatic organisms. Therefore, consumption of contaminated prey (e.g., lake trout) can represent an important exposure pathway for aquatic-dependent wildlife and humans. Indeed, ingestion of contaminated prey species represents the most important route of exposure for the majority of aquatic organisms and aquatic-dependent wildlife species for most bioaccumulative substances (such as polychlorinated biphenyls, mercury, organochlorine pesticides, and dioxins and furans). It is important to note that Traditional Knowledge (TK) is likely to provide essential information for identifying potentially-complete exposure pathways in the study area, thus highlighting the need for consultation with Aboriginal governments/organizations and other interested parties at this time.

6.0 Identification of Receptors Potentially at Risk

There are a wide variety of receptors that could be exposed to stressors of potential concern in aquatic ecosystems. Aquatic species can be classified into six main 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, amphibians, and reptiles. Birds and mammals represent the principal aquatic-dependent wildlife species that need to be considered in water quality assessments. Humans can also be exposed to contaminated surface water, groundwater, sediment, and/or biota. Development of a food web model provides one mechanism for illustrating 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 1).

Examination of the food web model provides a means of identifying the principal groups of aquatic organisms that are likely to be exposed to chemicals of potential concern in water. Under most circumstances, microorganisms, aquatic plants, aquatic invertebrates, fish, and amphibians represent the ecological receptor groups most likely to be exposed to toxic substances that partition into surface water. Although ingestion of surface water represents a potential exposure route for both birds and mammals, this pathway is likely to represent a relatively minor source of exposure for aquatic-dependent wildlife species. It is considered to be an important exposure route for humans, however. By comparison, aquatic invertebrates, pelagic fish, and aquatic-dependent birds and mammals (particularly those that wade or float in water) are likely to have the highest potential for exposure to toxic substances that partition into the surface microlayer.

For chemicals of potential concern that partition into sediments, microbiota, aquatic plants, benthic invertebrates, benthic fish, and amphibians represent the primary aquatic receptors that could be adversely affected by exposure to these stressors. However, sediment-probing birds and certain mammals can also be directly exposes to sediment-associated chemicals of potential concern. Indirect exposure to such chemicals can also occur due to bioaccumulation in aquatic food webs.

For chemicals of potential concern that partition into biological tissues, food web transfer represents the most important exposure pathway. In this respect, aquatic dependent birds, aquatic-dependent mammals, and humans all represent receptors potentially at risk. In addition, fish, amphibians, and mammals can be exposed to tissue-associated chemicals of potential concern via this pathway.

For physical and biological stressors, interactive matrices can be developed to establish linkages between disturbance activities and the responses of key ecological receptors (Bain *et al*. 1986; Shopley *et al*. 1990). This process involves identification of the types of changes to the environment that could result from the disturbance activities (e.g., changes in streamflow associated with hydroelectric power development) and receptors (e.g., dewatering incubation habitats after spawning). In this way, the receptors that are likely to be adversely affected by physical and/or biological stressors can be effectively identified (Irving and Bain 1993). Network analysis provides a similar approach that can be used to identify receptors potentially at risk (Smit and Spaling 1995; Conklin *et al*. 1992a; 1992b; Dixon and Montz 1995).

This step in the problem formulation process should culminate in the identification of all of the ecological and human receptors that could be exposed to stressors within the study area. These receptors should be sorted into taxonomic groups and feeding guilds to define the key groups of receptors that could be impacted by project-related activities within and nearby affected water bodies. The importance of TK in the identification of receptors potentially at risk cannot be overstated.

7.0 Development of a Conceptual Site Model

Development of a conceptual site model represents an important component of the AEMP development process because it enhances the level of understanding of the project under consideration and its potential interactions with the environment. Specifically, the conceptual site model describes key relationships between natural processes (i.e., natural stressors), human activities (i.e., project-related stressors), and the plants and animals that utilize habitats in the vicinity of the study area (i.e., human and ecological receptors). In so doing, the conceptual site model provides a framework for predicting the effects of developmental activities on the receptors and, hence, a template for generating risk questions (or effects questions) and testable hypotheses that can be evaluated using sampling data collected at the site (USEPA 1997; 1998; Golder Associates 2008). The conceptual site model also provides a means of highlighting what is known and what is not known about the study area. In this way, it provides a basis for identifying data gaps and designing sampling programs to acquire the information necessary to complete the assessment (i.e., to evaluate baseline conditions, reference conditions, and/or project-related effects).

Conceptual site models consist of two main elements, namely, a set of hypotheses that describe the predicted relationships between stressors, exposures, and assessment endpoint responses (along with a rationale for their selection) and a series of diagrams that illustrate the relationships presented in the risk hypotheses. Accordingly, development of a conceptual site model requires information on the natural processes that influence water quality conditions, on the sources and releases of stressors of potential concern, on the fate and transport of these substances, on the pathways by which ecological receptors are exposed to the stressors of potential concern, and on the potential effects of these stressors on ecological receptors and human health. In turn, this information is used to develop a set of hypotheses that provide predictions regarding how ecological receptors and humans will be exposed to and respond to the stressors of potential concern and a series of diagrams that illustrate these relationships.

Exposure to environmental contaminants and/or other stressors has the potential to adversely affect aquatic organisms and/or aquatic-dependent wildlife species. The nature and severity of such effects are dependent on the stressor under consideration, the bioavailability of the chemical of potential concern, 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 chemicals of potential concern and identification of the types of effects that could occur in the various groups of organisms that occur with a study area provides a basis for developing fate and effects hypotheses. In turn, such hypotheses provide a basis for evaluating the logical consequences of exposing ecological receptors to environmental contaminants and/or other stressors (i.e., predicting the responses of assessment endpoints when exposed to stressors; USEPA 1998). Hence, the development of testable hypotheses provides a basis for identifying the types of data and information that need to be collected in monitoring programs. As an example, MacDonald *et al.* (2002a) described the types of testable hypotheses that can be developed for contaminated site assessments.

The diagrams that illustrate the relationships presented in the risk hypotheses represent key elements of the conceptual site model. More specifically, conceptual site model diagrams highlight the relationships between stressors and receptors. Figures 2 to 6 provide examples of conceptual site model diagrams that illustrate these relationships. An example of a conceptual model that highlights potentially complete exposure pathways is shown in Figure 7 (BBL 2006). The conceptual site models that are developed at this stage of the process should be reviewed by TK holders and other interested parties to ensure that they adequately describe the relationships that apply to the project, as well as interactions with other projects located within the study area (i.e., illustrating potential cumulative effects).

8.0 Establishment of Assessment and Measurement Endpoints

In the context of this document, an assessment endpoint is defined as a valued ecosystem component that could be adversely affected by changes in environmental conditions associated with a development project (e.g., survival, growth and reproduction of benthic invertebrates).

The selection of assessment endpoints is an essential element of the problem formulation process because it provides a means of focussing monitoring activities on key environmental values (e.g., reproduction of sediment-probing birds) that could be adversely affected by exposure to environmental stressors of potential concern. Assessment endpoints must be selected based on the ecosystems, communities, and species that occur, have historically occurred, or could potentially occur at the site (Suter *et al.* 2000; 2007). The following factors need to be considered during the selection of assessment endpoints (USEPA 1997; Suter *et al.* 2000; 2007):

- The chemicals of potential concern that occur in environmental media and their concentrations, as well as the nature of other stressors;
- The mechanisms of toxicity of the chemicals of potential concern to various groups of organisms. The mechanisms through which other stressors can adversely affect ecological receptors and/or human health should also be considered;
- The ecologically-relevant receptor groups that are potentially sensitive or highly exposed to the stressor, based upon their natural history attributes; and,
- The presence of potentially complete exposure pathways.

Thus, the fate, transport, and mechanisms of ecotoxicity for each chemical of potential concern, group of chemicals of potential concern, and/or physical/biological stressors 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 stressor could be expressed (e.g., eggshell thinning in birds due to the pesticide DDT) and how the form of the chemical in the environment could influence its bioavailability and toxicity. The conceptual site model and associated information provide the basis for selecting the assessment endpoints that are most relevant for the water body under investigation. Some examples of assessment endpoints that may be considered in the development of AEMPs include:

- Activity of the microbial community;
- Survival and growth of the aquatic plants;
- Survival and growth, and reproduction of aquatic invertebrates;
- Survival, growth and reproduction of fish;
- Survival, growth and reproduction of amphibians;
- Survival, growth and reproduction of reptiles;
- Survival, growth and reproduction of aquatic-dependent birds;
- Survival, growth and reproduction of aquatic-dependent mammals; and/or,
- Health and welfare of humans.

A measurement endpoint is defined as ‘a measurable ecological characteristic that is related to a valued ecosystem component that is selected as the assessment endpoint’ and it is a measure of biological effects (e.g., mortality, reproduction, growth; USEPA 1997; Suter *et al*. 2000; 2007). 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 stressor or group of stressors at the site under consideration. Measurement endpoints can include measures of exposure (e.g., contaminant concentrations in water) 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 problem formulation documentation and must be based on scientific evidence (USEPA 1997).

After identifying receptors of concern and selecting assessment endpoints, it is useful to describe the linkages that are likely to exist between exposure media (i.e., stressors) and receptors within the study area. The results of this process facilitate identification of focal species (e.g., spotted sandpiper) for each group of receptors (e.g., sediment-probing birds) and each group of stressors (e.g., chemicals of potential concern). In turn, this information can be used to identify candidate measurement endpoints (e.g., concentrations of mercury in benthic invertebrates) that could be used to evaluate the status of each assessment endpoint (e.g., survival, growth, and reproduction of aquatic-dependent birds). Subsequently, the candidate measurement endpoints are prioritized to support identification of those that would provide the most useful information for evaluating aquatic effects in the study area. If, for example, the assessment endpoint selected is the survival, growth, and reproduction of pelagic fish and the effects hypothesis suggests that the concentrations of copper in surface water could exceed the water quality guideline for the protection of aquatic life, then the concentration of copper in surface water might be selected as a measurement endpoint in the investigation.

9.0 Development of a Preliminary Aquatic Effects Monitoring Program Analysis Plan

The problem formulation process should culminate in the development of a preliminary AEMP Analysis Plan. The AEMP Analysis Plan should describe the analytical approach that will be used to draw conclusions from the monitoring results. More specifically, this plan is intended to describe how the data collected under the AEMP will be used to determine the short-term and long-term effects of the project, to evaluate the accuracy of impact predictions, to assess the efficacy of mitigation measures, and to identify the need for further mitigation to reduce or eliminate project-related effects.

The measurement endpoints that are included in an AEMP can be classified into two general categories, including (Suter *et al.* 2000; 2007):

- Survey data that provide information on the state of receiving waters. Such data may include measurements of physical, chemical, and/or biological characteristics of the aquatic ecosystem, such as water levels, surface-water chemistry or benthic invertebrate community structure; and,
- Media-specific or *in-situ* toxicity data that indicate whether the contaminated media at the site are toxic to specific receptors (i.e., laboratory and/or *in-situ* toxicity testing of effluent, surface water, or sediment).

In some cases, single chemical toxicity data may also be generated to determine the expected toxic effects that a chemical could exert on a specific receptor. Toxicity identification evaluation procedures can also be applied to isolate the stressor(s) of potential concern that are causing any toxic effects that are identified.

The AEMP Analysis Plan should describe how the information on various measurement endpoints will be used to draw conclusions regarding the effects of the project and/or the cumulative effects of multiple disturbance activities on the aquatic ecosystem. For survey data, the AEMP Analysis Plan should identify how the data for each measurement endpoint will be interpreted to determine if project-related effects are occurring, either alone or in combination with other developmental activities. A central element of this analysis process is identification of the thresholds that will be used to determine if project-related effects are occurring at levels that necessitate management intervention. Such effects thresholds (termed Action Levels) can be based on background levels [i.e., using a reference envelope approach; MacDonald *et al.* 2002a), generic environmental quality guidelines, and/or site-specific environmental quality objectives (EQOs); see Volume 3 for more information on the establishment of Action Levels and on their application in Management Response Plans; MRPs; the MRP is the new term that will be used to replace the Adaptive Management Plan. This new term is also being used by the regulatory boards]. MacDonald *et al.* (2002b) provide detailed guidance for developing site-specific EQOs for aquatic ecosystems. For media-specific or in-situ toxicity data, reference envelope approaches also provide a defensible means of interpreting the resultant data.

For aquatic-dependent wildlife and human health, the AEMP Analysis Plan should describe how the resultant information on exposure and effects will be used to assess hazards. Accordingly, the procedures that will be used to estimate exposure point concentrations for each area of potential concern should be described, including any food web modelling that will be done and the associated assumptions. Effects thresholds for these receptor groups should also be defined in the AEMP Analysis Plan.

Finally, the AEMP Analysis Plan should provide a direct linkage to the MRP. More specifically the AEMP Analysis Plan should include a series of "if"..."then" statements that describe the management actions that will be taken if the monitoring results indicate that the effects thresholds are approached or exceeded. These "if"..."then" statements will represent key elements of the data quality objectives (DQOs) and the MRP that is developed in parallel with the AEMP.

10.0 Summary

This Technical Guidance Document provides an overview of the process that is recommended for developing a problem formulation document to support the design of the AEMP. The key elements of this process include: 1) refinement of the list of stressors of potential concern; 2) evaluation of the potential effects of physical, chemical, and biological stressors on human health and on ecological receptors; 3) evaluation of the transport and fate of chemicals of potential concern; 4) characterization of potential exposure pathways; 5) identification of receptors potentially at risk; 6) development of a conceptual site model; 7) selection of assessment and measurement endpoints; and, 8) development of a preliminary AEMP Analysis Plan.

As described in this document, problem formulation is a systematic, step-wise process for identifying the issues that will be evaluated by the AEMP. While none of the steps are particularly challenging, it can be difficult to fully grasp the integration of these steps without the aid of some tangible examples. For this reason, an example that illustrates each of these steps in the problem formulation process is provided at in Appendix 1 (i.e., for the Tri-State Mining District; MacDonald *et al.* 2007). This example was selected because it presents the problem formulation for a metal mining-related environmental contamination issue. Therefore, much of the underlying information could be relevant to mining projects in the NWT.

The problem formulation process integrates a great deal of information on the aquatic ecosystem and the potential effects of a development project. In so doing, this process establishes the goals, breadth, and focus on the AEMP. As such, consultation with Aboriginal governments/organizations and other interested parties is of fundamental importance throughout the problem formulation process. Project proponents are strongly recommended to avail themselves of the knowledge and experience of these parties throughout the problem formulation process. The resultant problem formulation document should be reviewed by these parties and relevant comments incorporated before proceeding with Step 3 of the framework for AEMP development.

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Figures

Figure 1. General conceptual site model showing the principal routes of exposure to contaminated water, sediment, soils, air, and biota.

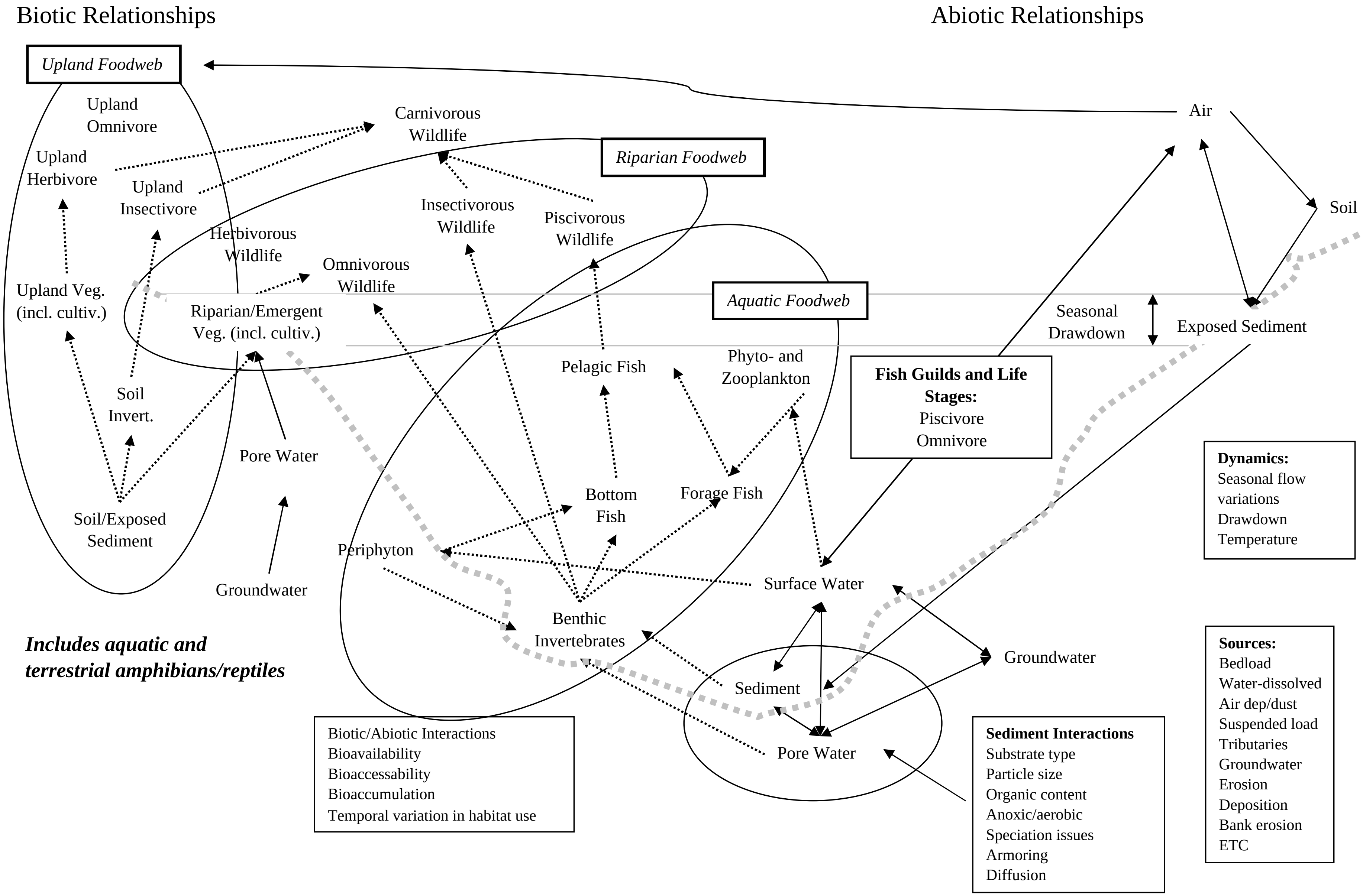


Figure 2. Conceptual model diagram illustrating exposure pathways and potential effects for bioaccumulative substances.

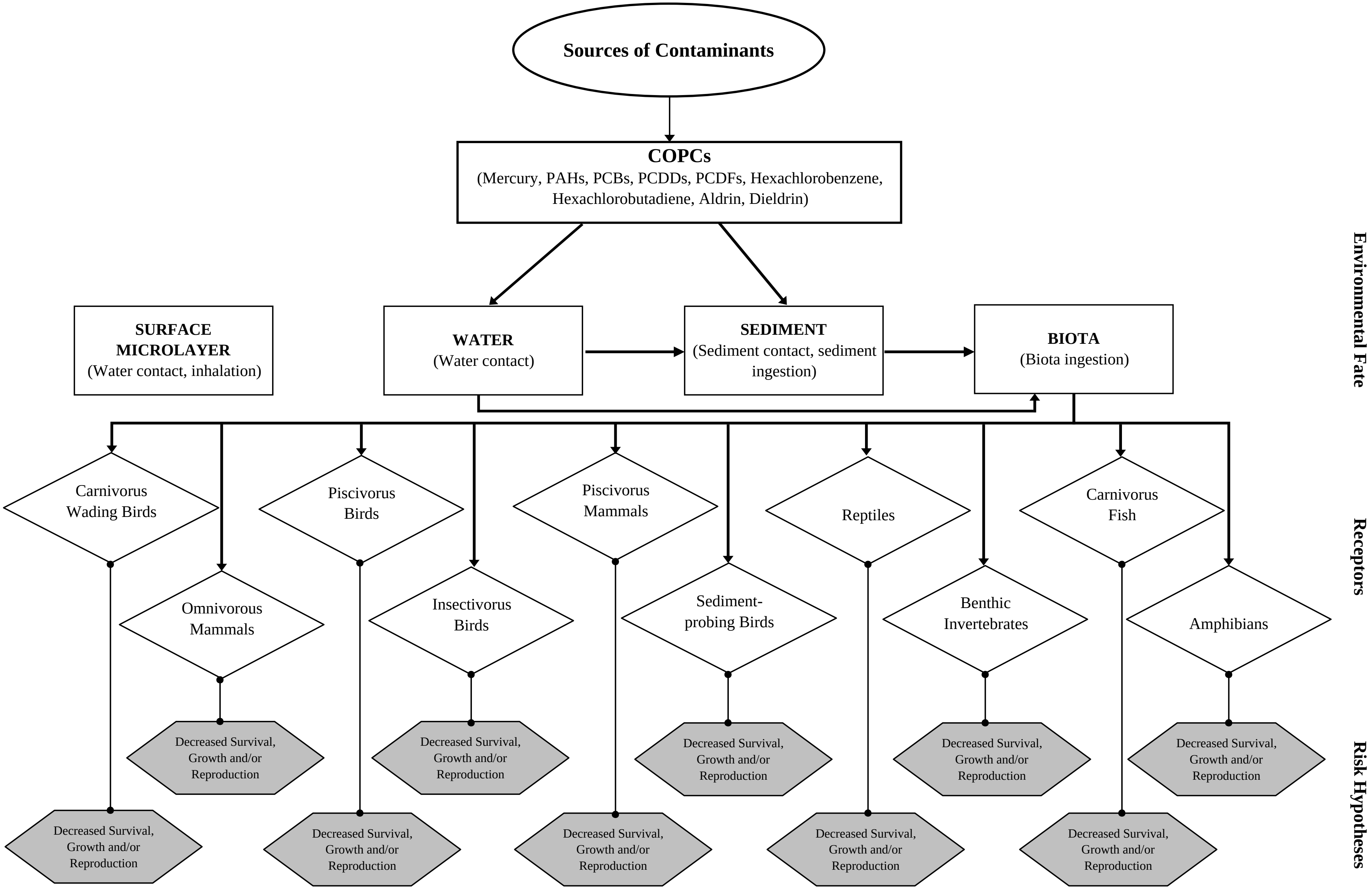


Figure 3. Conceptual model diagram illustrating exposure pathways and potential effects for toxic substances that partition into sediments.

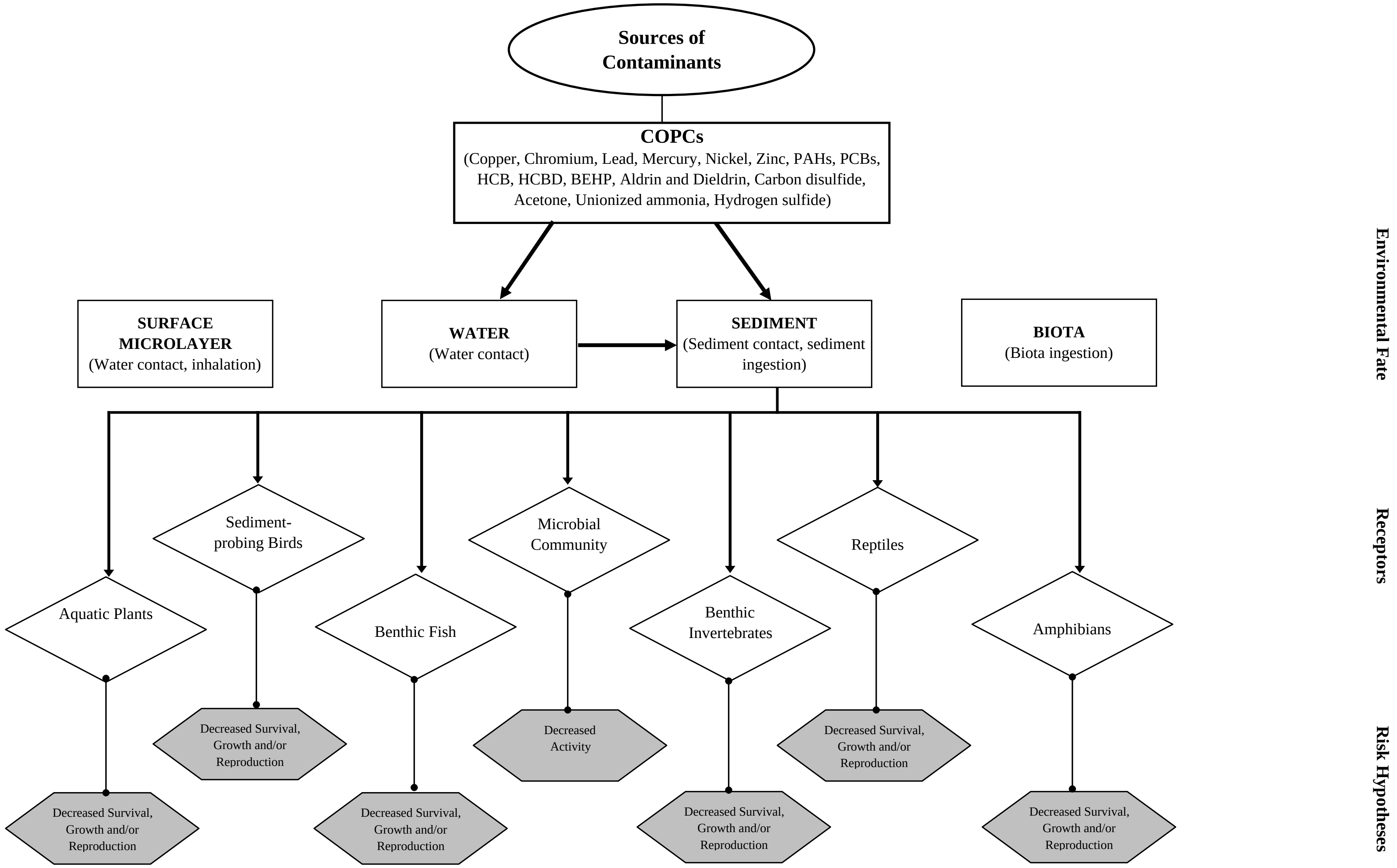


Figure 4. Conceptual model diagram illustrating exposure pathways and potential effects for toxic substances that partition into overlying water.

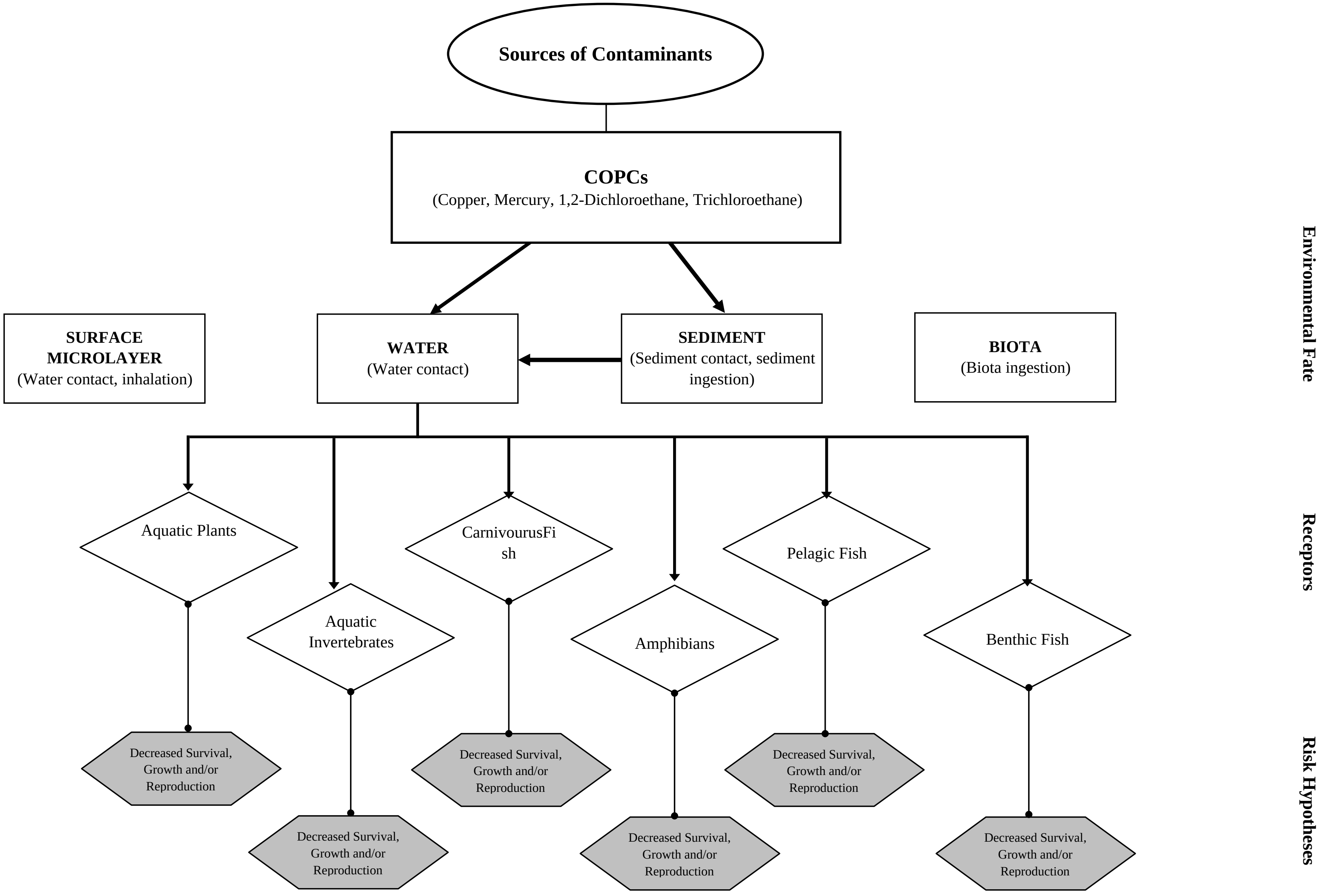


Figure 5. Conceptual model diagram illustrating exposure pathways and potential effects for toxic substances that partition into the surface microlayer.

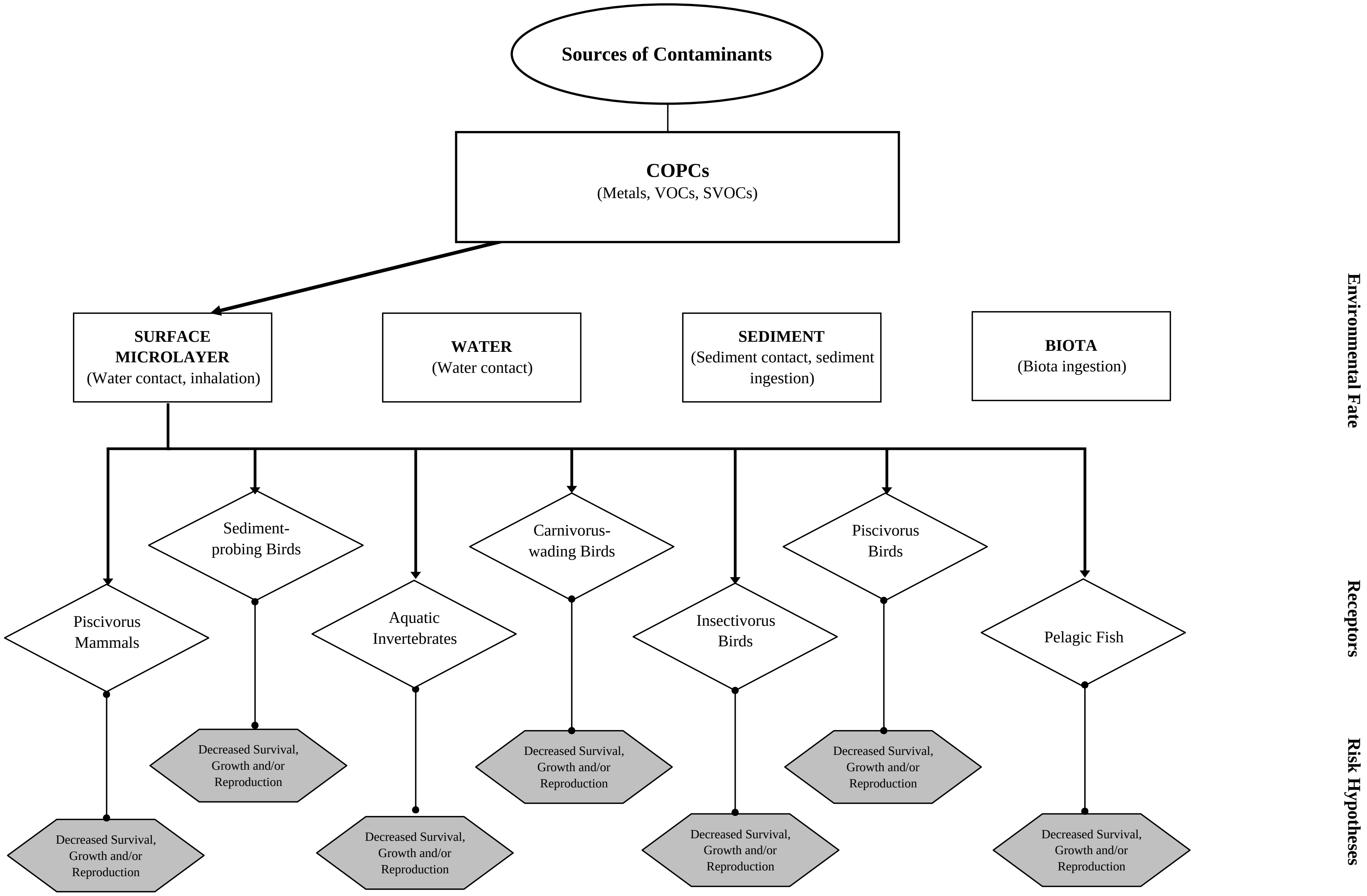


Figure 6. Conceptual model diagram illustrating exposure pathways and potential effects for all categories of COPCs.

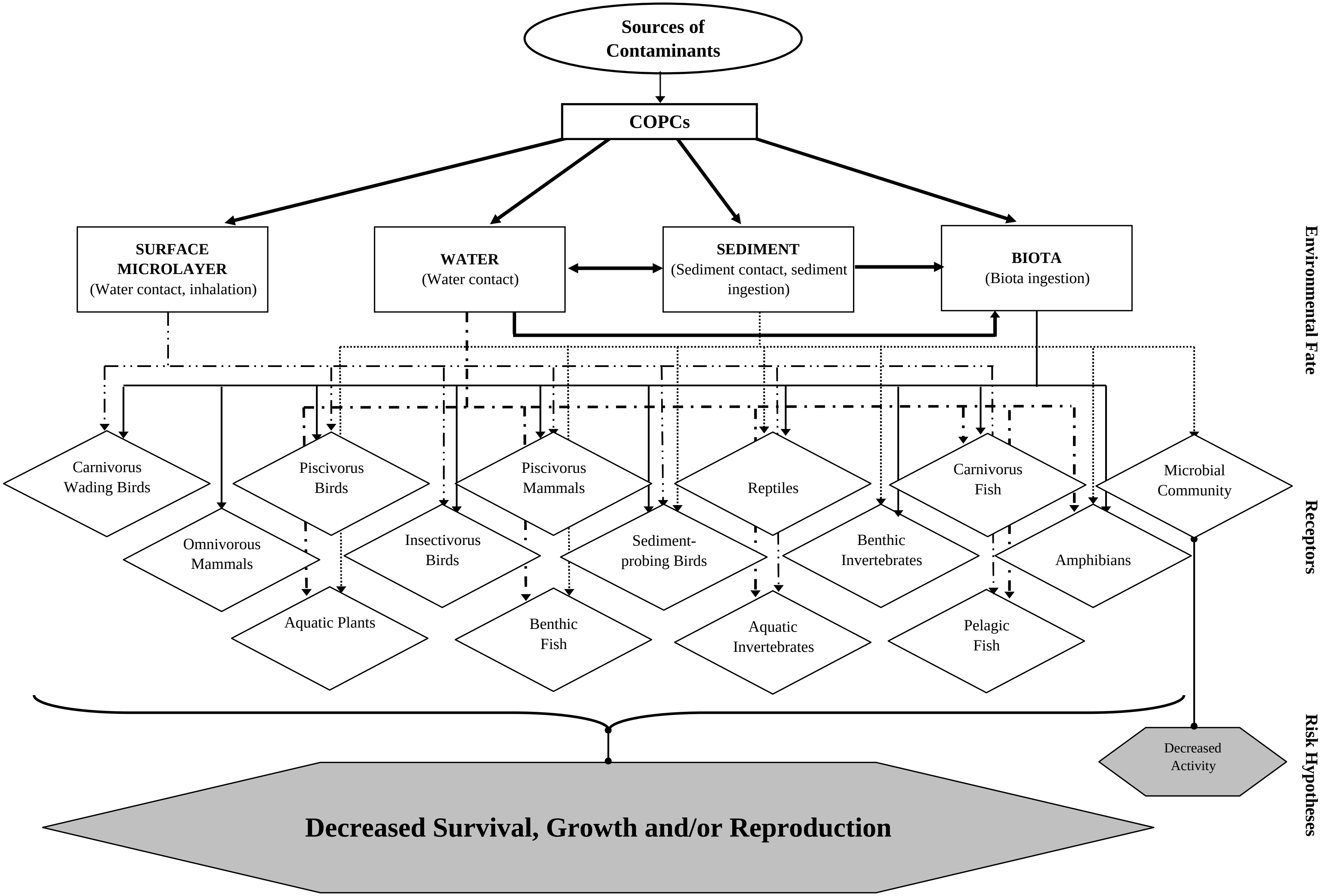
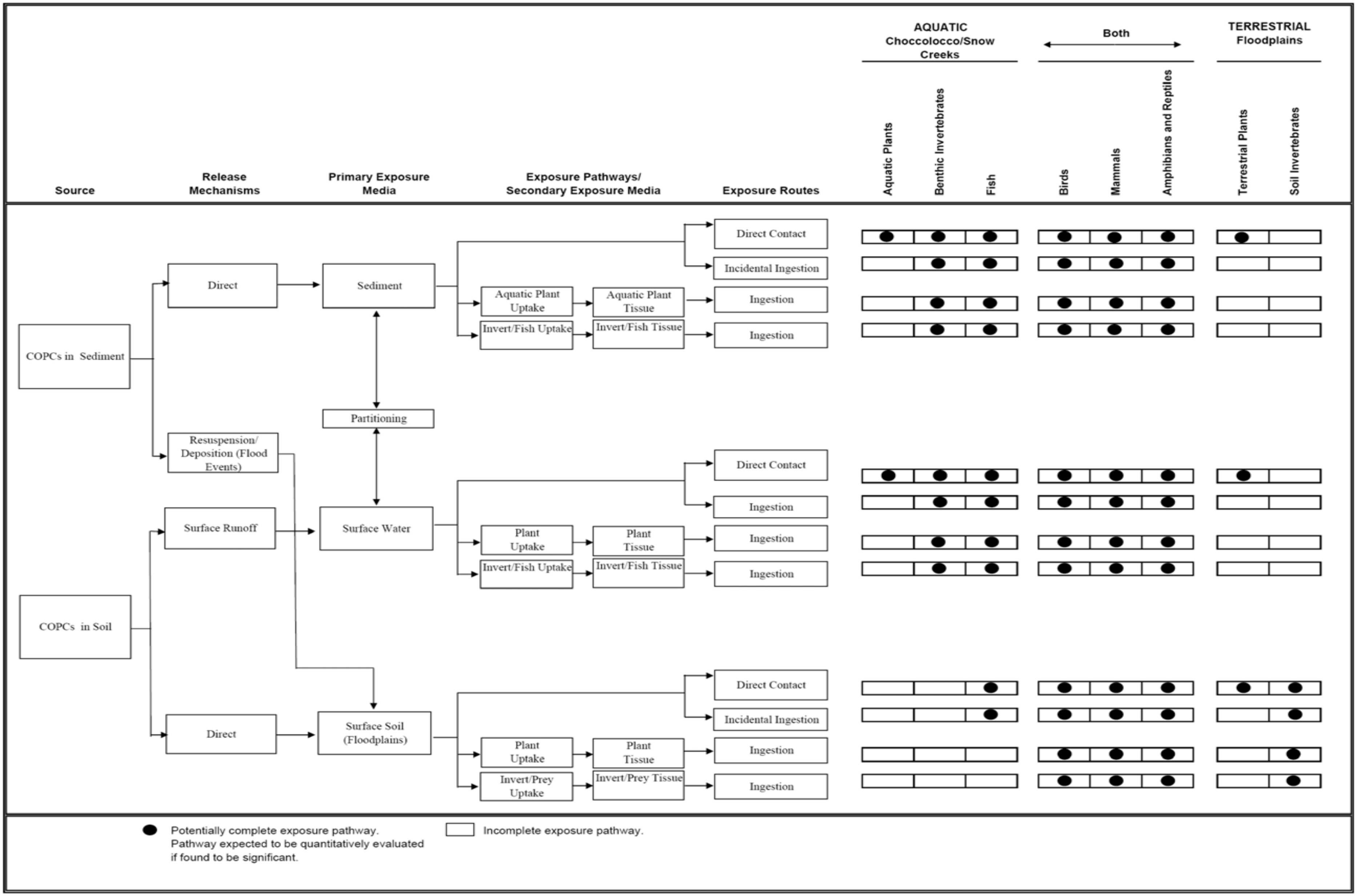


Figure 7. A conceptual model highlighting potentially complete exposure pathways (BBL 2006).



Primary Exposure Media	Exposure Pathways/ Secondary Exposure Media	Exposure Routes	Aquatic Plants	Benthic Invertebrates	Fish	Birds	Mammals	Amphibians and Reptiles	Terrestrial Plants	Soil Invertebrates
Sediment		Direct Contact	●	●	●	●	●	●	●	
		Incidental Ingestion		●	●	●	●	●		
	Aquatic Plant Tissue	Ingestion		●	●	●	●	●		
	Invert/Fish Tissue	Ingestion		●	●	●	●	●		
Surface Water		Direct Contact	●	●	●	●	●	●	●	
		Ingestion		●	●	●	●	●		
	Plant Tissue	Ingestion		●	●	●	●	●		
	Invert/Fish Tissue	Ingestion		●	●	●	●	●		
Surface Soil (Floodplains)		Direct Contact			●	●	●	●	●	●
		Incidental Ingestion			●	●	●	●		●
	Plant Tissue	Ingestion				●	●	●		●
	Invert/Prey Tissue	Ingestion				●	●	●		●

Appendix 1

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

Preliminary Problem Formulation
Version 2.0 (Drafted April, 2007)

Prepared for:

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Prepared – April, 2007 – by:

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ENVIRONMENTAL SCIENCES LTD.

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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 et seq.
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
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 *O*-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_2S = 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
SLERA = screening level ecological risk assessment
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
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 an advanced screening level ecological risk assessment (SLERA) 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 SLERA, 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 SLERA is limited to evaluating potential risks to aquatic receptors. As such, risks to aquatic-dependent wildlife and terrestrial receptors are not addressed in the problem formulation document.

1.1 Remedial Investigation and Feasability Study (RI/FS)

In response to concerns regarding environmental contamination, an advanced SLERA is being conducted in the TSMD. This SLERA will be conducted in 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.

In accordance with the USEPA guidance, the advanced SLERA of the TSMD is being conducted using this stepwise approach. The objectives of this advanced SLERA are:

- To estimate the risks posed to ecological receptors 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.

An advanced SLERA is being conducted for the TSMD because the results of the sediment sampling that has been conducted to date indicate that total metal concentrations exceed conservative toxicity thresholds (i.e., threshold effect concentrations; TELs; MacDonald *et al.* 2000) throughout much of the study area. As a result of the widespread sediment contamination, completion of a standard SLERA is unlikely to provide a basis for prioritizing subsequent risk assessment and risk management activities in the Spring River and Neosho River basins. For this reason, the SLERA will be focussed by developing site-specific toxicity thresholds that will provide a more reliable basis for identifying sediment samples that pose negligible risks to aquatic organisms and those that have the potential to adversely affect aquatic organisms. This site-specific calibration of the generic sediment quality guidelines should help focus any follow-up risk assessment and risk management activities on the areas that pose potential risks to sediment-dwelling organisms and other aquatic receptors.

1.2 Purpose of this Report

As indicated previously, the advanced SLERA 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 advanced SLERA. The process of defining the questions that will be addressed during the SLERA is termed problem formulation. Problem formulation is a systematic planning process that identifies the factors to be addressed in a SLERA and consists of five major activities (USEPA 1997), including:

- Identification of contaminant sources in the study area and development of the preliminary list of chemicals of potential concern (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 SLERA 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 SLERA. 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 SLERA. 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.

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 SLERA 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 1 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. MacDonald *et al.* (2007a) provides options for selecting assessment endpoints, risk questions, and measurement endpoints for a more thorough assessment of risks to ecological receptors.

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, an advanced SLERA is being conducted to assess risks to 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 SLERA 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 advanced SLERA, 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 divided into eight areas of interest (AoIs; see Section 3.3 of a list of AoIs).

Because mining activities have been conducted throughout the study area, it is difficult to identify reference areas within the TSMD. However, investigations conducted by the Quapaw Tribe recently suggest the Four-Mile Creek and upper Tar Creek represent suitable reference areas for the TSMD. For the 2007 field sampling program, the locations sampling in 2006 that qualified as reference samples were identified using whole-sediment chemistry data [Figure 4; i.e., based on mean PEC-Q_{metals} (DW@1%OC) <0.1 and GTM-AVS/foc <130 μmol/g, where PEC-Q is probable effects concentration quotient, TM is total metals, AVS is acid volatile sulfides, and foc is fraction organic carbon; MacDonald *et al.* 2007b]. A total of 29 of the 241 sediment samples collected during the 2006 field program met these criteria and were identified as reference samples (Figure 5; MacDonald *et al.* 2007b). These reference samples can be used to identify candidate sampling locations for collecting reference samples in the future.

Chapter 3 Identification of Chemicals of Potential Concern and Areas of Interest in the Tri-State Mining District

3.0 Introduction

The advanced SLERA that will be conducted as part of the overall RI/FS is intended to evaluate the risks posed to aquatic receptors associated with exposure to environmental contamination within the TSMD. In addition, the advanced SLERA 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 advanced SLERA and communicating this strategy to all stakeholders.

This chapter is intended to provide key background information needed to support the problem formulation for the advanced SLERA. 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 chemicals of potential concern (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 chemicals of potential concern (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 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);
- PAH (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);
- BTEX (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;
- 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);
- 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.

By considering the physical and chemical properties of these candidate COPCs, 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, including:

Toxic Substances that Partition into Water (log Kow < 3.5)

- Metals (As, Cd, Cu, Cr, Hg, Pb, Ni, Zn);
- Nutrients (ammonia, nitrite, and nitrate);

- Suspended solids;
- Certain herbicides, insecticides, and fungicides (identification pending pesticide use survey);
- BOD; and,
- Hydrogen sulfide.

Toxic Substances that Partition into Sediments or Soils (log Kow >3.5)

- Metals (arsenic, boron, cadmium, chromium, copper, lead, lithium, mercury, nickel, selenium, zinc);
- PAHs (13 parent PAHs + alkylated PAHs);
- BTEX (benzene, toluene, ethyl benzene, and xylene);
- Phenol;
- Chlorinated phenols;
- PCBs;
- Phthalates; and,
- Organochlorine pesticides.

Bioaccumulative Substances

- Metals (cadmium, lead, mercury, and zinc);
- High molecular weight PAHs [benz(a)anthracene, benzo(a)pyrene, chrysene, dibenz(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 areas of interest with respect to environmental contamination will be considered in the advanced SLERA of the TSMD (Figure 6):

- Upper Spring River (i.e., Spring River and associated tributaries located upstream of the confluence with Center Creek; Figure 7);
- Spring River Mainstem (i.e., Spring River and associated tributaries located between the confluence with Center Creek and Grand Lake; Figure 8);
- Center Creek (i.e., Center Creek and associated tributaries; Figure 9);
- Turkey Creek (i.e., Turkey Creek and associated tributaries; Figure 10);
- Shoal Creek (i.e., Shoal Creek and associated tributaries; Figure 11);
- Lost Creek (i.e., Lost Creek and associated tributaries; Figure 12);
- Neosho River (i.e., Neosho River and associated tributaries between the confluence with Elm Creek and Grand Lake; Figure 13); and,
- Tar Creek (i.e., Tar Creek and associated tributaries; Figure 14).

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 SLERA of the TSMD is focussed 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 advanced SLERA. The strategy for addressing this apparent limitation of the advanced SLERA 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 Δrisk) 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 1 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 abiota 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 specie (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 Boron (B)

To be prepared subsequently.

4.3 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).

4.4 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 1 for more information on the environmental fate and effects of Cu.

4.5 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 1 for more information on the environmental fate and effects of Cr.

4.6 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 1 for more information on the environmental fate and effects of Pb.

4.7 Lithium (Li)

To be prepared subsequently.

4.8 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 1 for more information on the environmental fate and effects of Hg.

4.9 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 1 for more information on the environmental fate and effects of Ni.

4.10 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).

4.11 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 1 for more information on the environmental fate and effects of Zn.

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 1 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 1 for more information on the environmental fate and effects of PCBs.

4.14 Bis(2-ethylhexyl)phthalate (BEHP)

Bis(2-ethylhexyl)phthalate (BEHP) belongs to the group of chemicals called semi-volatile organic compounds (SVOCs). This group of chemical compounds includes chemicals that are moderately volatile and may be present as liquids or solids. BEHP is used as a plasticizer in PVC films, sheets, flooring, and other vinyl products (CIS 1992). The release of BEHP into the atmosphere is the most important route of entry to the environment. The sources of such releases include emissions associated with the production and use of BEHP as well as the incomplete combustion of plastic materials (IPCS 1992).

The most important processes influencing the distribution and transformation of BEHP in the environment include atmospheric photo-oxidation, partitioning to soil, sediment, and biota, and aerobic degradation (Howard 1989). In water, aerobic biodegradation half-lives of BEHP range from five days to one month (Howard *et al.* 1991). In anaerobic conditions, BEHP persists between 42 and 389 days. The photolysis half-life of BEHP in water is at least 144 days. Volatilization of BEHP from water is considered to be very slow. Bis(2-ethylhexyl)phthalate has a strong tendency to partition to sediments from the water column (Al-Omran and Preston 1987). Some BEHP may desorb from the sediments back into the water column (Atwater *et al.* 1990).

For aquatic organisms, the lowest identified acutely toxic concentration was a 48-hour LC_{50} (median lethal concentration) of 133 μg/L for the cladoceran, *Daphnia pulex*

(Passino and Smith 1987). The lowest reported chronic toxicity value was a 21-day LOEL (lowest observed effect level; survival reduced by 25%) of 160 µg/L for *Daphnia magna* and a 21-day NOEL (no observed effect level) of 77 µg/L for the same organism (Springborn Bionomics 1984). The Chemical Manufacturer's Association (CMA; 1990) reported 96-hour LC_{50} values of 320 µg/L and 670 µg/L for the rainbow trout (*Oncorhynchus mykiss*) and the fathead minnow (*Pimephales promelas*). DeFoe *et al.* (1990) reported a 96-hour LC_{50} of 327 µg/L for the fathead minnow. Chronic toxicity of BEHP in sediments to frog eggs was investigated by Larson and Thuren (1987). A no observed effects level (NOEL) of 10 mg/kg fresh weight was determined for the hatchability of frog eggs over a 60 day exposure.

4.15 Chlorinated Phenols

To be prepared subsequently.

4.16 Benzene, Toluene, Ethyl benzene, and Xylene (BTEX)

To be prepared subsequently.

4.17 Total Suspended Solids (TSS)

Suspended matter consists of silt, clay, and fine particles of organic and inorganic matter, (CCME 1999). Total suspended solids provide a measure of mineral and organic particles transported in the water column. A closely related water quality parameter is turbidity and at sites where the relationship between suspended solids concentration and turbidity is known, turbidity can be used as a surrogate to predict suspended solids concentrations. The relationships between turbidity and suspended solids are site-specific, as turbidity is affected by factors such as the concentration, size, shape, and refractive index of suspended solids and the water colour (CCME 1999).

Mechanisms regulating deposition of sediment particles are gravity, which controls the suspended particle settling velocity, and entrapment of particles within the interstitial areas of stream beds (Anderson *et al.* 1996). Suspended sediment particles that are equal to or greater than 0.5 mm (e.g., coarse sand and gravel) will be redeposited quickly (Caux *et al.* 1997). Silt and clay sediment particles (<62 µm), perhaps the most pernicious of sediments particle types for aquatic biota, can remain in suspension for much longer periods of time as the upward component of fluid turbulence in streams is often just enough to keep these from being deposited (Caux *et al.* 1997). Other factors affecting the variability in suspended sediment concentrations are pools, gravel bars, and debris jams, acting as sediment storage sites during low flows and as supply sources during high flows.

Aquatic organisms are sensitive to the effects of TSS, with survival, growth, and reproduction adversely affected at elevated levels of suspended solids. For invertebrates, lethal concentrations of TSS ranged from 8 to 25,000 mg/L. By comparison, short-term ($\leq$96 hr) lethal concentrations of TSS ranged from 20 to 207,000 mg/l. In longer-term exposures ($\geq$96 hr), lethal concentrations of TSS for fish ranged from 7 to 200 mg/L. Newcombe and MacDonald (1991) and Newcombe and Jensen (1996) developed models that described the effects of suspended sediments in aquatic ecosystems, based on both the concentration and duration of exposure to TSS. Fish (all life stages) are sensitive to low levels of suspended solids. Chronic LC_{50}s for adults and juvenile fish range from 0.27 to 35 mg TSS/L.

4.18 Nitrate

Nitrate (NO_3^-) is a naturally occurring anion in fresh and saline waters. Nitrate is the primary form of inorganic nitrogen found in surface waters and, along with nitrite and ammonia, are important components of the aquatic portion of the nitrogen cycle (Nordin and Pommen 1986). Microorganisms perform four processes in the nitrogen cycle that result in production or transformation of nitrate and the other forms of nitrogen: nitrogen fixation, nitrification, denitrification, and ammonification (ATSDR 2004). Nitrate is manufactured in large amounts and used primarily in the form of potassium nitrate and ammonium nitrate, most of which is used for fertilizer. Potassium nitrate, sodium nitrate, calcium nitrate, silver nitrate and other metal nitrates and used in a variety of applications including; oxidants in chemical processes, explosives, fireworks, matches, photography, engraving, textile dyes, food processing, and as a raw material for manufacturing nitric acid (Nordin and Pommen 1986).

Nitrate is commonly released directly to the environment in the form of its potassium and ammonium salts, via their use as fertilizer. Ammonia and nitrite released to the environment can subsequently be transformed into nitrate by nitrification (Nordin and Pommen 1986). Ammonium is oxidized to nitrite by chemolithotroph *Nitrosomonas* spp., and nitrite is oxidized to nitrate by *Nitrobacter* spp.(WHO 1978). Nitrate is stable under aerobic conditions, although it is incorporated into tissue by both terrestrial and aquatic plants. However, little nitrate is found in sediments below a depth of 10 cm (Hill 1986).

Studies on salmonid sensitivity to nitrate (Westin 1974) indicate that chinook salmon (1-10 g) and rainbow trout (1-5g) are very resistant to nitrate poisoning with 96 h LC_{50} (at 13-17 °C) values for sodium nitrate in freshwater being 5,800 and 6,000 mg/L (as nitrogen) respectively for the two species. In contrast, the eggs of coho salmon and rainbow trout are more sensitive to nitrate than other life history stages, with threshold toxic values in the 40-80 mg/L range. In other studies with early life stages, nitrate concentrations in the range of 1-10 mg/L have been shown to be lethal to eggs and, to a lesser extent, fry of salmon and trout species (Kincheloe *et al.* 1979). Exposure of tadpoles from various amphibian species to nitrate has led to behavioural changes, reduced survivorship, and other effects at concentrations as low as 11 mg/L (nitrate; Hecnar 1995). Furthermore, tadpoles exposed to 11-44 mg/L nitrate for 24 hours showed developmental abnormalities, reduced feeding activity, and weight loss, swam less vigorously, and displayed disequilibrium and eventually paralysis (Hecnar 1995). In a long-term study, Knepp and Arkin (1973) observed that largemouth bass (*Micropterus salmoides*), and channel catfish (*Ictalurus punctatus*), could be maintained at concentrations up to 400 mg/L nitrate (90 mg/L nitrate nitrogen) without significant effect upon their growth and feeding activities.

4.19 Nitrite

Nitrite (NO_2^-) is a naturally occurring anion in fresh and saline waters. Nitrite is intermediate in oxidation state between ammonium (NH_3) and nitrate (NO_3^-), and is typically found in oxygenated waters at concentrations less than 0.005mg/L (Lewis and Morris 1986). Nitrite, and along with nitrate and ammonia, is an important component of the nitrogen cycle in aquatic environments (Nordin and Pommen 1986). Nitrite is not considered such a severe environmental problem because it does not usually occur in natural (well aerated) surface water systems at concentrations considered harmful to aquatic organisms (CCREM 1987). It may comprise a significant fraction of dissolved nitrogen in hypoxic lake hypolimnia or where water chemistry slows the nitrification of nitrite to nitrate relative to the rate of nitrification of ammonia to nitrite (Nordin and Pommen 1986; Lewis and Morris 1986).

Nitrite can be released directly to the environment in the effluents from industries producing metals, dyes, and celluloids, from sewage effluents, and from some types of aquaculture (Nordin and Pommen 1986; Lewis and Morris 1986). Ammonia and nitrate released to the environment can subsequently be transformed into nitrite by processes that occur in both the water column and associated sediments (Nordin and Pommen 1986). Runoff from fertilized agricultural fields and feedlots, and effluent from municipal waste treatment facilities are major sources of ammonia and nitrates (CCME 2000). Sediments are commonly the location of denitrification processes, which require the absence of oxygen (Hill 1986). Nitrate diffusing from overlying water is quickly converted to nitrite (as well as nitrogen oxide and ammonia) in the upper few cm of sediments.

Nitrite toxicity decreases as the pH increases, particularly at high pH (>8.6), and has some dependence on sulphate, phosphate and nitrate concentrations (Russo *et al.* 1981). Russo *et al.* reported 96-h LC_{50}s for rainbow trout (*Oncorhynchus mykiss*) at pH 6.44, 7.52, 8.10 and 9.00 of 0.21 mg/L, 0.32 mg/L, 0.28 mg/L and 1.67 mg/L respectively (all in terms of NO_2^- nitrogen). For chinook salmon (*O. tshawytscha*), 96-hour and 7-day LC_{50} values, were found to be 0.9 and 0.7 mg/L nitrite nitrogen in fresh water (Westin 1974). Minnows *(Phoxinus laevis)* suffered a 50 percent mortality within 1.5 hours of exposure to 2,030 mg/L nitrite nitrogen, but required 14 days of exposure for mortality to occur at 10 mg/L (Klingler 1957), and carp, *Cyprinus carpio* , when raised in a water reuse system, tolerated up to 1.8 mg/L nitrite nitrogen (Saeki 1965). Sub-lethal effects of nitrite on rainbow trout (increased methemoglobin, decreased hemoglobin) have been observed at levels of 0.015 to 0.10 mg/L N as NO_2^- (Russo and Thurston 1977). Nitrite toxicity has been investigated as a possible influence on world-wide amphibian population declines. In recent studies of Cascades frogs (*Rana cascadae*), nitrite concentrations of 3.5 mg/L induced behavioural and morphological changes, retarded development, and altered the age at emergence from tadpole to frog (Marco and Blaustein 1999). Nitrites also decrease the oxygen-carrying capacity of the blood by transforming hemoglobin, which transports oxygen, into methemoglobin, which does not. Nitrite concentrations as low as 1 mg/L have been shown to increase the amount of methemoglobin in the blood of bullfrog tadpoles (Huey and Beitinger 1980).

4.20 Ammonia

Ammonia is colourless gas, with a pungent, suffocating odour and an atomic mass of 17.03 (CCME 2000). In aqueous solutions, and 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 a 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 LC_{50} 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 enpoint. 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).

4.21 Phosphorus

Phosphorus (P), as a pure solid, occurs in three allotropic forms; white phosphorus (sometimes called yellow phosphorus, although the colour of the waxy crystals is due to impurities), black phosphorus (resembles graphite in texture) and red phosphorus (a red to violet powder; Budavari *et al.* 1989). Phosphorus exists naturally in rocks and soils as calcium phosphate minerals, of which apatite is the most common, containing some 95% of all P in the Earth's crust (Smil 2000). In freshwater systems, phosphorus occurs in three forms; inorganic phosphorus, particulate organic phosphorus, and dissolved organic phosphorus. Most scientific investigations regarding bioavailability have been directed toward defining bioavailable phosphorus (Nordin 1985). In most lakes and rivers, phosphorus is the primary nutrient that limits the growth of algae and plants.

The fate and transport in the environment is determined by the processes that influence the cycling of phosphorus. Unlike the cycles of elements such as carbon, nitrogen and sulfur, phosphorus does have a significant gaseous phase and so the dominant mechanisms regulating phosphorus distribution are erosion and fluvial transport. Phosphates have low solubility and are rapidly transformed into insoluble forms (e.g,. precipitates with aluminum in freshwaters with low pH), resulting in low concentrations in natural freshwater systems (Smil 2000).

Phosphorus can be toxic, but toxicity occurs rarely in nature and is generally not a concern. Of more concern are the indirect effects of phosphorus. All algae and plants require phosphorus to grow. Elevated phosphorus levels, however, can increase a freshwater system's productivity and result in large amounts of organic matter falling to the bottom. Bacteria and other organisms decompose this matter. In very productive freshwater systems, the oxygen levels can be in such short supply that fish kills occur. A type of algae, called cyanobacteria, grows particularly well in high levels of phosphorus. Cyanobacterial blooms can cause a range of water quality problems, including summer fish kills, and even soluble exotoxins that can harm wildlife (Environment Canada 2005).

4.22 Biological Oxygen Demand (BOD)

To be prepared subsequently.

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 in the estuary 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 1 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 conducting 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;
- Piscivorus 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 sheathes. 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., pyrrophytes; 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 (*Orocnectes 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 lead 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., mayfiles, 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 detrivores. Fish represent important prey species for piscivorus (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 dolomieui*), spotted bass (*Micropterus punctulatus*), white crappie (*Poxomis annularus*), rock bass (*Ambloplites constellatus*), channel catfish (*Ictalurus punctatus*), and rainbow trout (*Oncornchus 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 redspot 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*), redfin 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 piscivorus 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, piscivorus 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 advanced SLERA 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 (As, Bo,Cd, Cu, Cr, Hg, Li, Pb, Ni, Se, Zn);
- PAHs (13 parent PAHs + alkylated PAHs);
- BTEX;
- PCBs;
- Phthalates;
- Phenol;
- Chlorinated phenols;
- Organochlorine pesticides;
- Nutrients (ammonia, nitrite, nitrate, and phosphorus);
- Suspended solids;

- Certain herbicides, insecticides, and fungicides;
- Hydrogen sulphide; and,
- BOD.

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 1, 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 SLERA will focus on the five receptor groups that occur within the aquatic portions of the TSMD. Figures 15 to 18 present examples of a riverine food webs for Ozark stream ecosystems at various times of the year, while Figure X (to be prepared) illustrates a food web for a prairie stream ecosystem in the study area. 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 19). 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, 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 (Table 12) provides a basis for developing fate and effects hypotheses (i.e., using the information presented in Appendix 1). 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, 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 1 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., Kows) 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, lead, mercury, zinc, certain PAHs, PCBs, organochlorine pesticides, and/or PCDDs/PCDFs 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. Although not addressed in the SLERA, 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, 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 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 (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 porewater, 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 SLERA, 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 metals (As, Cd, Cu, Cr, Hg, Pb, Ni, Zn), nutrients, TSS, BOD, H_2S, and certain pesticides (e.g., water-soluble herbicides, insecticides, and/or fungicides). 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, metals (As, Cd, Cu, Cr, Hg, Pb, Ni, Zn), nutrients, TSS, BOD, H_2S and certain pesticides (e.g., water-soluble herbicides, insecticides, and/or fungicides) 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 20 to 22, respectively. In addition, Figure 23 integrates the linkages that were identified for all four categories of COPCs. Furthermore, Figure 24 provides a more explicit linkage diagram that highlight the potentially complete exposure pathways that need to be evaluated in the advanced SLERA.

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 1). 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 advanced SLERA for the TSMD.

8.2 Preliminary 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 BERA (Note: the candidate assessment endpoints, risk questions, and measurement endpoints for the BERA are presented in MacDonald *et al.* 2007a to provide a perspective on those that are recommended for the SLERA). Importantly, the scope of the advanced SLERA has been limited to aquatic receptors, including microbiota, aquatic plants, aquatic invertebrates (i.e., benthic invertebrates and zooplankton), and amphibians. Accordingly, aquatic-dependent reptiles, birds, and mammals and all terrestrial receptor groups have been excluded from the assessment. The preliminary list of assessment endpoints for the advanced SLERA includes:

- Protection of aquatic organisms from any adverse effects associated with exposure to COPCs in surface water; and,
- Protection of aquatic organisms from any adverse effects associated with exposure to COPCs in sediment and/or pore water.

8.3 Preliminary 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 advanced SLERA for the TSMD includes:

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

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

8.4 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 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 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 growth of amphipods in 10-d toxicity tests). At the SLERA stage of the process, the measured or estimated concentrations of COPCs in environmental media are selected measurement endpoints. 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 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 SLERA, 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 (RQs) and the highest priority measurement endpoints (MEs) for evaluating the status of the candidate assessment endpoints (AEs) include:

AE-1: Protection of aquatic organisms from any adverse effects associated with exposure to COPCs in surface water.
RQ-1: Are the concentrations of COPCs in surface-water water from the TSMD greater that conservative benchmarks for the protection of aquatic organisms (i.e., benchmarks that are equivalent to no observed effect levels; NOELs)?
ME-1: The concentrations of COPCs in surface-water samples collected from the TSMD.

AE-2: Protection of aquatic organisms from any adverse effects associated with exposure to COPCs in sediment and/or pore water.
RQ-2a: Are the concentrations of COPCs in whole-sediment samples from the TSMD greater that conservative benchmarks for the protection of aquatic organisms (i.e., benchmarks that are equivalent to NOELs)?
ME-2a: The concentrations of COPCs in whole-sediment samples collected from the TSMD.

RQ-2b: Are the concentrations of COPCs in pore-water samples from the TSMD greater that conservative benchmarks for the protection of aquatic organisms (i.e., benchmarks that are equivalent to NOELs)?

ME-2a: The concentrations of COPCs in pore-water samples collected from the TSMD.

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 advanced SLERA 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, or associated pore water 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 advanced SLERA 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 three types of data, including surface-water chemistry data, whole-sediment chemistry data, and pore-water chemistry data. The advanced SLERA 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, three types of data (i.e., surface-water chemistry data, whole-sediment chemistry data, and pore-water chemistry data) will be used to evaluate the potential risks to aquatic organisms associated with exposure to COPCs within the TSMD. These three 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 maximum 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 advanced SLERA. 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 metals (where HQ = measured concentration ÷ conservative benchmark). The maximum 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 evaluated during the advanced SLERA. 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);
- STM-AVS;
- STM-AVS/f_{oc}
- ΣSEM-AVS; and,
- ΣSEM-AVS/f_{oc}.

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); and USEPA (2005). 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 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 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.

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 1 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*** - While the ambient water quality criteria (i.e., final chronic values; FCVs) could be used to evaluate the surface-water chemistry data, such values represent lowest observed adverse effect levels (LOAELs, which are not preferred for use in SLERA; USEPA 1997; i.e., no observed adverse effect levels, NOAELs, are preferred). For this reason, it may be more appropriate to screen the surface water chemistry data against the Canadian water quality guidelines (WQGs).

> ***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 SLERA. 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 SLERA 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. 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 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 STT-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. 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 - While the ambient water quality criteria (i.e., final chronic values; FCVs) could be used to evaluate the pore-water chemistry data, such values represent lowest observed adverse effect levels (LOAELs, which are not preferred for use in SLERA; USEPA 1997; i.e., no observed adverse effect levels, NOAELs, are preferred). For this reason, it may be more appropriate to screening the surface water chemistry data against the Canadian water quality guidelines (WQGs).

9.3 Risk Characterization

In the risk calculation step of the SLERA, 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 NOAEL (i.e., the selected conservative benchmark). For surface water and pore water, the Canadian WQGs will be used to calculate the HQs. For whole sediments, the SSTTs-LR 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 advanced SLERA 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 advanced SLERA are likely to support the identification of COPCs that require further evaluation during the SLERA and/or those that need to be considered in the BERA. 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 SSTTs-LR and SSTTs-HR that are derived to support the advanced SLERA 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 advanced SLERA 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 advanced SLERA will not provide a basis for evaluating risks to:

- 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 SLERA 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. Importantly, the uncertainties that are identified in the CSM will be further addressed during problem formulation for the BERA, if required, and by conducting additional

investigations during the remedial investigation (i.e., the CSM will be further developed to address, to the extent possible, the uncertainties that are identified).

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, whole-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 SLERA. First, indicator species have been selected to evaluate the potential for exposure for certain groups of aquatic receptors (e.g., information on the amphipod, *H. azteca,* 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 SLERA 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 is not recommended for the sampling program. Rather, focused water quality sampling in conjunction with detailed source identification activities should be conducted 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 SLERA. 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. 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
Oklahoma Portion of the TSMD				
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; NO_3 = nitrate, NH_4 = ionized ammonia.

Table 2. Mussels collected in the Spring River Basin in Missouri (Oesch 1984).

Common Name	Scientific Name
Paper floater	*Anodonta imbecilis*
Giant floater	*Anodonta grandis grandis*
Squaw foot	*Strophitus undulatus undulatus*
Elk toe	*Alasmidonta marginata*
Slipper shell	*Alasmidonta viridis*
White heel-splitter	*Lasmigona complanata*
Fluted shell	*Lasmigona costata*
Pistol-grip	*Tritogonia verrucosa*
Maple leaf	*Quadrula quadrula*
Rabbit's foot	*Quadrula cylindrica cylindrica*
Monkey face	*Quadrula metanevra*
Pimple-back	*Quadrula pustulosa*
Three-ridge	*Amblema plicata plicata*
Wabash pig-toe	*Fusconaia flava*
Ozark shell	*Fusconaia ozarkensis*
Round pig-toe	*Pleurobema coccineum*
Lady-finger	*Elliptio dilata*
Kidney-shell	*Ptychobranchus occidentalis*
Western fanshell	*Cyprogenia aberti*
Mucket	*Actinonaias ligamentina carinata*
Plea's mussel	*Venustaconcha ellipsiformis*
Fawn's foot	*Truncilla donaciformis*
Deer-toe	*Truncilla truncata*
Fragile paper shell	*Leptodea fragilis*
Liliput shell	*Toxolasma parvus*
Little purple	*Toxolasma lividus glans*
Pond mussel	*Ligumia subrostrata*
Slough sand shell	*Lampsilis teres teres*
Yellow sand shell	*Lampsilis teres anodontoides*
Fat mucket	*Lampsilis radiata luteola*
Neosho mucket	*Lampsilis rafinesqueana*
Pocketbook	*Lampsilis ventricosa*
Broken rays	*Lampsilis reeviana brevicula*
Purple pimpleback	*Cyclonaias tuberculata*
Black sand shell	*Ligumia recta*

Table 3. Fish species found in the Spring River Basin (MDC 1991 and Beckman 1995).

Common Name	Scientific Name
Percidae (Perches)	
Arkansas darter	*Etheostoma cragini*
Fantail darter	*Etheostoma flabellare*
Orangethroat darter	*Etheostoma spectabile*
Stippled darter	*Etheostoma punctulatum*
Cyprinidae (Minnows or carps)	
Cardinal shiner	*Luxilus cardinalis*
Common carp	*Cyprinus carpio*
Creek chub	*Semotilus atromaculatus*
Southern redbelly dace	*Phoxinus erythrogaster*
Stoneroller	*Campostoma sp.*
Lepisosteidae (Gars)	
Longnose gar	*Lepisosteus osseus*
Shortnose gar	*Lepisosteus platostomus*
Catostomidae (Suckers)	
Black buffalo	*Ictiobus niger*
Black redhorse	*Moxostoma duquesnei*
Golden redhorse	*Moxostoma erythrurum*
Northern hog sucker	*Hypentelium nigricans*
River carpsucker	*Carpiodes carpio*
River redhorse	*Moxostoma carinatum*
Shorthead redhorse	*Moxostoma macrolepidotum*
Spotted sucker	*Minytrema melanops*
White sucker	*Catostomus commersoni*
Centrarchidae (Sunfishes)	
Green sunfish	*Lepomis cyanellus*
Warmouth	*Lepomis gulosus*
Ictaluridae (North American freshwater catfishes)	
Blue catfish	*Ictalurus punctatus*
Black bullhead	*Ameiurus melas*
Flathead catfish	*Pylodictis olivaris*
Yellow bullhead	*Ameiurus natalis*
Neosho madtom	*Noturus placidus*
Salmonidae (Salmonids)	
Rainbow trout	*Oncorhynchus mykiss*
Clupeidae (Herrings, shads, sardines, menhadens)	
Gizzard shad	*Dorosoma cepedianum*

Table 4. Amphibian species found in the Spring River Basin (Johnson 1987).

Common Name	Scientific Name	Range
Salamanders		
Ringed salamander	*Ambystoma annulatum*	Basinwide
Spotted salamander	*Ambystoma maculatum*	Basinwide
Marbled salamander	*Ambystoma opacum*	Eastern counties of the basin
Smallmouth salamander	*Ambystoma texanum*	Western counties of the basin
Eastern tiger salamander	*Ambystoma tigrinum tigrinum*	Basinwide
Central newt	*Notophthalmus viridescens louisianensis*	Basinwide
Longtail salamander	*Eurycea longicauda*	Basinwide
Cave salamander	*Eurycea lucifuga*	Basinwide
Graybelly salamander	*Eurycea multiplicata griseogaster*	Basinwide
Oklahoma salamander	*Eurycea tynerensis*	Basinwide
Ozark zigzag salamander	*Plethodon dorsalis angusticlavius*	Basinwide
Slimy salamander	*Plethodon glutinosus glutinosus*	Basinwide
Grotto salamander	*Typhlotriton spelaeus*	Basinwide
Red River mudpuppy	*Necturus maculosis louisianensis*	Basinwide
Frogs and Toads		
Dwarf American toad	*Bufo americanus charlesmithi*	Basinwide
Fowler’s toad	*Bufo woodhousei fowleri*	Basinwide
Woodhouse’s toad	*Bufo woodhousei woodhousei*	possibly in Newton County
Blanchard’s cricket frog	*Acris crepitans blanchardi*	Basinwide
Northern spring peeper	*Hyla crucifer crucifer*	Basinwide
Cope’s gray treefrog	*Hyla chrysoscelis*	Basinwide
Western chorus frog	*Pseudacris triseriata*	Basinwide
Eastern narrowmouth toad	*Gastrophryne carolinensis*	Basinwide
Great Plains narrowmouth toad	*Gastrophryne olivacea*	Western counties of the basin
Northern crawfish frog	*Rana areolata circulosa*	Western counties of the basin
Bullfrog	*Rana catesbeiana*	Basinwide
Green frog	*Rana clamitans*	Basinwide
Pickerel frog	*Rana palustris*	Basinwide
Southern leopard frog	*Rana sphenocephala*	Basinwide
Wood frog	*Rana sylvatica*	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	*Chelydra serpentina serpentina*	Basinwide
Alligator snapping turtle	*Macroclemys temminckii*	Southern counties of the basin
Yellow mud turtle	*Kinosternon flavescens*	Western counties of the basin
Stinkpot	*Sternotherus odoratus*	Basinwide
Western painted turtle	*Chrysemys picta bellii*	Basinwide
Common Map turtle	*Graptemys geographica*	Basinwide
Mississippi map turtle	*Graptemys kohnii*	Basinwide
Ouachita map turtle	*Graptemys pseudogeographica ouachitensis*	Basinwide
River cooter	*Pseudemys concinna concinna*	Basinwide
Three-toed box turtle	*Terrapene carolina triunguis*	Basinwide
Ornate box turtle	*Terrapene ornata ornata*	Basinwide
Red-eared slider	*Trachemys scripta elegans*	Basinwide
Midland smooth softshell	*Apalone mutica mutica*	Basinwide
Eastern spiny softshell	*Apalone spinfera spinifera*	Basinwide
Lizards		
Eastern collared lizard	*Crotaphytus collaris collaris*	Basinwide
Texas horned lizard	*Phrynosoma cornutum*	Western counties of the basin
Northern fence lizard	*Sceloporus undulatus hyacinthinus*	Basinwide
Southern coal skink	*Eumeces anthracinus pluvialis*	Basinwide
Five-lined skink	*Eumeces fasciatus*	Basinwide
Broadhead skink	*Eumeces laticeps*	Basinwide
Great Plains skink	*Eumeces obsoletus*	Western counties of the basin
Northern Prairie Skink	*Eumeces septentrionalis*	Western counties of the basin
Ground skink	*Scincella lateralis*	Basinwide
Six-lined racerunner	*Cnemidophorus sexlineatus sexlineatus*	Basinwide
Western slender glass lizard	*Ophisaurus attenuatus attenuatus*	Basinwide
Snakes		
Western worm snake	*Carphophis vermis*	Basinwide
Eastern yellowbelly racer	*Coluber constrictor flaviventris*	Basinwide
Prairie ringneck snake	*Diadophis punctatus arnyi*	Basinwide
Great Plains rat snake	*Elaphe guttata emoryi*	Basinwide
Black rat snake	*Elaphe obsoleta obsoleta*	Basinwide
Eastern hognose snake	*Heterodon platirhinos*	Basinwide
Prairie kingsnake	*Lampropeltis calligaster calligaster*	Basinwide
Speckled kingsnake	*Lampropeltis getula holbrooki*	Basinwide
Red milk snake	*Lampropeltis triangulum syspila*	Basinwide
Eastern coachwhip	*Masticophis flagellum flagellum*	Basinwide

Table 5. Reptile species found in the Spring River Basin (Johnson 1987).

Common Name	Scientific Name	Range
Blotched water snake	*Nerodia erythrogaster transversa*	Basinwide
Diamondback water snake	*Nerodia rhombifer rhombifer*	Western counties of the basin
Midland water snake	*Nerodia sipedon pleuralis*	Basinwide
Rough green snake	*Opheodrys aestivus*	Basinwide
Bullsnake	*Pituophis catenifer sayi*	Basinwide
Graham’s crayfish snake	*Regina grahamii*	Western counties of the basin
Ground snake	*Sonora semiannulata*	Basinwide
Midland brown snake	*Storeria dekayi wrightorum*	Eastern counties of the basin
Texas brown snake	*Storeria dekayi texana*	Basinwide
Northern redbelly snake	*Storeria occipitomaculata occipitomaculata*	Basinwide
Flathead snake	*Tantilla gracilis*	Basinwide
Western ribbon snake	*Thamnophis proximus proximus*	Basinwide
Eastern garter snake	*Thamnophis sirtalis sirtalis*	Basinwide
Red-sided garter snake	*Thamnophis sirtalis parietalis*	Western counties of the basin
Lined snake	*Tropidoclonion lineatum annectens*	Western counties of the basin
Rough earth snake	*Virginia striatula*	Basinwide
Western earth snake	*Virginia valeriae elegans*	Basinwide
Osage copperhead	*Agkistrodon contortrix phaeogaster*	Northwest counties of the basin
Southern copperhead	*Agkistrodon contortrix contortrix*	Southern counties of the basin
Western cottonmouth	*Agkistrodon piscivorus leucostoma*	Southern counties of the basin
Timber rattlesnake	*Crotalus horridus*	Basinwide
Western pygmy rattlesnake	*Sistrurus miliarius streckeri*	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).

Larks

Horned Lark

Swallows

Bank Swallow
Barn Swallow
Cliff Swallow
Northern Rough-winged Swallow
Purple Martin
Tree Swallow

Jays & Crows

American Crow
Blue Jay
Fish Crow

Titmice, Chickadees, Nuthatches & Creepers

Brown Creeper
Carolina Chickadee
Red-breasted Nuthatch
Tufted Titmouse
White-breasted Nuthatch

Wrens

Bewick's Wren
Carolina Wren
House Wren
Marsh Wren
Sedge Wren
Winter Wren

Kinglets, Thrushes & Gnatcatchers

American Robin
Blue-gray Gnatcatcher
Eastern Bluebird
Golden-crowned Kinglet
Gray-cheeked Thrush
Hermit Thrush
Ruby-crowned Kinglet
Swainson's Thrush
Veery
Wood Thrush

Mockingbirds & Thrashers

Brown Thrasher
Gray Catbird
Northern Mockingbird

Shrikes

Loggerhead Shrike

Starlings

European Starling

Vireos

Bell's Vireo
Philadelphia Vireo
Red-eyed Vireo
Solitary Vireo
Warbling Vireo
White-eyed Vireo
Yellow-throated Vireo

Warblers

American Redstart
Bay-breasted Warbler
Black-and-white Warbler
Blackburnian Warbler
Blackpoll Warbler
Black-throated Green Warbler
Blue-winged Warbler
Canada Warbler
Cerulean Warbler
Chestnut-sided Warbler
Common Yellowthroat
Golden-winged Warbler
Kentucky Warbler
Louisiana Waterthrush
Magnolia Warbler
Mourning Warbler
Nashville Warbler
Northern Parula
Northern Waterthrush
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 Sparow
- 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	*Taxidea taxus*
Beaver	*Castor canadensis*
Black-tailed jack rabbit	*Lepus californicus*
Bobcat	*Felis rufus*
Chipmunk	*Eutamias spp.*
Coyote	*Canis latrans*
Deer	*Odocoileus spp.*
Gray bat	*Myotis grisescens*
Gray fox	*Urocyon cinereoargenteus*
Long-tailed weasel	*Mustela frenata*
Mink	*Mustela vison*
Muskrat	*Ondatra zibethicus*
Opossum	*Monodelphis spp.*
Rabbit	*Oryctolagus cuniculus*
Raccoon	*Procyon lotor*
Red fox	*Vulpes vulpes*
River otter	*Lontra canadensis*
Skunk	*Mephitis spp*
Squirrel	*Spermophilus spp.*

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	*Lepus californicus*	✓		
Gray bat	*Myotis grisescens*	✓		
Long-tailed weasel	*Mustella frenata*		✓	
Plains spotted skunk	*Spilogale putorius intemipta*	✓		
Swamp rabbit	*Sylvilagus aquaticus*		✓	
Birds				
Barn owl	*Tyto alba*		✓	
Cooper's hawk	*Accipiter cooperii*		✓	
Greater prairie-chicken	*Tympanuchus cupido*		✓	
Henslow's sparrow	*Ammodramus henslowii*		✓	
Northern harrier	*Circus cyaneus*	✓		
Ozark wake robin	*Trillium pusillum var ozarkanum*		✓	
Pied-billed grebe	*Podilymbus podiceps*		✓	
Upland sandpiper	*Bartramia longicauda*			✓
Fish				
Arkansas darter	*Etheostoma cragini*		✓	
Bluntface shiner	*Cyprinella camura*		✓	
Ghost shiner	*Notropis buchanani*			✓
Least darter	*Etheostoma microperca*			✓
Neosho madtom	*Noturus placidus*	✓		
Ozark cavefish	*Amblyopsis rosae*	✓		

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
Fish (cont)				
Pugnose minnow	*Opsopoeodus emiliae*			✓
Redfin darter	*Etheostoma whipplei*	✓		
Western slim minnow	*Pimephales tenellus tenellus*		✓	
Reptiles/Amphibians				
Great plains skink	*Eumeces obsoletus*		✓	
Grotto salamander	*Typhlotriton spelaeus*			✓
Northern crayfish frog	*Rana areolata circulosa*			✓
Invertebrates				
Bristly cave crayfish	*Cambarus setosus*			✓
Neosho mucket	*Lampsilis rafinesqueana*		✓	
Rabbits foot (bivalve)	*Quadrula cylindrica cylindrica*	✓		
Western fanshell (bivalve)	*Cyprogenia aberti*		✓	
Insects				
Arkansas snaketail dragonfly	*Ophiogomphus westfalli*		✓	
Prairie mole cricket	*Gryllotalpa major*		✓	
Regal fritillary (butterfly)	*Speyeria idalia*			✓
Plants				
False foxglove spp.	*Agalinis auriculata*		✓	✓
Moss spp.	*Leska polycarpa*		✓	
Venus' looking glass spp.	*Triodanis lamprosperma*		✓	

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
Plants (cont.)				
Wild pea spp.	*Lathyrus pusillus*	✓		
Alabama lip-fern	*Chalanthes alabamensis*	✓		
Adder's tongue fern spp.	*Ophioglossum vulgatum*			✓
Brush's poppy mallow	*Callirhoe bushii*			✓
Drummond's halfchaff sedge	*Lipocarpha drummondii*	✓		
Geocarpon	*Geocarpon minimum*	✓		
Green false foxglove	*Agalinis viridis*	✓		
Joint grass	*Coelorachis cylindrica*	✓		
Kansas arrowhead	*Sagittaria ambigua*	✓		
Lake-bank sedge	*Carex lacustris*	✓		
Low prickly pear *Opuntia macrorhiza*	*Opuntia macrorhiza*		✓	
Marsh bellflower	*Campanula aparinoides*	✓		
Mead's milkweed	*Asclepias meadii*	✓		
Mudbank paspalum	*Paspalum dissectum*	✓		
Oklahoma sedge	*Carex oklahomensis*		✓	
Pinnate dog shade	*Limnosciadium pinnatum*	✓		
Prairie false foxglove	*Agalinis heterophylla*	✓		
Purple lilliput	*Toxolasma lirudus*			✓
Royal catchfly	*Silene regia*			✓
Running buffalo clover	*Trifolium stoloniferum*	✓		
Sixteenweeks three-awn	*Aristida adscensionis*			✓
Slender ladies' tresses	*Spiranthes lacera var gracilis*			✓
Slender pondweed	*Potamogeton pusillus var pusillus*	✓		

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
Plants (cont)				
Small spike rush	*Eleocharis parvula var anachaeta*		✓	
Soapberry	*Sapindus drummondii*			✓
Tansy mustard	*Descurainia pinnata*	✓		
Tradescant aster	*Aster dumosus var strictior*		✓	
Water hyssop	*Mecardonia acuminata*	✓		
Western prairie fringed orchid	*Planthera praeclara*	✓		
Yellow-eyed grass	*Xyris torta*	✓		
Yellow false mallow	*Malvastrum*			✓
Yellow-flowered leafcup	*Smallanthus wedalius*			✓

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 (H_2S)
Toxic substances that partition into sediments and/or soils	**Metals**
	Arsenic, boron, cadmium, chromium, copper, lead, lithium, mercury, nickel, selenium, zinc
	PAHs
	Parent PAHs (*Acenaphthene, Acenaphthylene, Anthracene, Fluorene, 2-Methylnaphthalene, Naphthalene, PhenanthreneBenz(a)anthracene, Benzo(a)pyrene, Chrysene, Dibenz(a,h)anthracene, Fluoranthene, Pyrene*), 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
	Benz(a)anthracene, Benzo(a)pyrene, Chrysene, Dibenz(a,h)anthracene, Fluoranthene, Pyrene
	PCBs
	Aroclors, PCB congeners, Total PCBs
	Organochlorine pesticides

PCBs = Polychlorinated biphenyls; PAHs = Polycyclic aromatic hydrocarbons; NO_2 = nitrite; NO_3 = nitrate, NH_3 = 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_2S	✓				✓
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; NO_3 = nitrate, NH_3 = ammonia; P = phosphorous; TSS = total suspended solids; BOD = biological oxygen demand; H_2S = 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_2S	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	Insectivorus birds, Sediment-probing birds, Carnivorous-wading birds, Piscivorus birds	Piscivorus mammals, Omnivorous mammals

PCBs = Polychlorinated biphenyls; PAHs = Polycyclic aromatic hydrocarbons; OC = organochlorine; NO_2 = nitrite; NO_3 = nitrate, NH_3 = ammonia; P = phosphorous;
TSS = total suspended solids; BOD = biological oxygen demand; H_2S = 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; NO_2 = nitrite;
NO_3 = nitrate, NH_3 = ammonia; P = phosphorous; TSS = total suspended solids; BOD = biological oxygen demand.

Figures

Figure 1. Map of the Tri-State Mining District study area.

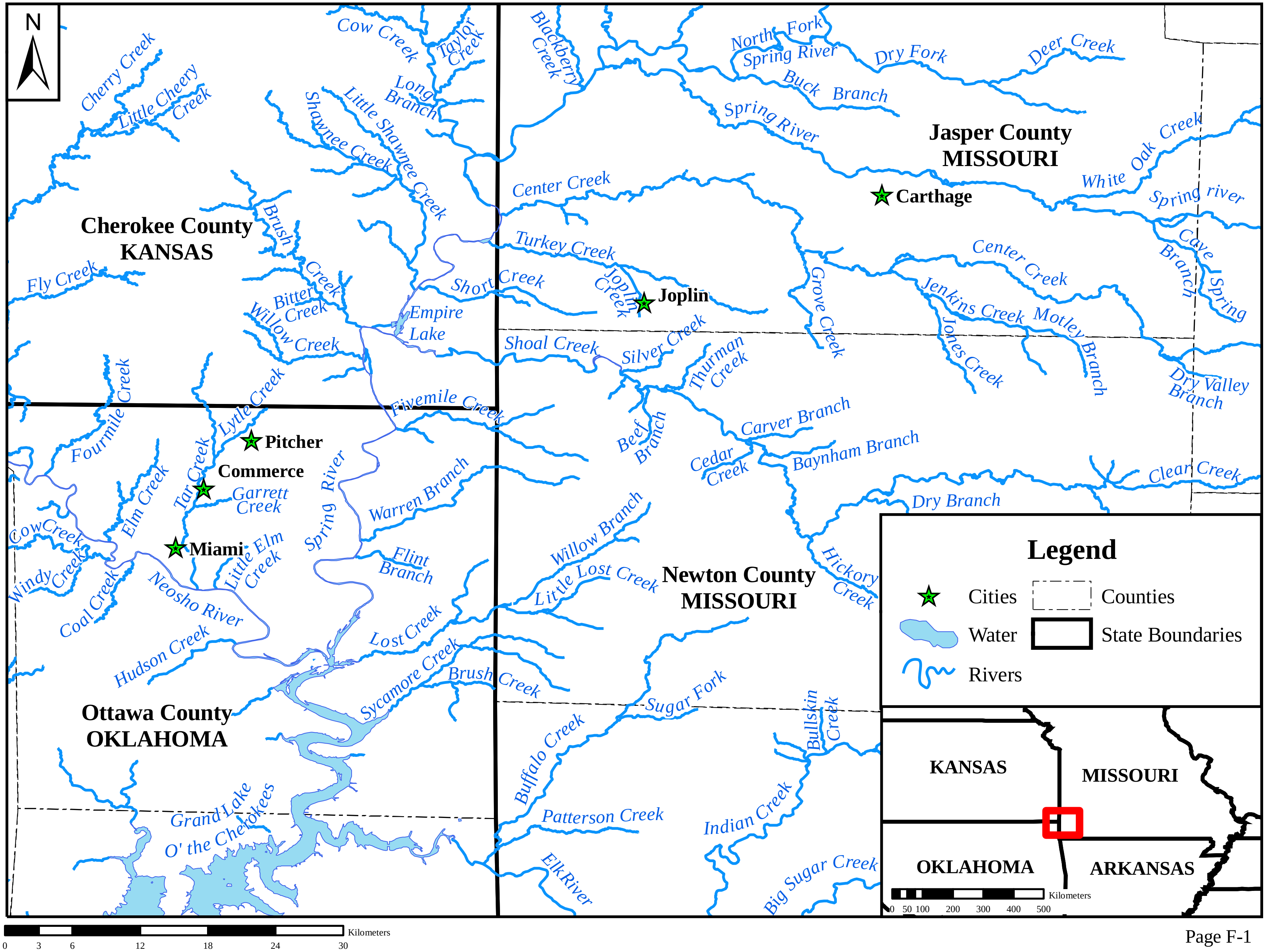


Figure 2. The framework for ecological risk assessment (modified from USEPA 1997).

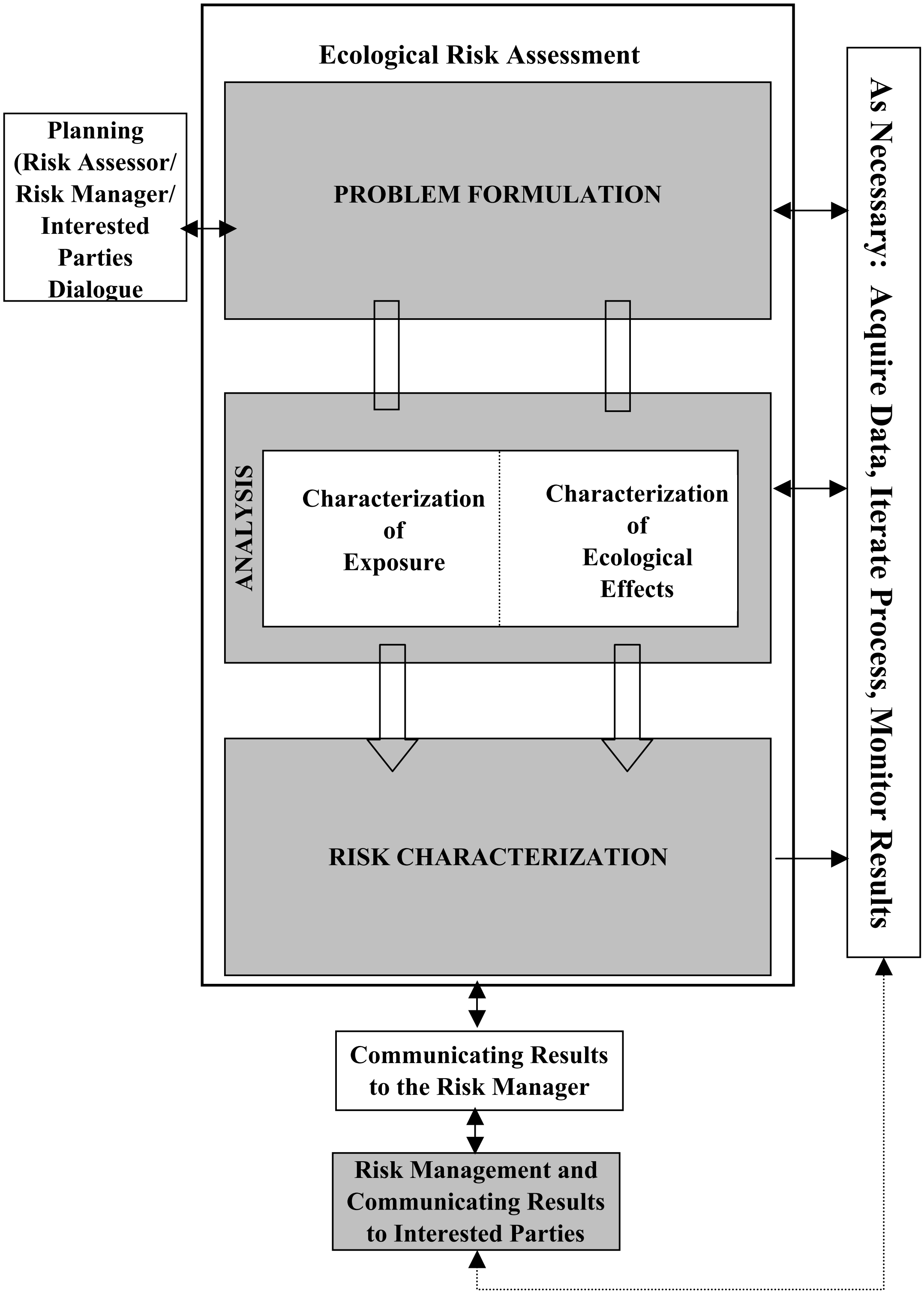
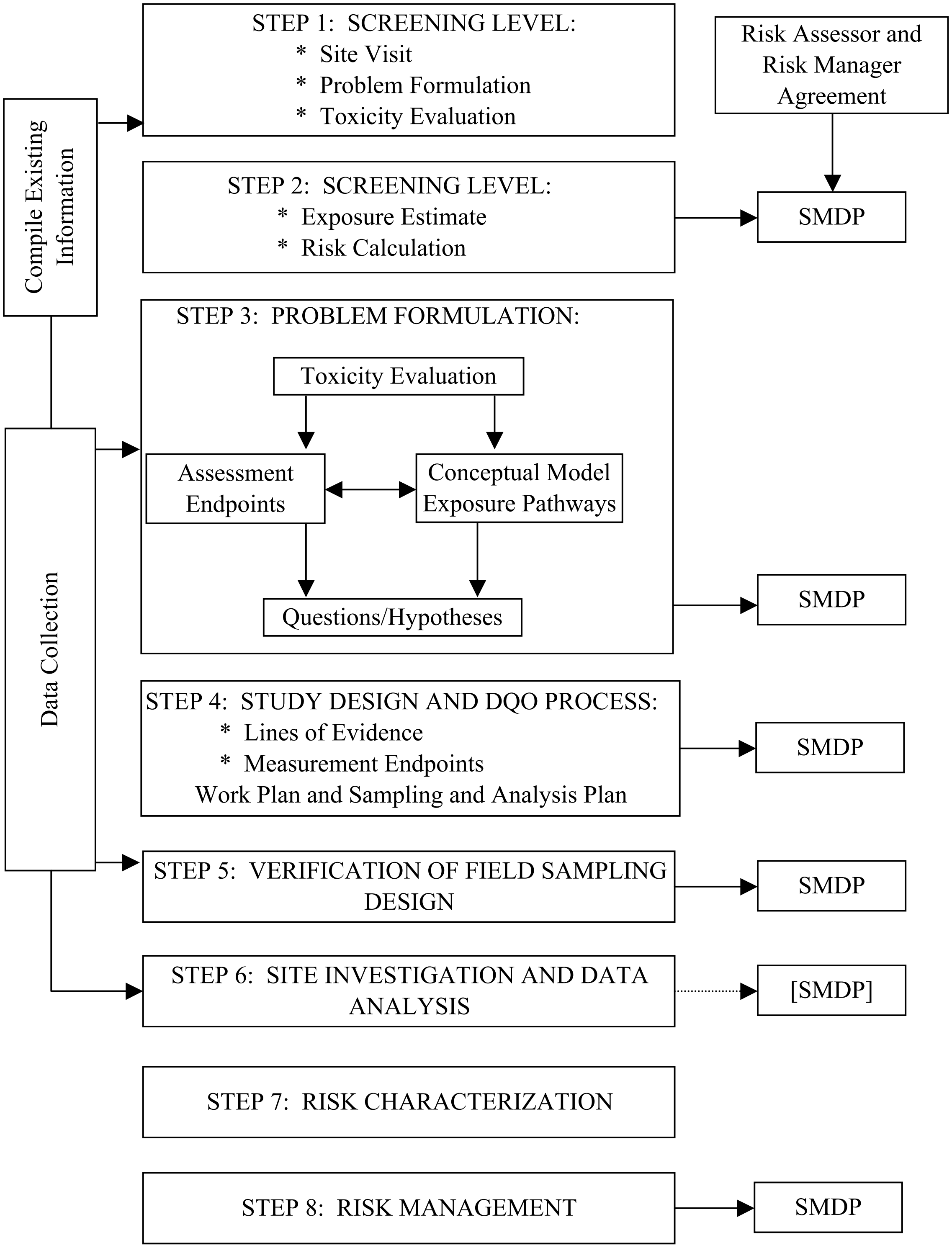


Figure 3. Eight-step ecological risk assessment process for Superfund (USEPA 1997).



SMDP = Scientific/Management Decision Point

Figure 4. Map of the Tri-State Mining District, showing distributions of stations sampled in 2006 to obtain whole-sediment chemistry and associated data.

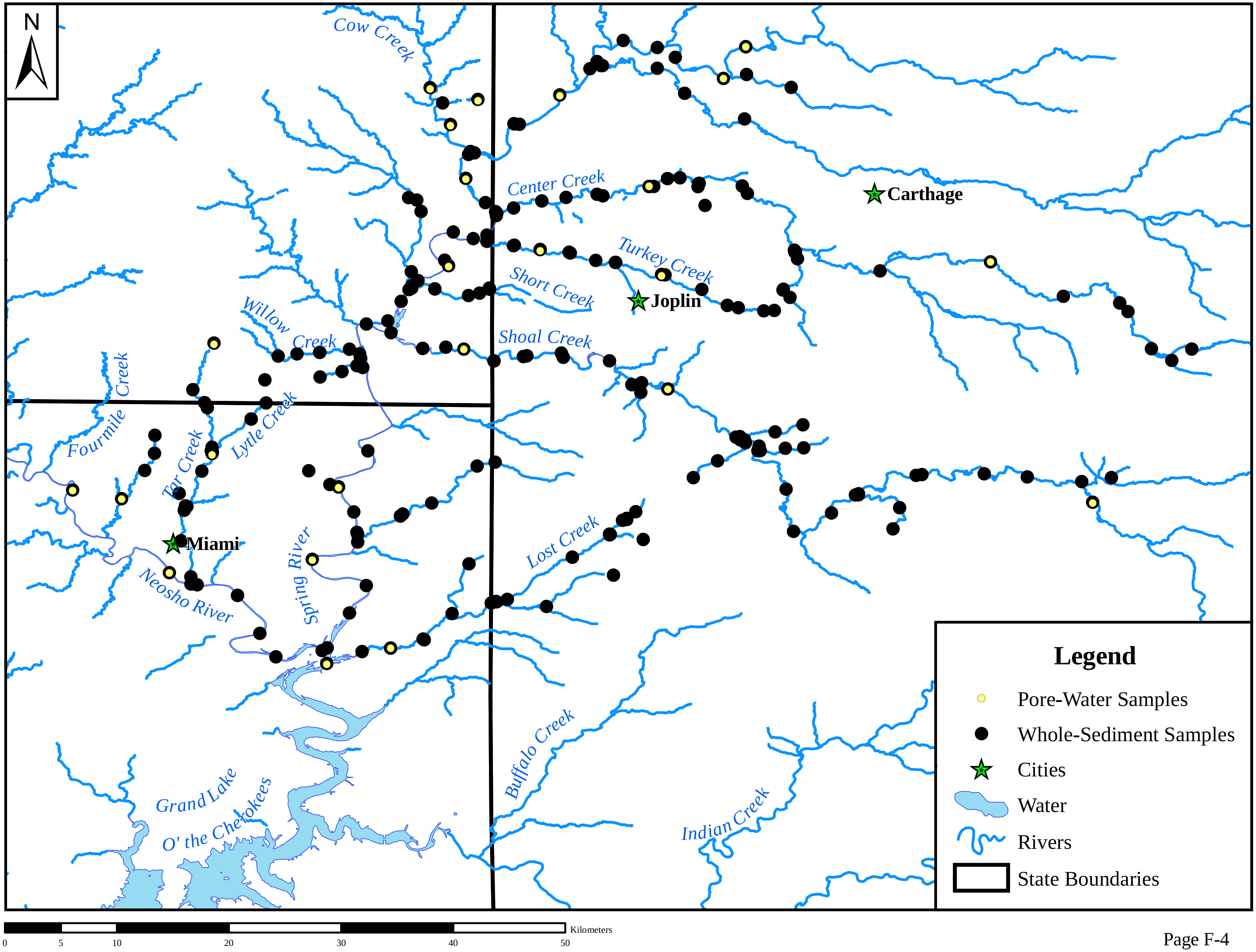


Figure 5. Map of the Tri-State Mining District, showing locations of selected and alternate candidate sampling locations for reference samples for the 2007 field sampling program.

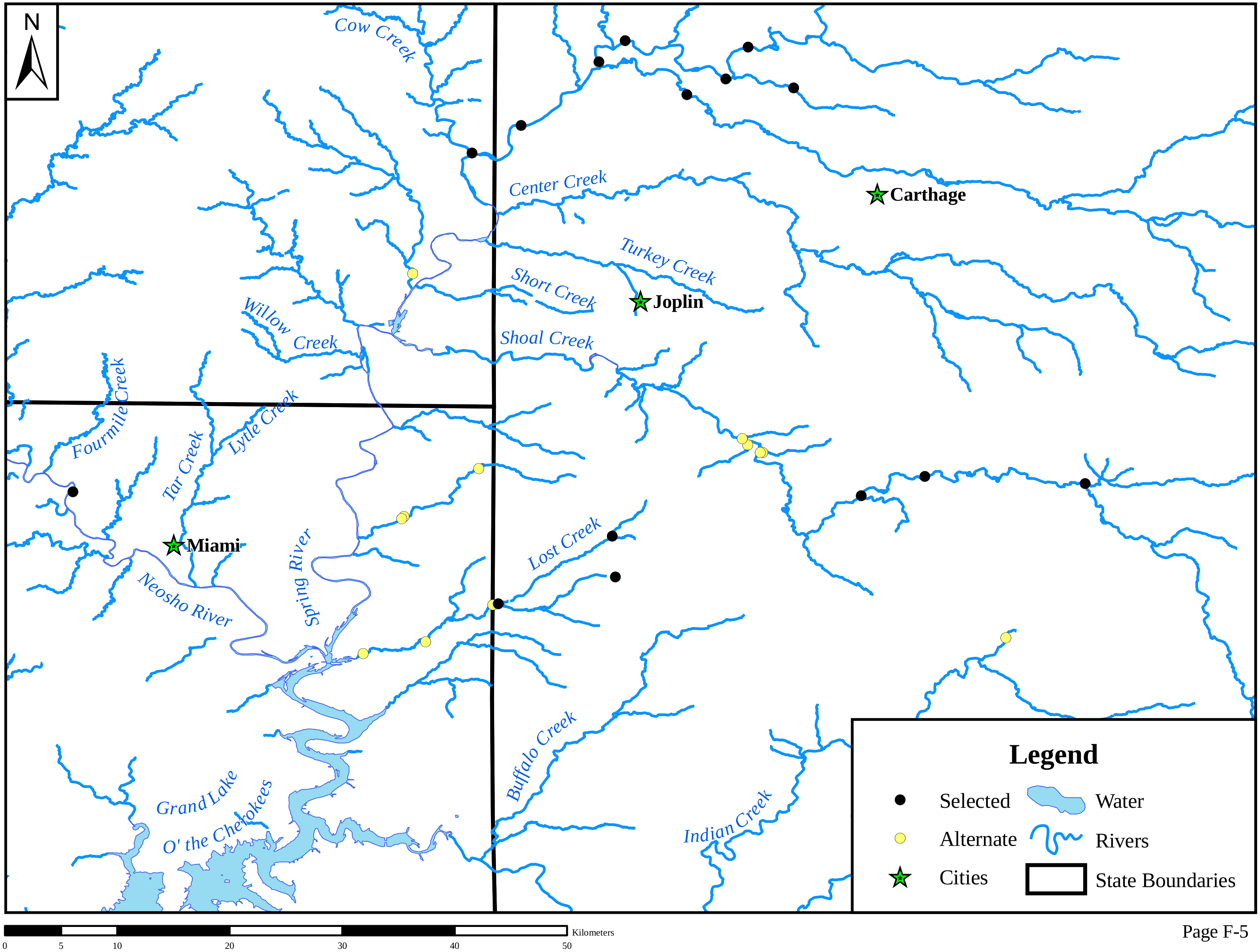


Figure 6. Map of the Tri-State Mining District, showing the eight Areas of Interest (AoIs).

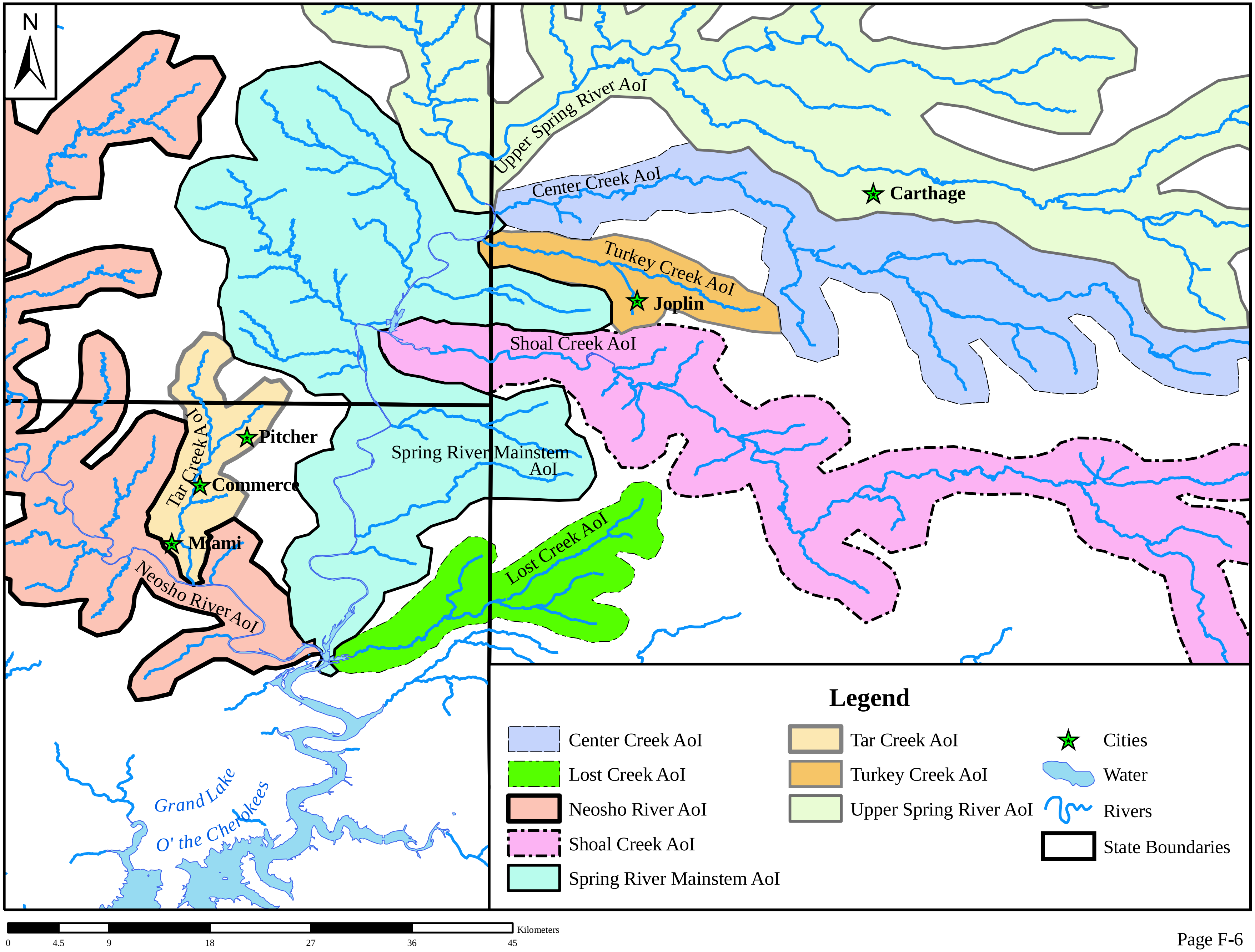
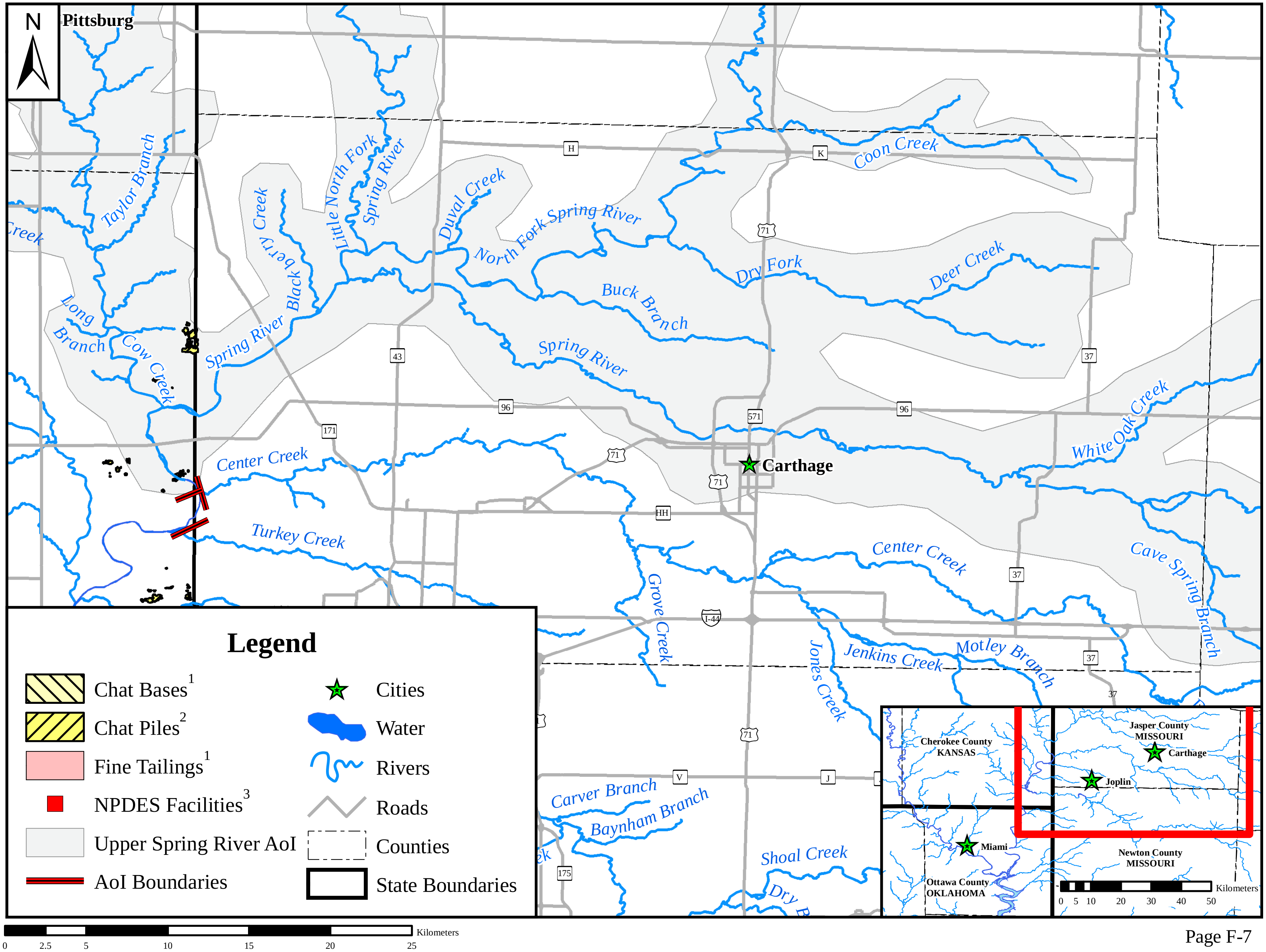


Figure 7. Map of the Tri-State Mining District, showing the Upper Spring River Area of Interest (AoI).

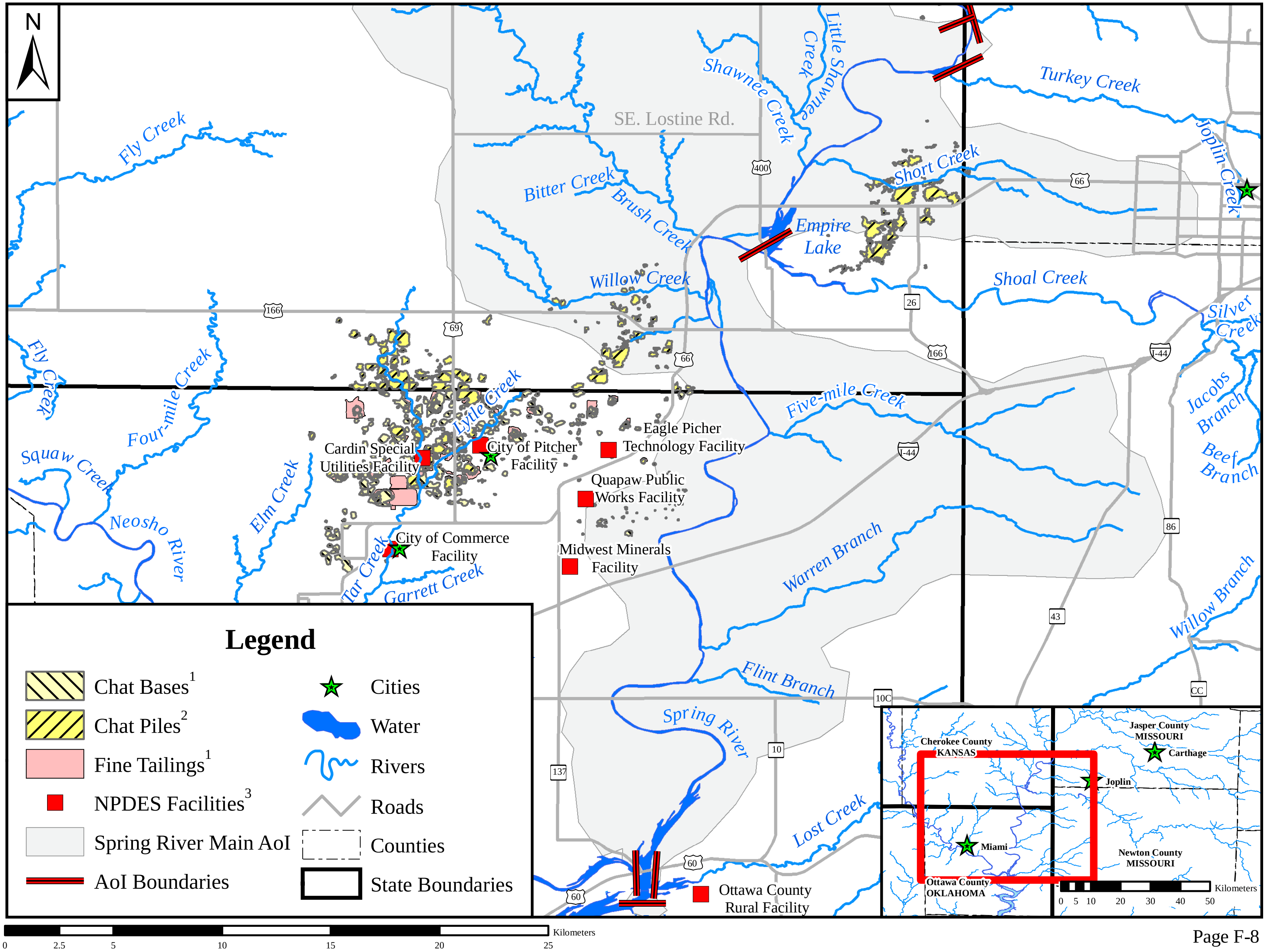


[1] OK only; MO and KS to be determined.

[2] OK and KS Chat Piles; MO to be determined.

[3] Facilities with NPDES permits (OK only; MO and KS to be determined).

Figure 8. Map of the Tri-State Mining District, showing the Spring River Mainstem Area of Interest (AoI).

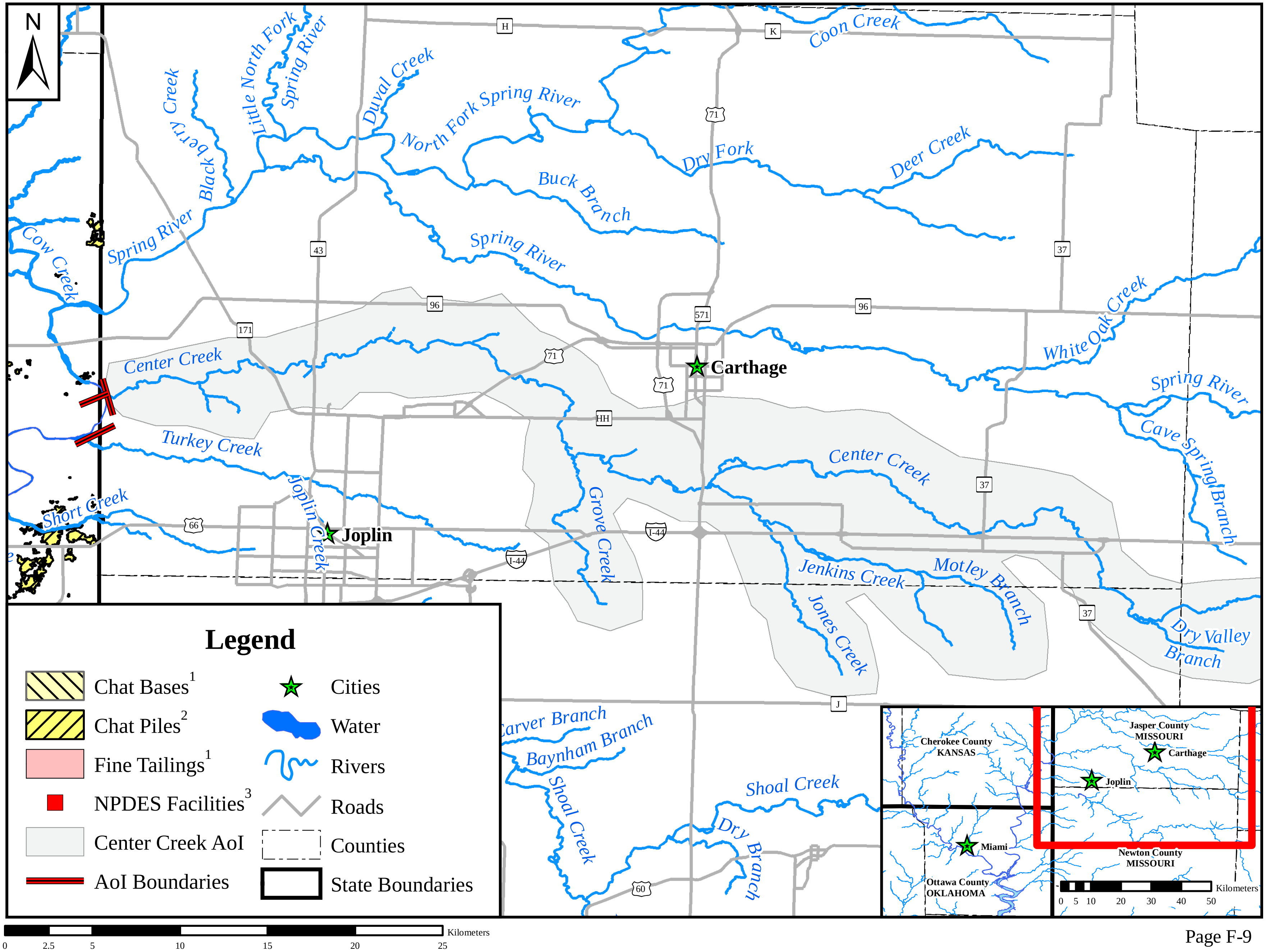


[1] OK only; MO and KS to be determined.

[2] OK and KS Chat Piles; MO to be determined.

[3] Facilities with NPDES permits (OK only; MO and KS to be determined).

Figure 9. Map of the Tri-State Mining District, showing the Center Creek Area of Interest (AoI).

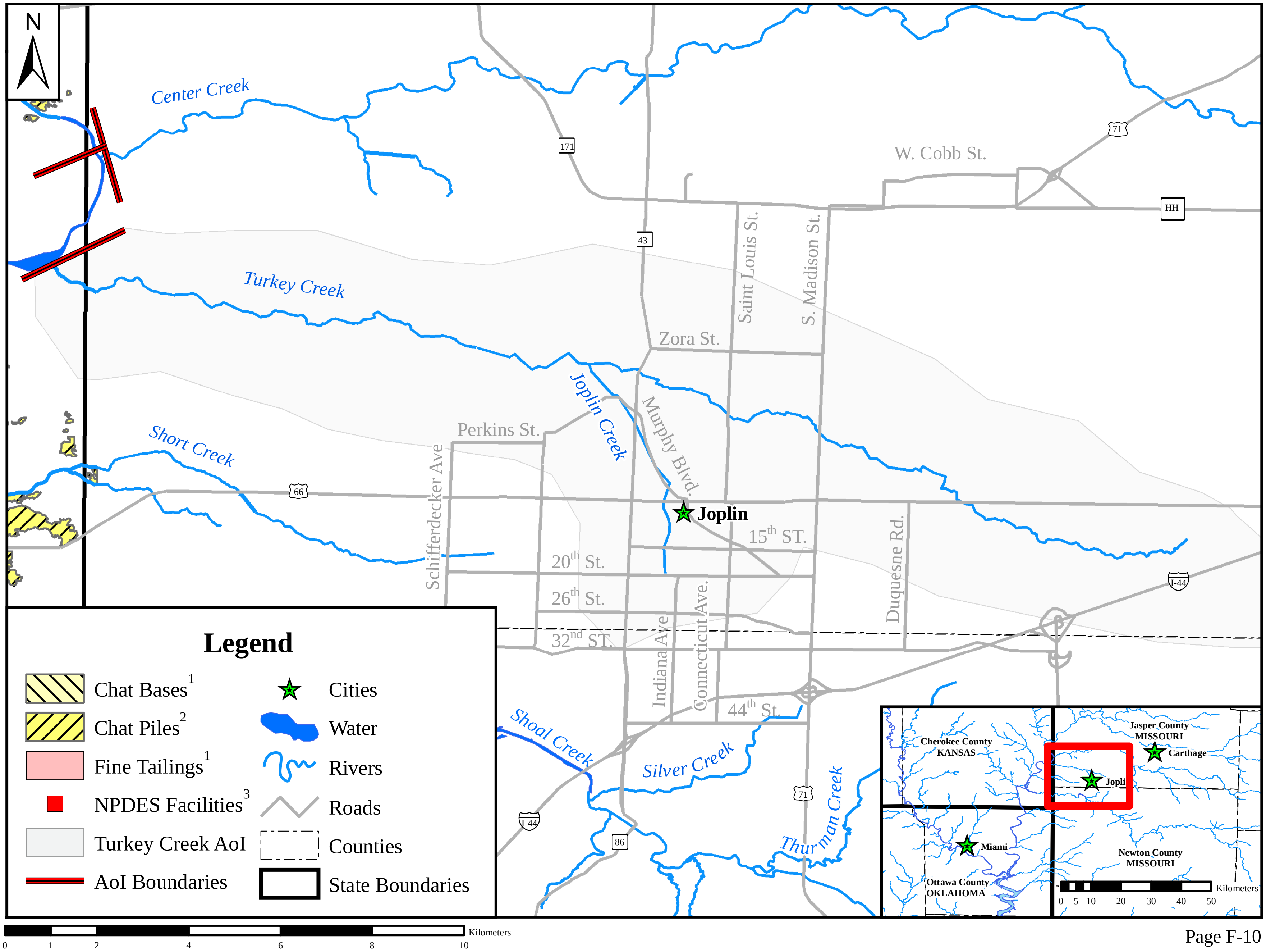


[1] OK only; MO and KS to be determined.

[2] OK and KS Chat Piles; MO to be determined.

[3] Facilities with NPDES permits (OK only; MO and KS to be determined).

Figure 10. Map of the Tri-State Mining District, showing the Turkey Creek Area of Interest (AoI).

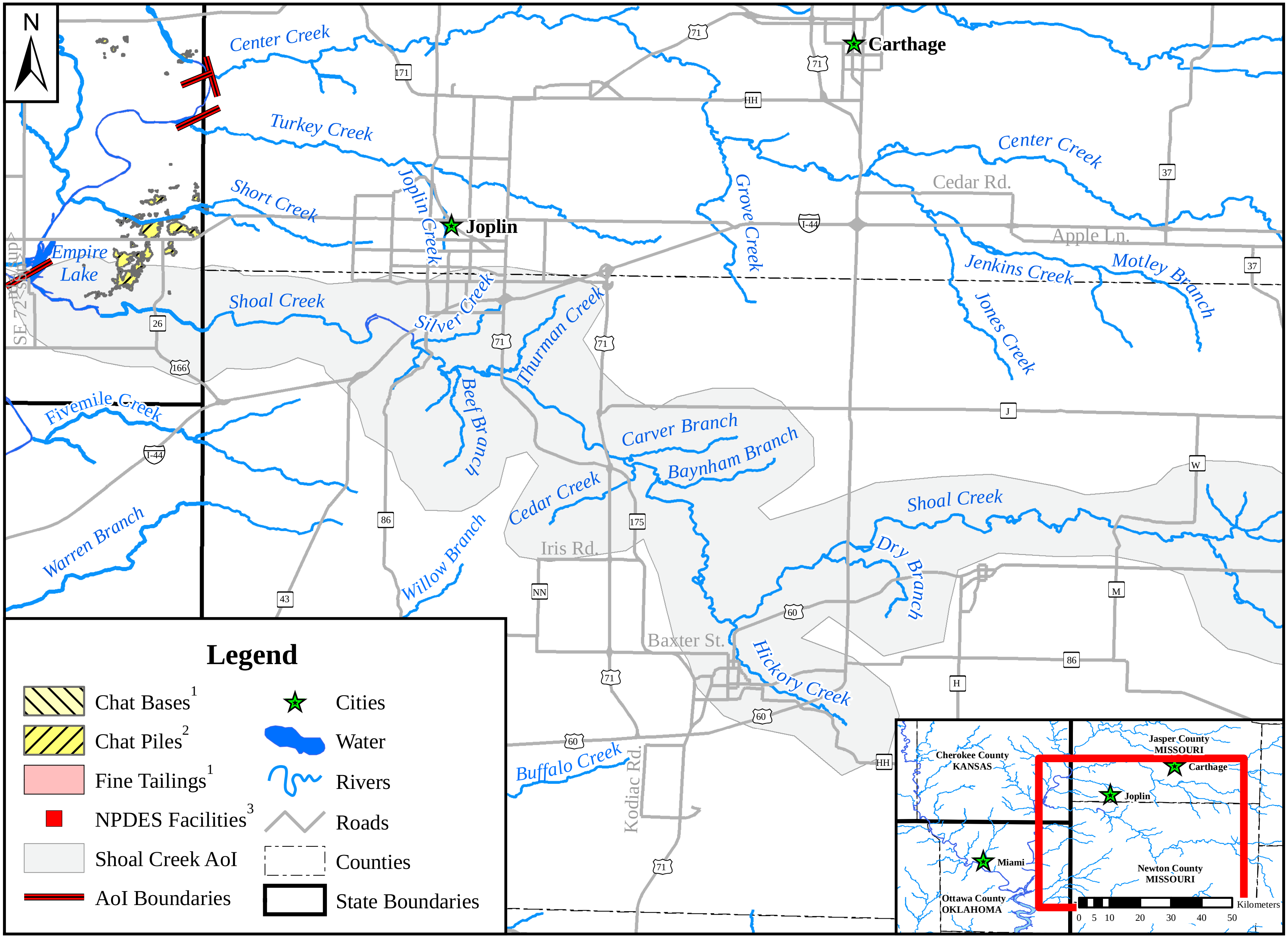


[1] OK only; MO and KS to be determined.

[2] OK and KS Chat Piles; MO to be determined.

[3] Facilities with NPDES permits (OK only; MO and KS to be determined).

Figure 11. Map of the Tri-State Mining District, showing the Shoal Creek Area of Interest (AoI).

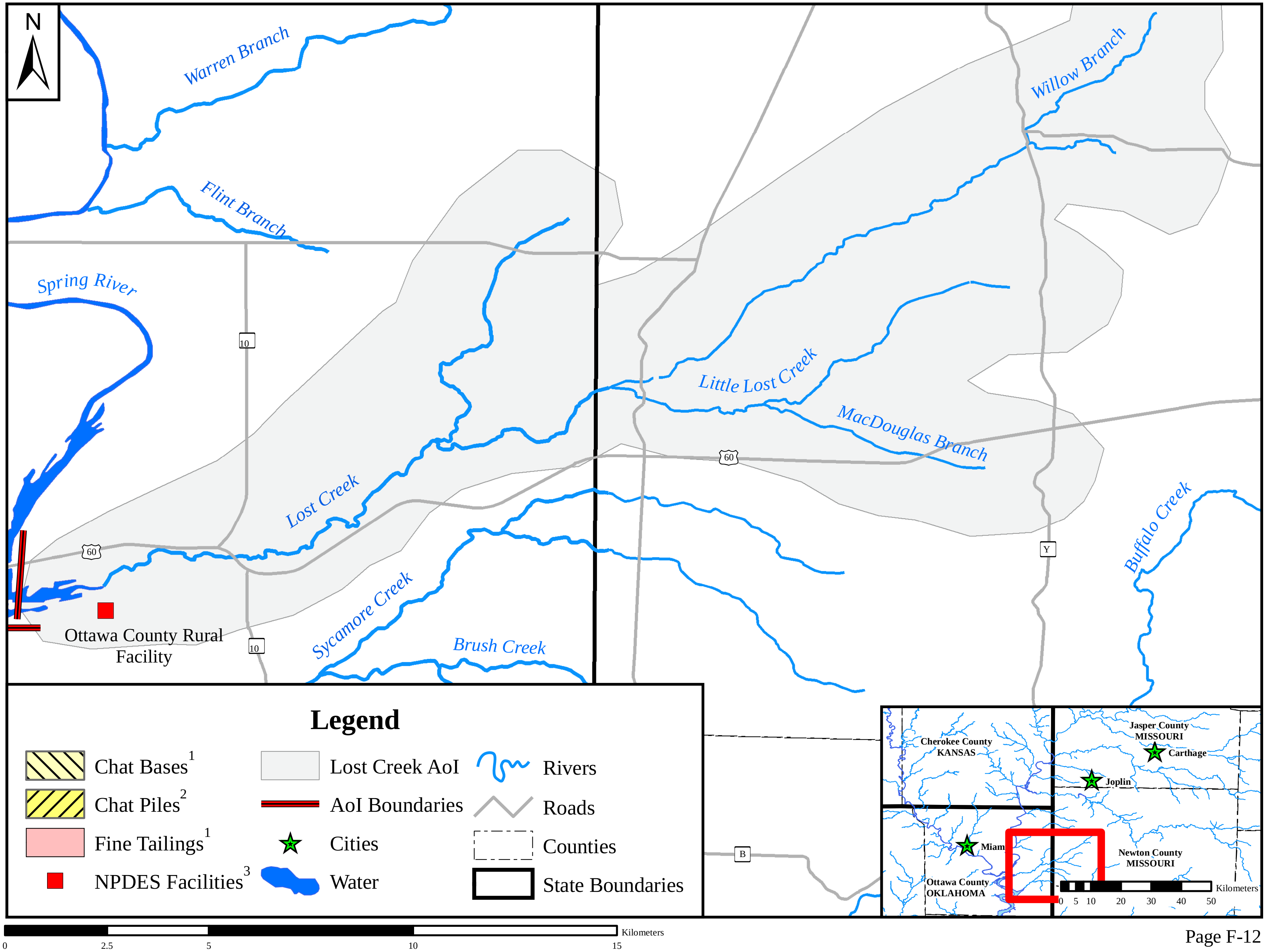


[1] OK only; MO and KS to be determined.

[2] OK and KS Chat Piles; MO to be determined.

[3] Facilities with NPDES permits (OK only; MO and KS to be determined).

Figure 12. Map of the Tri-State Mining District, showing the Lost Creek Area of Interest (AoI).

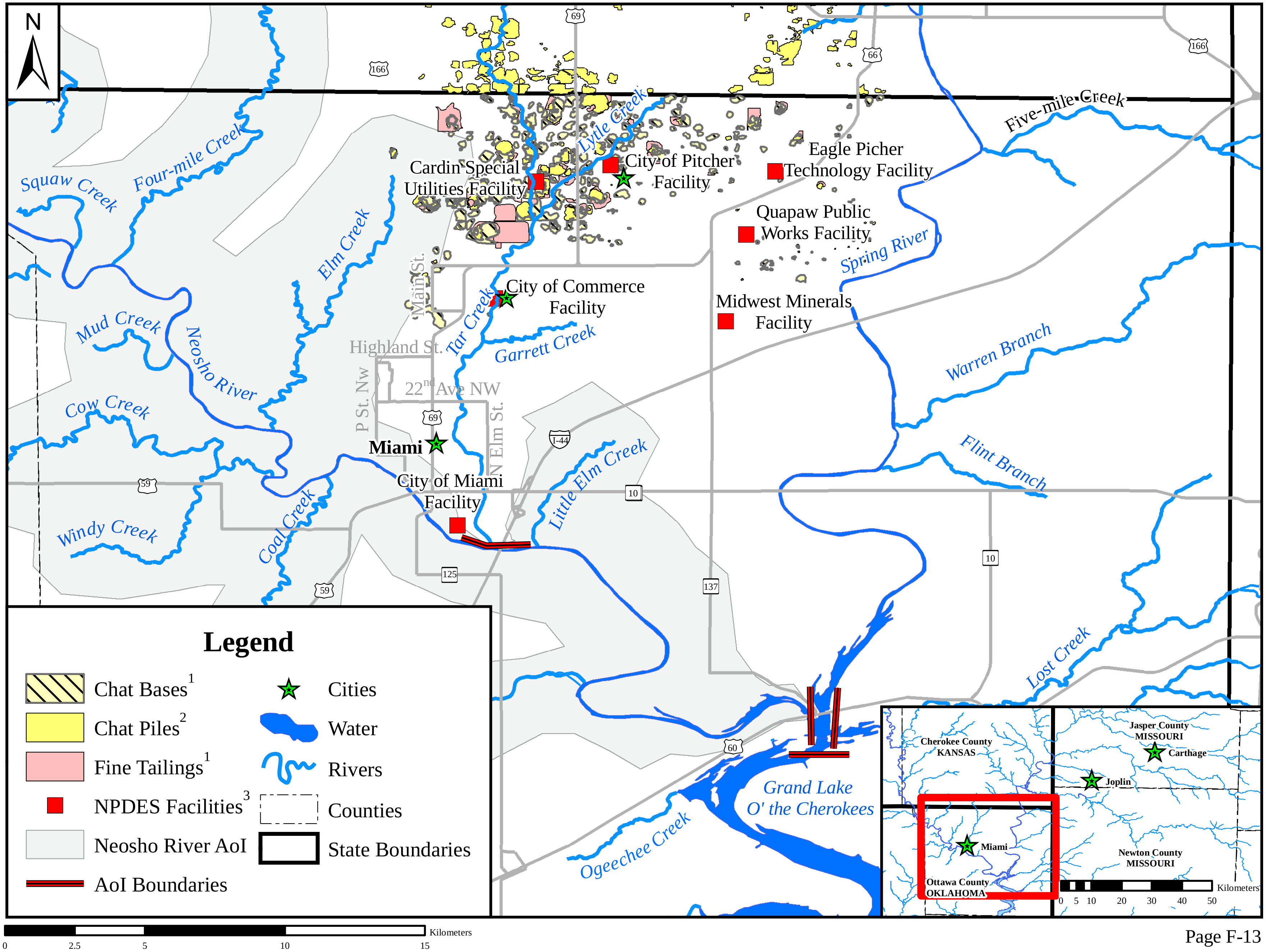


[1] OK only; MO and KS to be determined.

[2] OK and KS Chat Piles; MO to be determined.

[3] Facilities with NPDES permits (OK only; MO and KS to be determined).

Figure 13. Map of the Tri-State Mining District, showing the Neosho River Area of Interest (AoI).

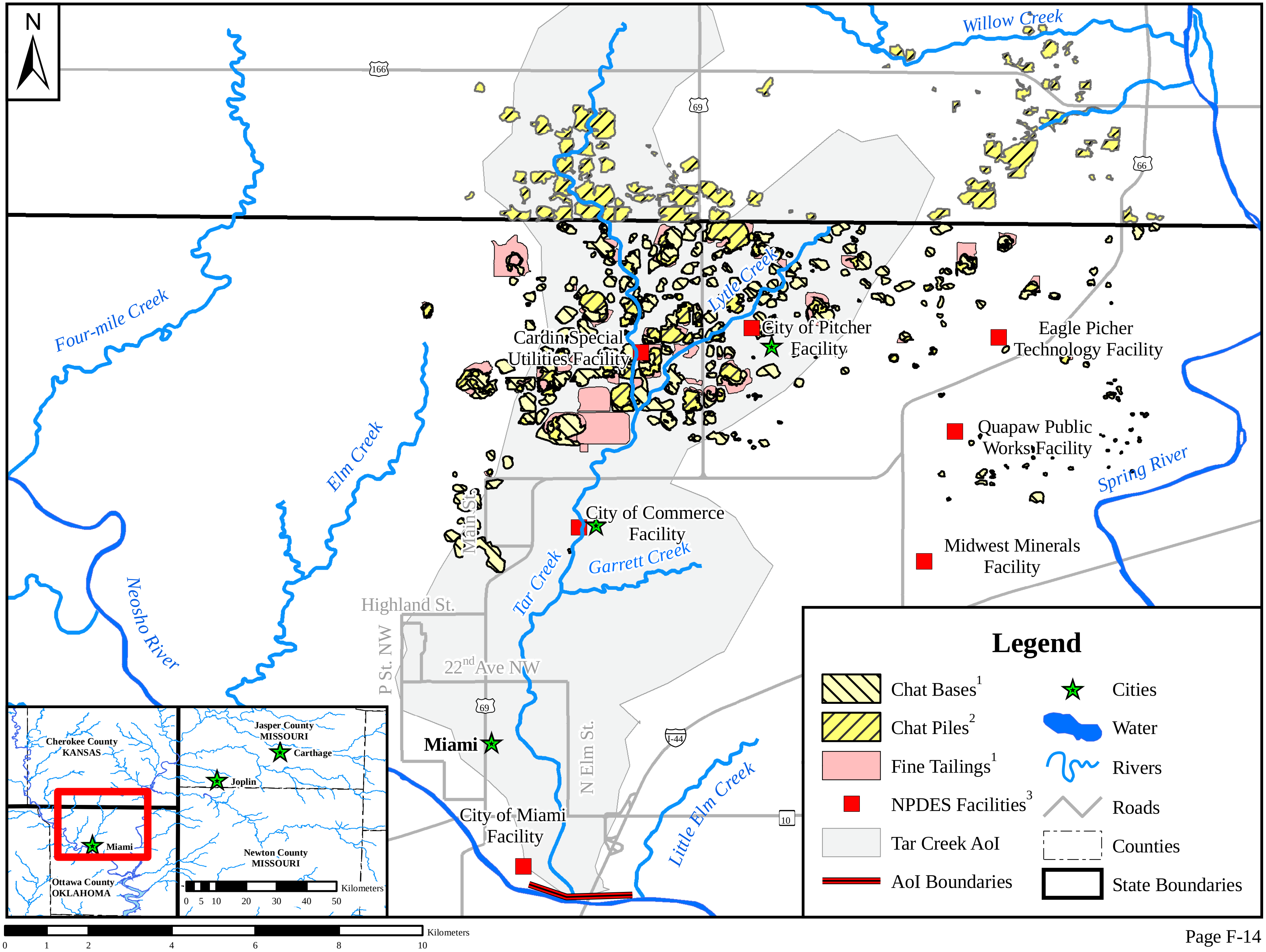


[1] OK only; MO and KS to be determined.

[2] OK and KS Dhat Piles; MO to be determined.

[3] Facilities with NPDES permits (OK only; MO and KS to be determined).

Figure 14. Map of the Tri-State Mining District, showing the Tar Creek Area of Interest (AoI).



[1] OK only; MO and KS to be determined.

[2] OK and KS Chat Piles; MO to be determined.

[3] Facilities with NPDES permits (OK only; MO and KS to be determined).

Figure 15. Simplified aquatic food web for a low order, cool water Ozark stream (Meyer, unknown).

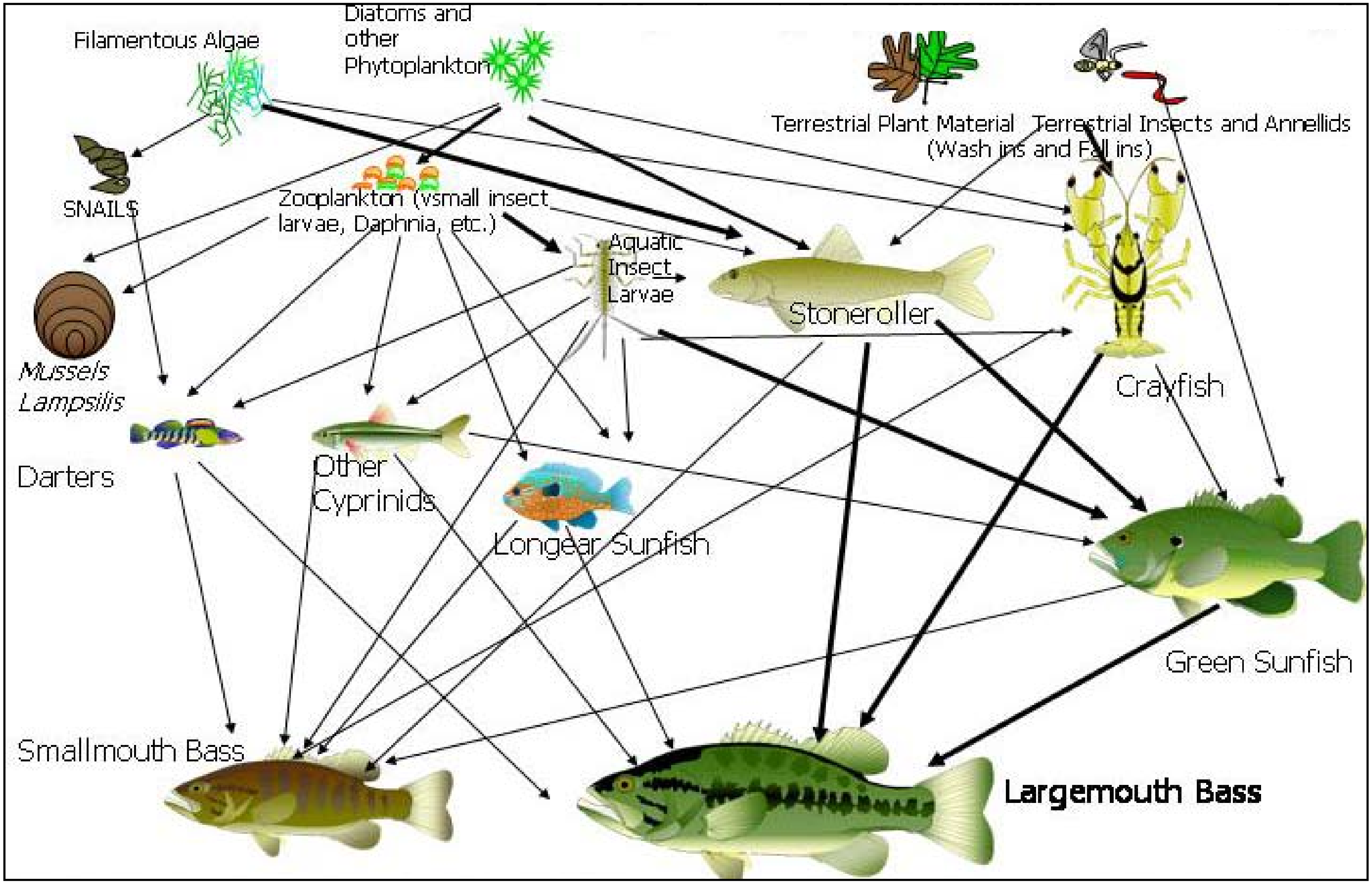


Figure 16. Simplified aquatic food web for a moderate order Ozark stream, after spring warming (Meyer, unknown).

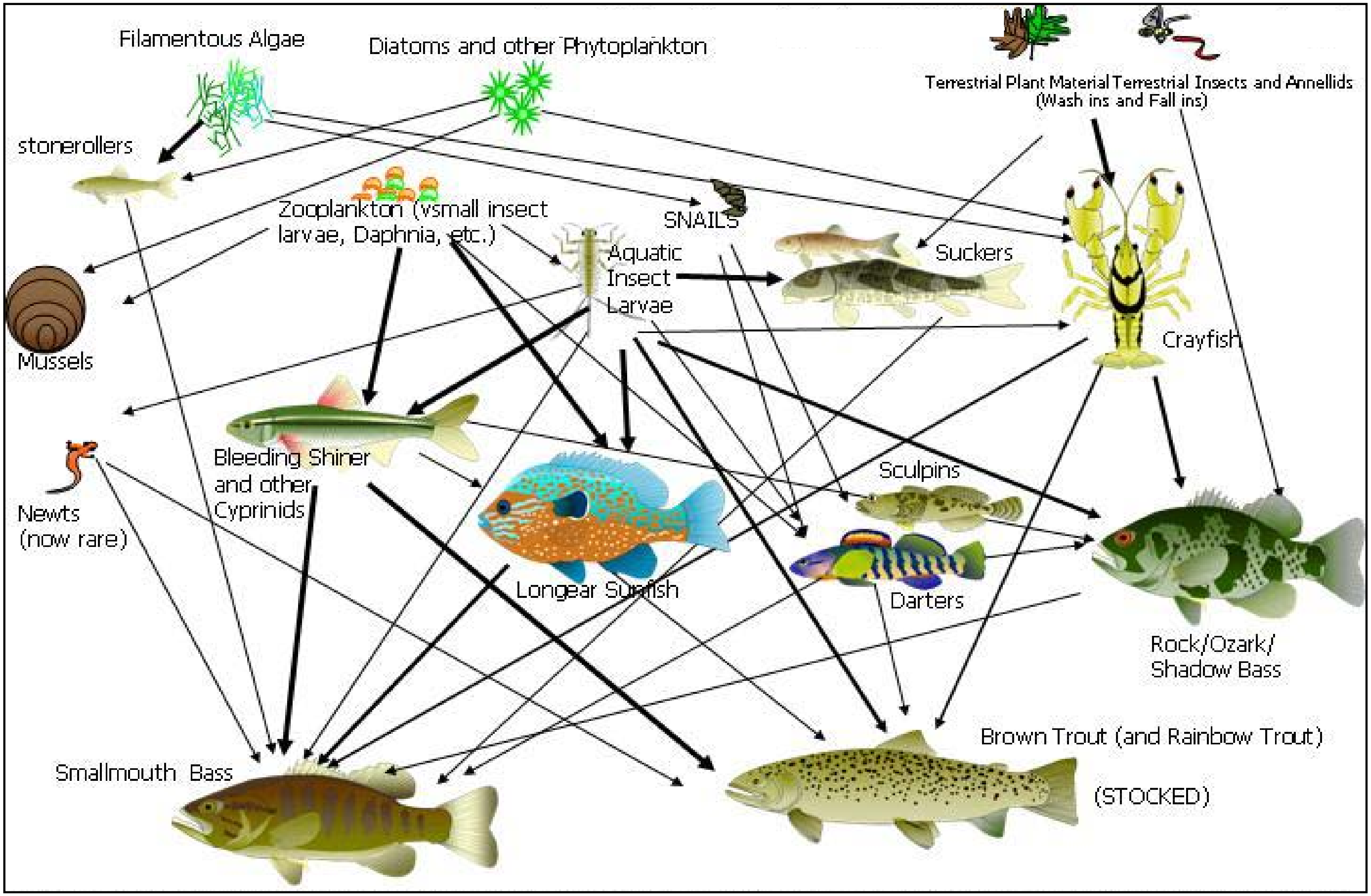


Figure 17. Simplified aquatic food web for a moderate order Ozark stream, after fall cooling (Meyer, unknown).

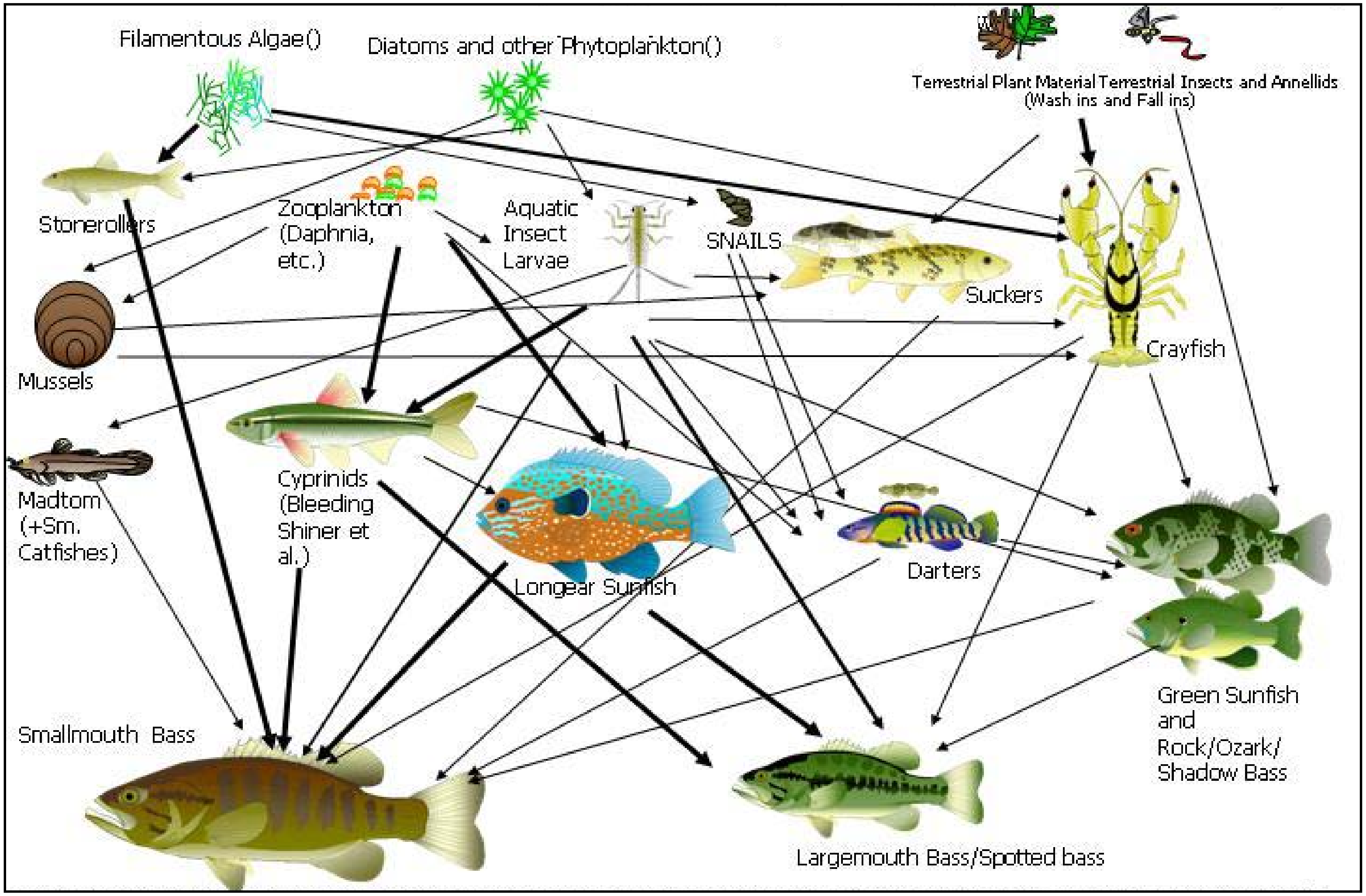


Figure 18. Simplified aquatic food web for Ozark streams, near springs or spring riffles (Meyer, unknown).

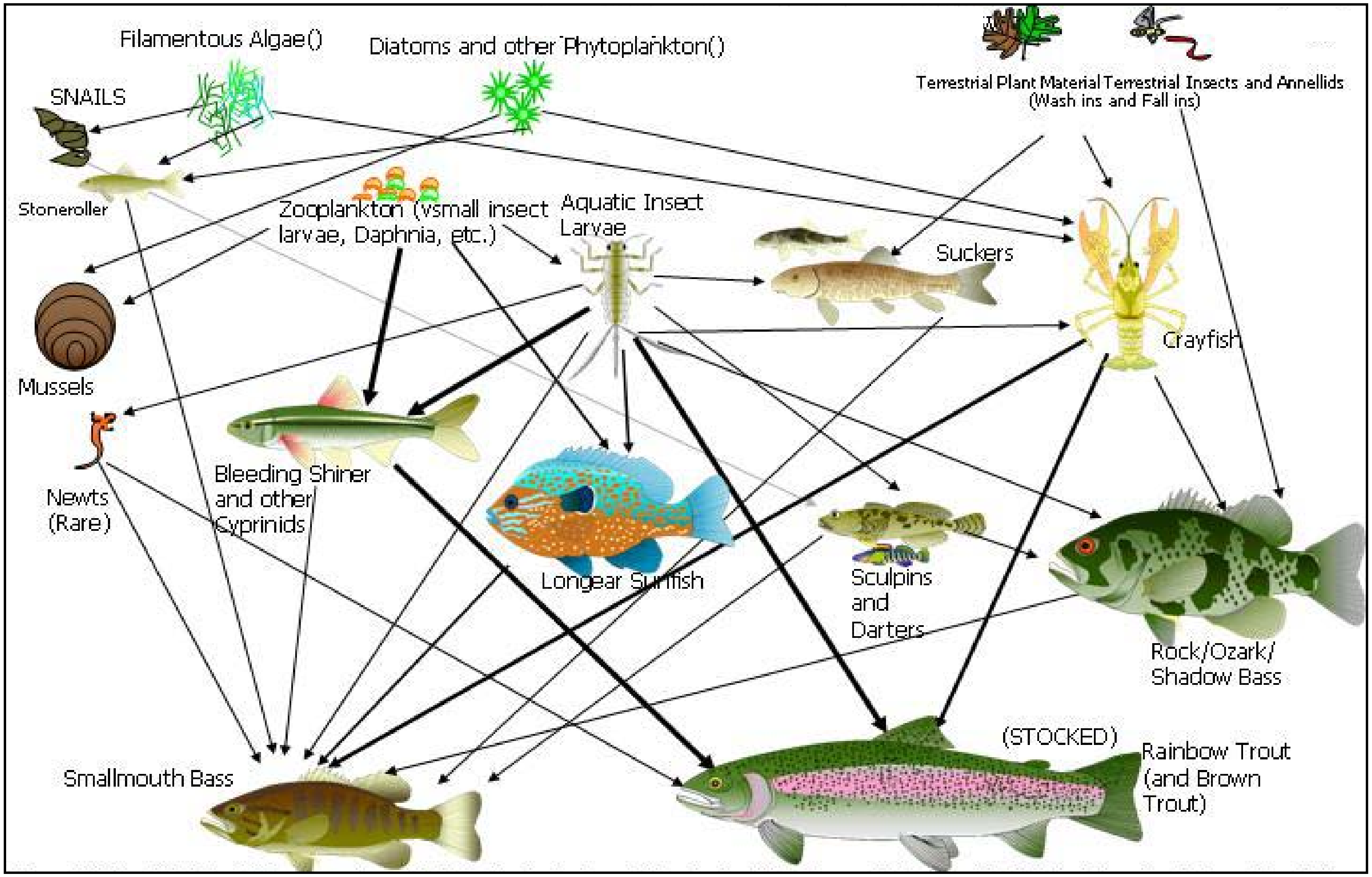
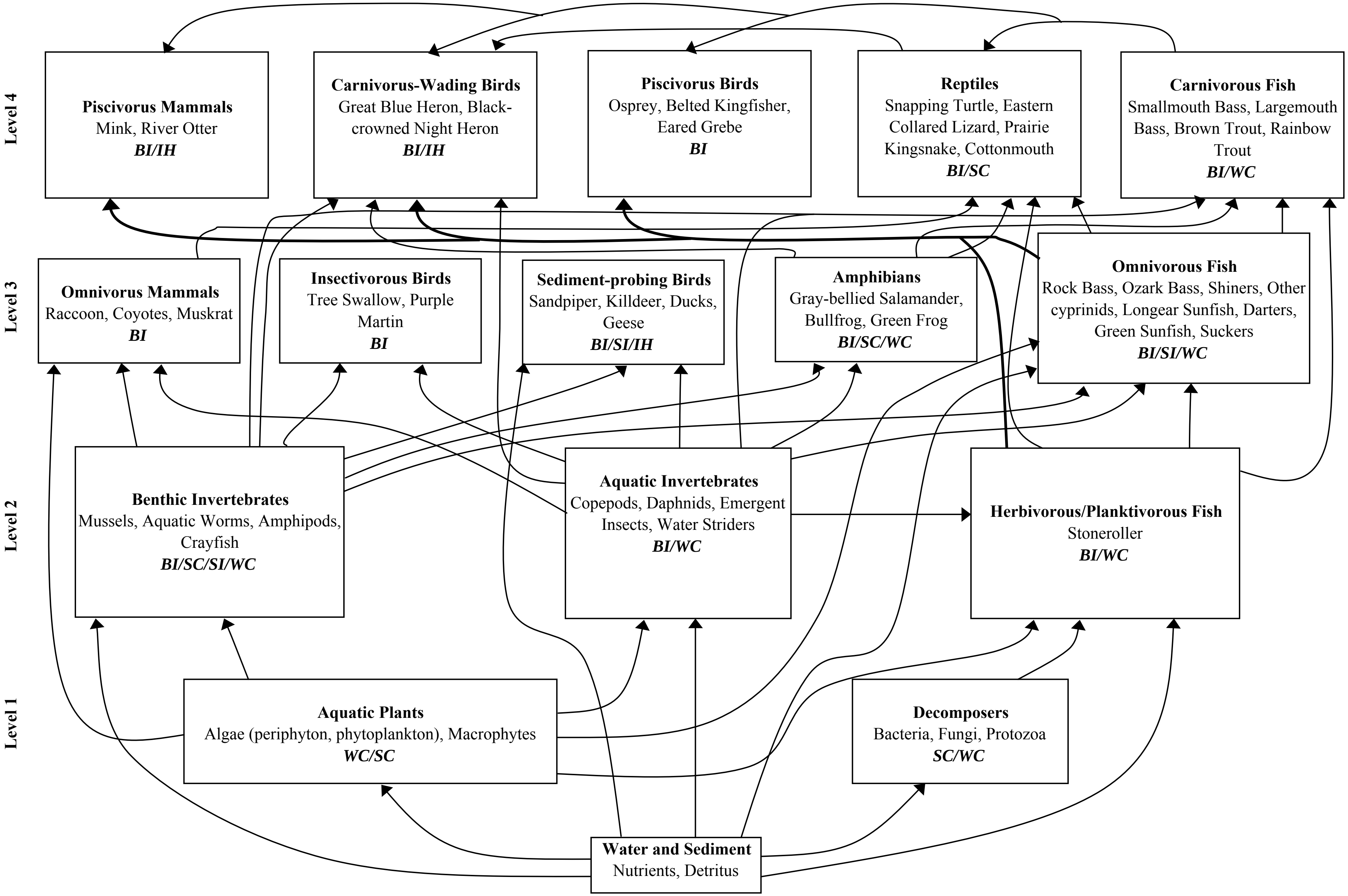


Figure 19. A generalized aquatic food web for the study area, showing the principal routes of exposure to contaminated water, sediment and biota.



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 20. Conceptual model diagram illustrating exposure pathways and potential effects for bioaccumulative substances.

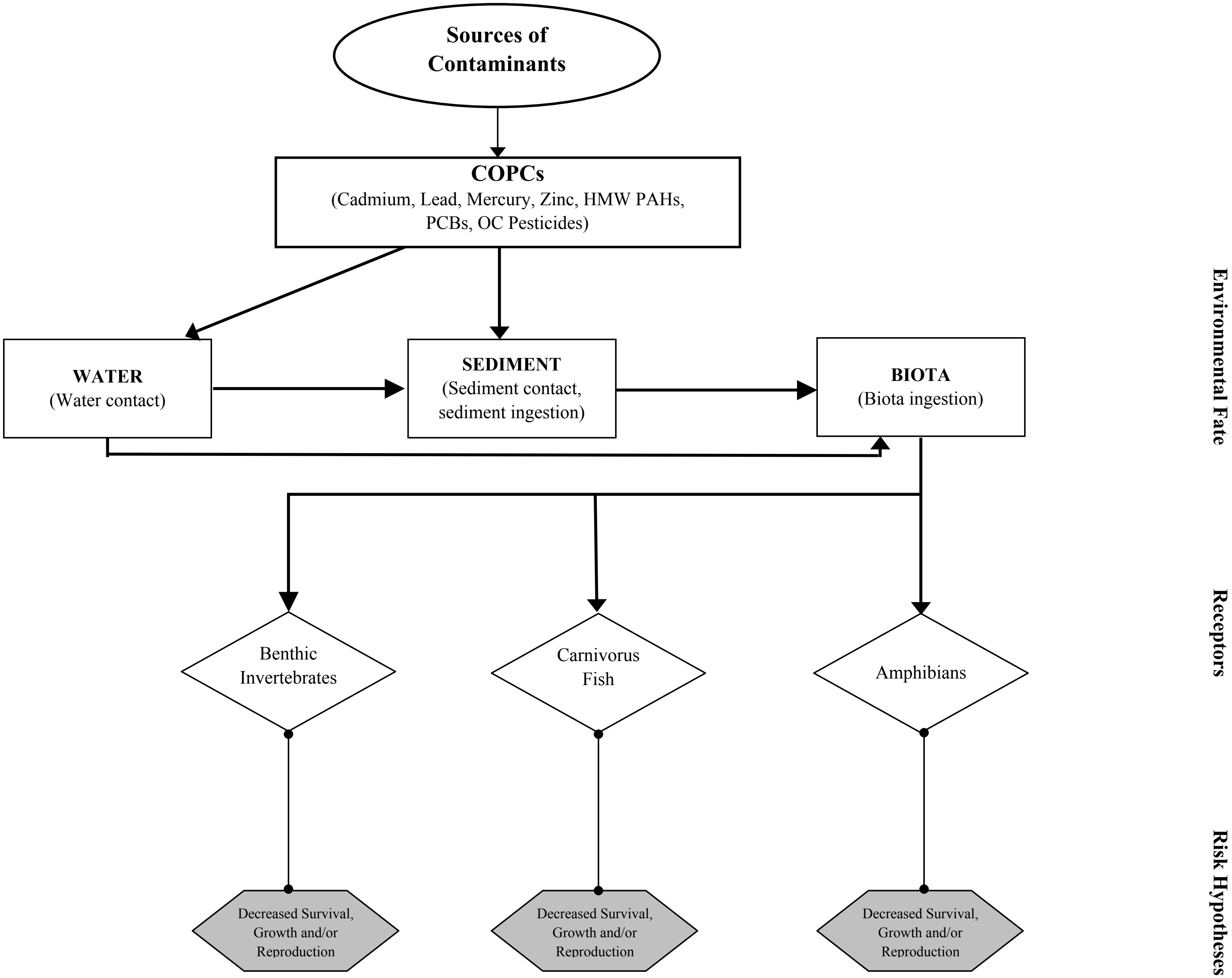


Figure 21. Conceptual model diagram illustrating exposure pathways and potential effects for toxic substances that partition into sediments.

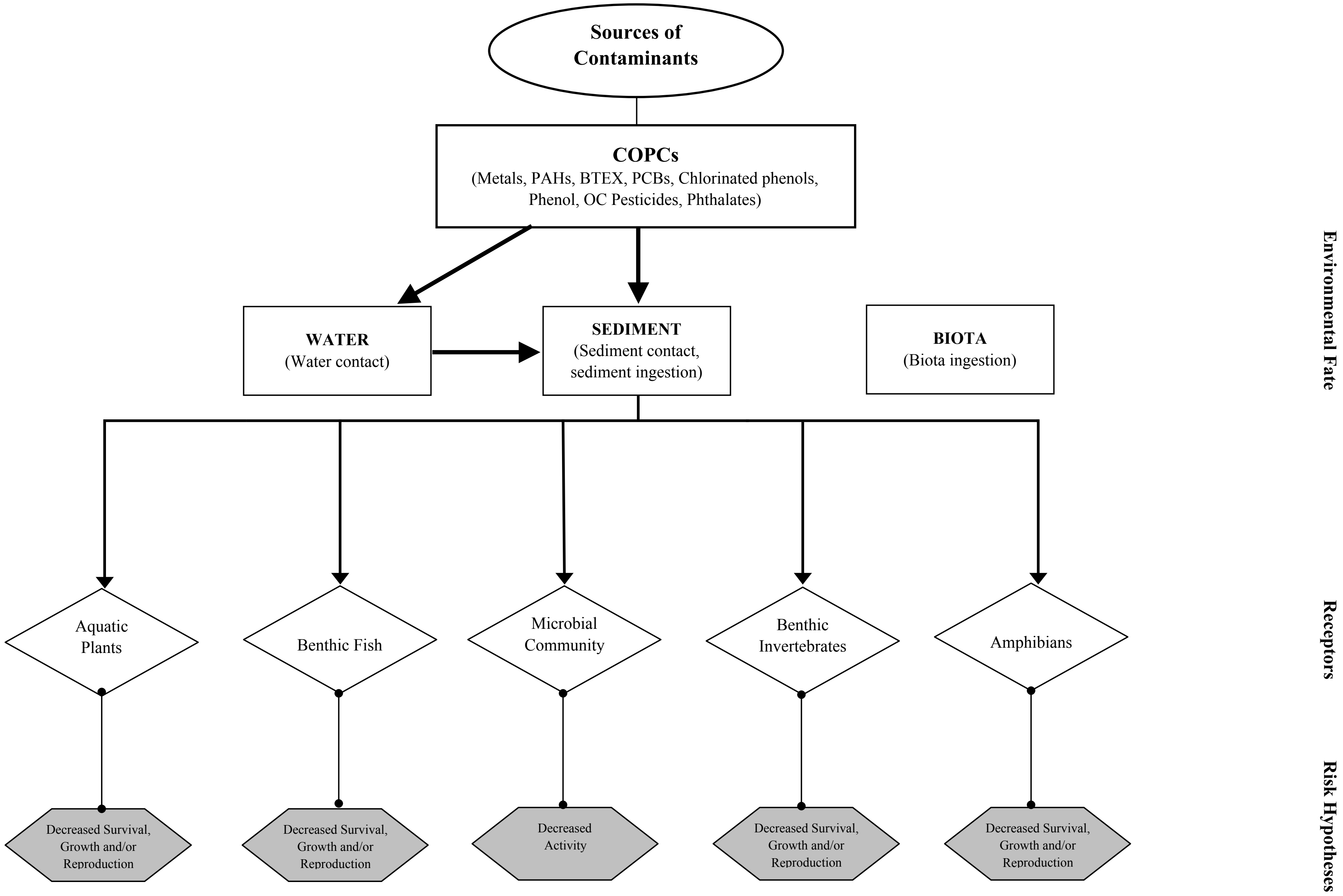


Figure 22. Conceptual model diagram illustrating exposure pathways and potential effects for toxic substances that partition into overlying water.

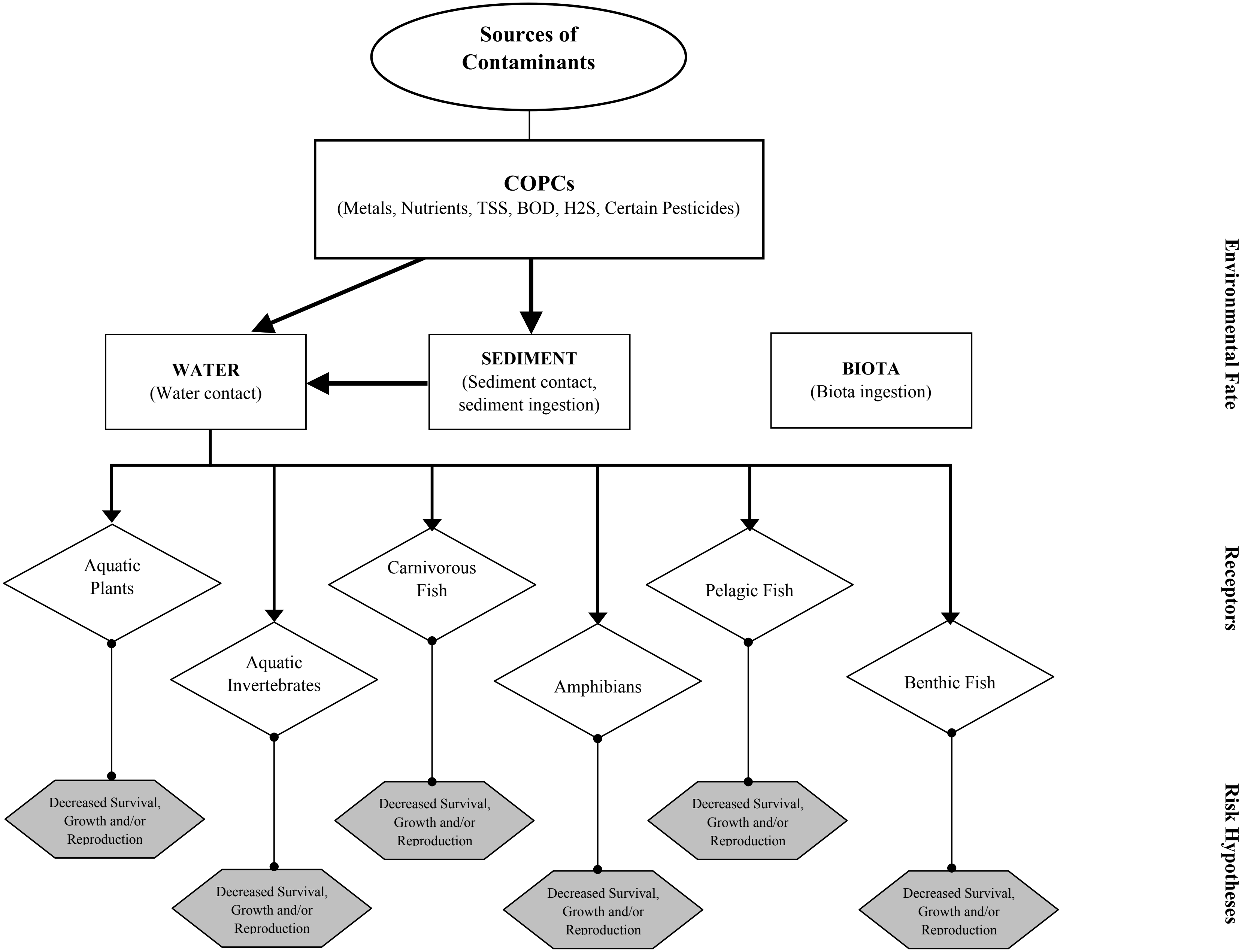


Figure 23. Conceptual model diagram illustrating exposure pathways and potential effects for all categories of COPCs.

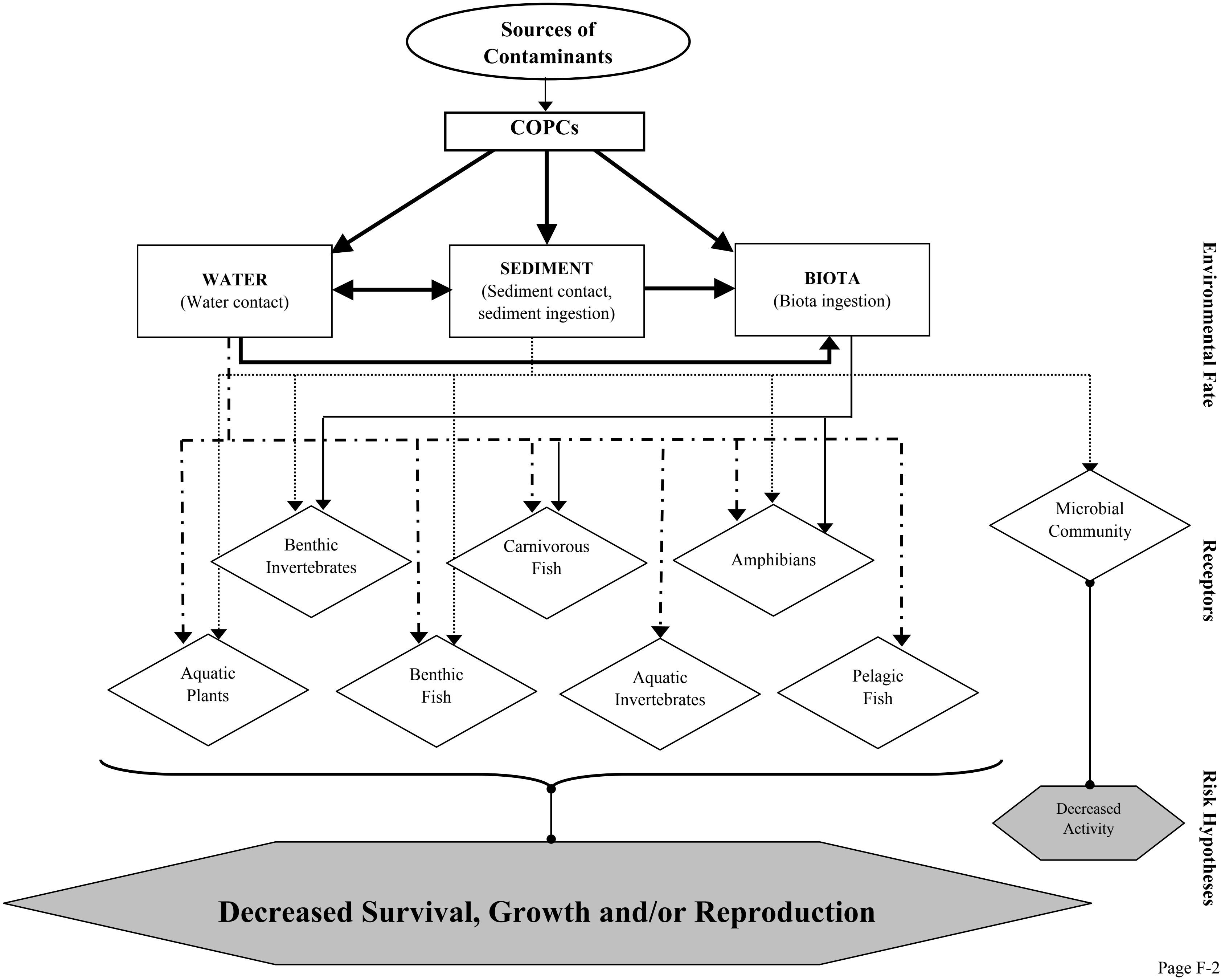
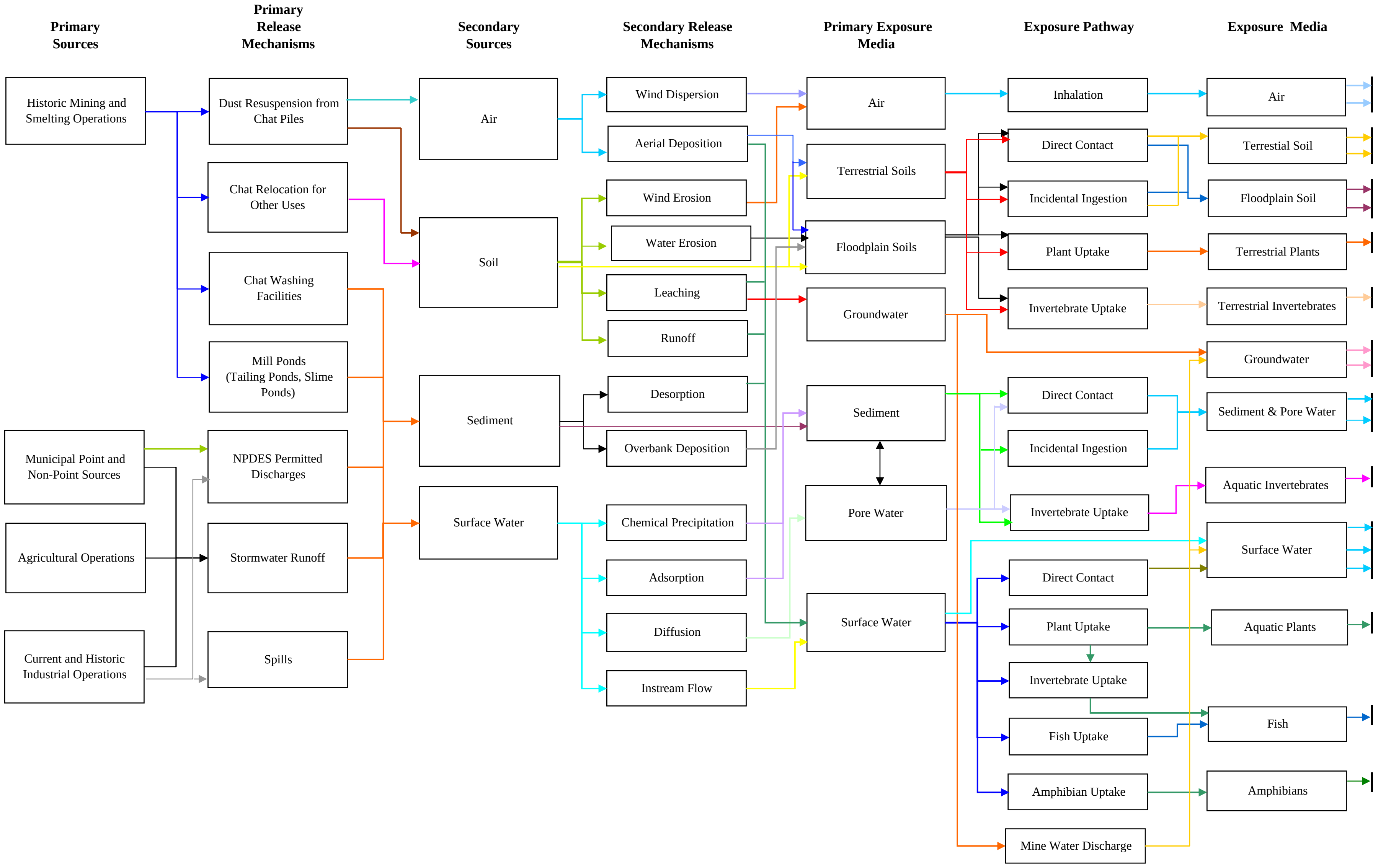


Figure 24. Multi-pathway ecological conceptual site model for the Tri-State Mining District.



		Aquatic Foodweb								Aquatic Dependent Riparian/ Upland Foodweb											
Exposure Media	Exposure Route	Plankton	Periphyton	Aquatic Macrophytes	Pelagic Invertebrates	Benthic Invertebrates	Pelagic Fish	Benthic Fish	Amphibians	Terrestrial Plants	Terrestrial Invertebrates	Reptiles	Sediment-Probing Birds	Soil-Probing Birds	Carnivorous-Wading Birds	Insectivorous Birds	Piscivorous Birds	Herbivorous Mammals	Omnivorous Mammals	Insectivorous Mammals	Piscivorous Mammals
Air	Inhalation								✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	Foliar Uptake			✓						✓											
Terrestrial Soil	Direct Contact								✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	
	Ingestion										✓			✓				✓			
Floodplain Soil	Direct Contact									✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	
	Ingestion										✓		✓	✓				✓			
Terrestrial Plants	Ingestion										✓							✓	✓		
Terrestrial Invertebrates	Ingestion								✓			✓		✓		✓			✓	✓	
Groundwater	Direct Contact					✓															
	Root Uptake			✓							✓										
Sediment & Pore Water	Direct Contact		✓	✓		✓		✓	✓				✓						✓		
	Ingestion					✓		✓	✓				✓						✓		
Aquatic Invertebrates	Ingestion						✓	✓	✓			✓	✓			✓	✓		✓	✓	
Surface Water	Direct Contact	✓	✓	✓	✓	✓	✓	✓	✓												
	Ingestion								✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	Root Uptake			✓						✓											
Aquatic Plants	Ingestion				✓	✓	✓	✓										✓			
Fish	Ingestion						✓	✓				✓			✓		✓				✓
Amphibians	Ingestion											✓			✓		✓		✓		✓

✓ = Potentially Complete Exposure Pathway