Susitna-Watana Hydroelectric Project
(FERC No. 14241)

Mercury Assessment and Potential for Bioaccumulation Study
Study Plan Section 5.7

Appendix A:
Mercury Assessment Pathways Analysis
Technical Memorandum

Prepared for

Alaska Energy Authority

SUSITNA-WATANA HYDRO
Clean, reliable energy for the next 100 years.

Prepared by

Tetra Tech

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Appendix A: Susitna-Watana Hydroelectric Project: Mercury Pathways Literature Review & Summary

LIST OF ACRONYMS AND ABBREVIATIONS

Abbreviation	Definition
ADEC	Alaska Department of Environmental Conservation
AEA	Alaska Energy Authority
APA	Alaska Power Authority
DO	Dissolved Oxygen
FA(s)	Focus Area(s)
FERC	Federal Energy Regulatory Commission
ILP	Integrated Licensing Process
MeHg	Methyl-mercury
NTU	Nephelometric turbidity unit
PRM	Project River Mile
Project	Susitna-Watana Hydroelectric Project
RSP	Revised Study Plan
SPD	Study Plan Determination
TSS	Total Suspended Solids
USACE	U.S. Army Corps of Engineers
USGS	U.S. Geological Survey

1. INTRODUCTION

The Alaska Energy Authority (AEA) is preparing a License Application that will be submitted to the Federal Energy Regulatory Commission (FERC) for the Susitna-Watana Hydroelectric Project (Project) using the Integrated Licensing Process (ILP). The Project is located on the Susitna River, an approximately 300-mile-long river in Southcentral Alaska. The Project's dam site would be located at Project River Mile (PRM) 187.1.

On December 14, 2012, Alaska Energy Authority (AEA) filed with the Federal Energy Regulatory Commission (FERC or Commission) its Revised Study Plan (RSP), which included 58 individual study plans (AEA 2012). Included in the Study Plan was the Mercury Assessment and Potential for Bioaccumulation Study, Section 5.7. Section 5.7 focuses on determining the current concentrations and methylation rates for mercury in the study area, and what changes could occur with construction of the Susitna-Watana Project (Project) reservoir.

On February 1, 2013, FERC staff issued its study determination (February 1 SPD; Study Plan Determination) for 44 of the 58 studies, approving 31 studies as filed and 13 with modifications. On April 1, 2013 FERC issued its study determination (April 1 SPD) for the remaining 14 studies; approving one study as filed and 13 with modifications. Study Plan Section 5.7 was one of the 13 approved with modifications. In its April 1 SPD, FERC recommended the following:

> *Use of Harris and Hutchinson and EFDC Models for Mercury Estimation*
> *We recommend that AEA use the more sophisticated Phosphorus Release Model to predict peak methylmercury levels in fish tissue, regardless of the outcome of the other two models.*

> *Mercury Effects on Riverine Receptors*
> *We recommend that AEA include likely riverine receptors (i.e., biota living downstream of the reservoir that may be exposed to elevated methyl mercury concentrations produced in the reservoir and discharged to the river) as part of the predictive risk analysis. The additional study element would have a low cost (section 5.9(b)(7)) because AEA would simply add consideration of additional receptors to the existing analysis. This information is necessary to evaluate potential project effects downstream of the reservoir (section 5.9 (b)(5)).*

2. STUDY OBJECTIVES

Previous studies have documented increased mercury concentrations in fish and wildlife following the flooding of terrestrial areas to create hydroelectric reservoirs. The purpose of this study is to assess the potential for such an occurrence in the proposed Project area. The study objectives as established in Study Plan (Section 5.7.1) are as follows:

- Summarize available and historic mercury information for the Susitna River basin, including data collection from the 1980s Alaska Power Authority (APA) Susitna Hydroelectric Project.

- Characterize the baseline mercury concentrations of the Susitna River and tributaries. This will include collection and analyses of vegetation, soil, water, sediment pore water, sediment, piscivorous birds and mammals, and fish tissue samples for mercury.

- Utilize available geologic information to determine if a mineralogical source of mercury exists within the inundation area.

- Map mercury concentrations of soils and vegetation within the proposed inundation area. This information will be used to develop maps of where mercury methylation may occur.

- Use the water quality model to predict where in the reservoir conditions (pH, dissolved oxygen [DO], turnover) are likely to be conducive to MeHg formation.

- Use modeling to estimate MeHg concentrations in fish.

- Assess potential pathways for MeHg to migrate to the surrounding environment.

- Coordinate study results with other study areas, including fish, instream flow, and other piscivorous bird and mammal studies.

3.   STUDY AREA

The Susitna River, located in Southcentral Alaska, drains an area of approximately 20,010 square miles and flows about 320 miles from its headwaters at the Susitna, West Fork Susitna, and East Fork Susitna glaciers to the Cook Inlet (USGS 2012). The Susitna River basin is bounded on the west and north by the Alaska Range, on the east by the Talkeetna Mountains and Copper River Lowlands and on the south by Cook Inlet. The highest elevations in the basin are at Mt. McKinley at 20,320 feet while its lowest elevations are at sea level where the river discharges into Cook Inlet. Major tributaries to the Susitna River between the headwaters and Cook Inlet include the Chulitna, Talkeetna and Yentna rivers that are also glacially fed in their respective headwaters. The basin receives, on average, 35 inches of precipitation annually with average annual air temperatures of approximately 29°F.

As established in Study Plan Section 5.7.3, the study area begins at PRM 19.9 (RM 15.1) and extends upstream from the proposed reservoir to PRM 235.2 (RM 233.4) (Figure 3-1).
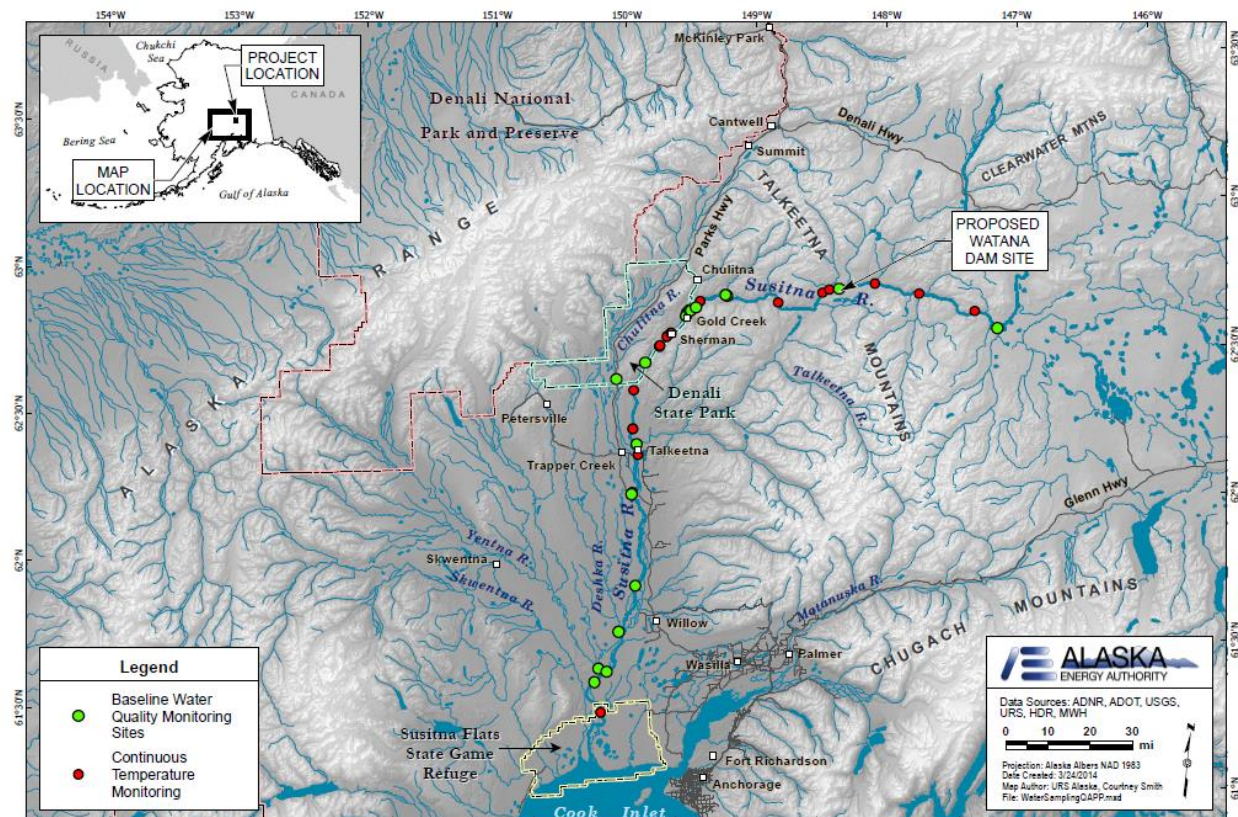
Figure 1-1. Overview of Baseline Water Quality and Temperature Data Collection Sites.

Mercury of non-atmospheric origin has been occasionally found in water bodies. The source can be industrial processes, mercury mining, or simply the presence of sulfate-rich mercury ores, which occur in very limited areas. In the study area, no widespread mining has occurred, and there are no industrial sources. Point sources have been documented on the Kuskokwim River in Alaska, but are relatively rare, and are associated with known sulfate-rich ore bodies (Saiki and Martin 2010; Gray et al 2000). Based on the available geologic information, the inundation area consists largely of diorite and granodiorite, which are not typically associated with massive sulfide mineral deposits. For this reason, such a point source appears to be unlikely in the inundation area of the dam.

In areas that lack the necessary mercury mineralization, the mercury concentration in parent geologic materials is typically very low, and cannot explain the mercury concentrations observed in sediment in aquatic ecosystems (Fitzgerald et al. 1998; Wiener et al. 2006).

4. METHODS

4.1 Background Information

Samples for surface water, porewater, sediment, vegetation, soil, fish, and piscivorous mammal hair were collected and analyzed for mercury and methylmercury. These data were used in the

pathways models to predict Project effects on the potential for mercury availability and bioaccumulation.

Assessment of the potential pathways for mercury in the environment is based on available literature and additional mercury studies, to ensure the most applicable methods are used to meet Project needs. The pathway assessment incorporates both existing conditions, and conditions with the reservoir and dam in place. The Water Quality Modeling Study (Section 5.6) provides for a three-dimensional model to be developed for the proposed reservoir to represent the spatial variability in hydrodynamics and water quality in longitudinal, vertical, and lateral directions. The model will be able to simulate flow circulation in the reservoir, turbulence mixing, temperature dynamics, nutrient fate and transport, interaction between nutrient and algae, and potentially sediment and metal transport.

Table 4-1 below contains the general outline describing the potential sources of select contaminants associated with presence of mercury, major factors affecting bioavailability, and route of exposure.

Table 4-1. Potential sources, bioaccumulation potential, major factors affecting bioavailability, and routes of exposure for each toxic of concern.

Contaminant of Concern	Potential Sources	Bioaccumulation Potential	Critical Factors Affecting Bioaccumulation/Toxicity Potential	Route of Exposure		
				Sediment	Water	Food
Zinc	Upstream	Low	Sediment Redox Potential (AVS/SEM), Organic matter concentration/DOC, Water hardness; Water DOC; Sediment particle size; Suspended solids; pH; Temperature	Low	High	Low
Cadmium	Upstream	Low-Med	Sediment Redox Potential (AVS/SEM); Water hardness; Water DOC; Sediment particle size; Suspended Solids; pH; Chloride; Temperature	High	Med	Med
Lead	Upstream	Low-Med	Sediment redox potential (AVS/SEM); Organic matter concentration/DOC; Water hardness; Suspended solids; Sediment particle size; pH; Temperature	High	Med	Med
Mercury	Atmospheric, Upstream	High	Aquatic vegetation; Sediment redox potential (AVS/SEM); Organic matter concentration/ DOC; Nutrients; Temperature; Microbial respiration; pH; Selenium concentration	High	Low	High

Contaminant of Concern	Potential Sources	Bioaccumulation Potential	Critical Factors Affecting Bioaccumulation/Toxicity Potential	Route of Exposure		
				Sediment	Water	Food
Arsenic	Upstream	Med	Sediment redox potential (AVS/SEM); pH; Suspended solids; Sediment particle size; Microbial respiration; Nitrification	Med	Med	Med

Notes:
> Critical factors are often the most important factors affecting bioavailability for that toxicant.
> AVS – acid volatile sulfide
> DOC – dissolved organic carbon
> PCB – polychlorinated biphenyl
> SEM – simultaneously extracted metals

Metals included in Table**Error! Reference source not found.** are categorized as divalent (zinc, cadmium, and lead) or organometals (mercury, arsenic) and when present in bioaccumulative form, can have identifiable chronic and acute effects on aquatic life. Specific water quality conditions can promote mobilization of toxic forms of these metals from a sequestered state. These are known as "critical factors affecting bioaccumulation" that promote release of metals from media and then absorbed through respiratory tissue in aquatic organisms or through consumption of organic particles (food) in the case of organometals. Route of exposure is included in TableTable 4-1 and a prediction for risk of exposure when bioavailable in each of three media.

4.2   Pathway Model Development

4.2.1   Riverine Model

The riverine model reflects conditions downstream of the reservoir both with and without impoundment. Running water has a different set of conditions that influence either mobilization or sequestration of metals in comparison to lentic ecosystems (e.g., lakes or reservoirs). Moving water in a stream has a lower risk of developing critical factors that would increase metals bioavailability to aquatic organisms. Existing conditions in the mainstem Susitna River generally have a lower risk for releasing sequestered metals from sediment (organic or inorganic) as many of the factors are not in a range that would promote release in a bioavailable form. Metals that affect aquatic life through absorption or consumption of food can remain sequestered for a long period of time in the particulate compartment (Newbold et al. 1981) of the riverine ecosystem (contained within microbes and attached algae).
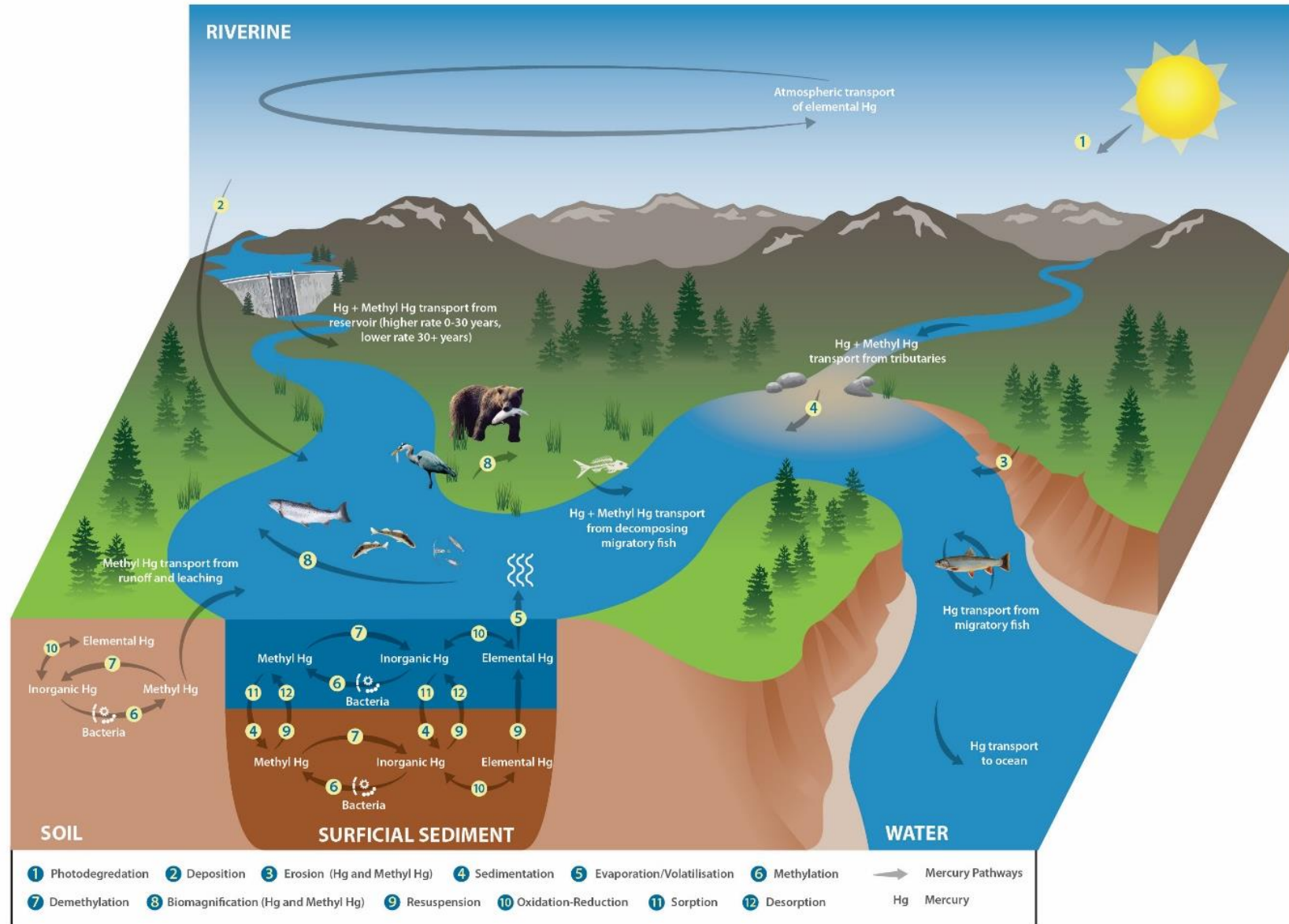
Figure 4-1. The riverine model mercury pathways following impoundment

The organo-metals will be closely associated with organics, including microbes and attached algae, in the riverine aquatic ecosystem. Physical movement of organics into locations where critical factors that cause release of organo-metals increase the potential for bioavailability are evaluated using the toxics pathway models. The riverine pathway model describes how a toxic metal will be transferred between media and the monitoring data gathered in Study 5.5 and Study 5.7 used as evidence to affirm mobilization as influenced by critical factors (Figure 4-1).

4.2.2   Mature Reservoir Model

The mature reservoir model reflects physical and chemical conditions after the reservoir has been in existence for 40 or more years. While there have been noticed increases in mercury concentrations in all media in newly formed reservoirs following impoundment, concentrations are expected to return to background levels after approximately 30 years based on previous research (Bodaly et al., 2007). For example, mercury concentrations in fish tissue from boreal reservoirs are above background conditions for three decades following impoundment (Bodaly et al., 2007). Concentrations in lake whitefish are usually the highest within 6 years of impoundment, and it takes 10 to 20 years following impoundment for decline in fish tissue concentrations to background conditions (Bodaly et al., 2007). MeHg concentrations in zooplankton from flooded wetlands remain elevated for 14 years following impoundment (Hall et al., 2009). It should be noted that background methylmercury concentrations are rarely zero, and many natural water bodies have shown elevated concentrations of methylmercury.

Mercury and methylmercury data collected during field sampling will be used as input data for the mature reservoir pathway model and will reflect how Project operations would influence the dominant form of mercury (e.g., elemental, methylated) and partitioning among media (e.g., sediment, pore water, and water column) after 40 years of operation. The reservoir representation has been developed based on local bathymetry and dimensions of the proposed dam. The mature reservoir pathways model is presented below in Figure 4-2.
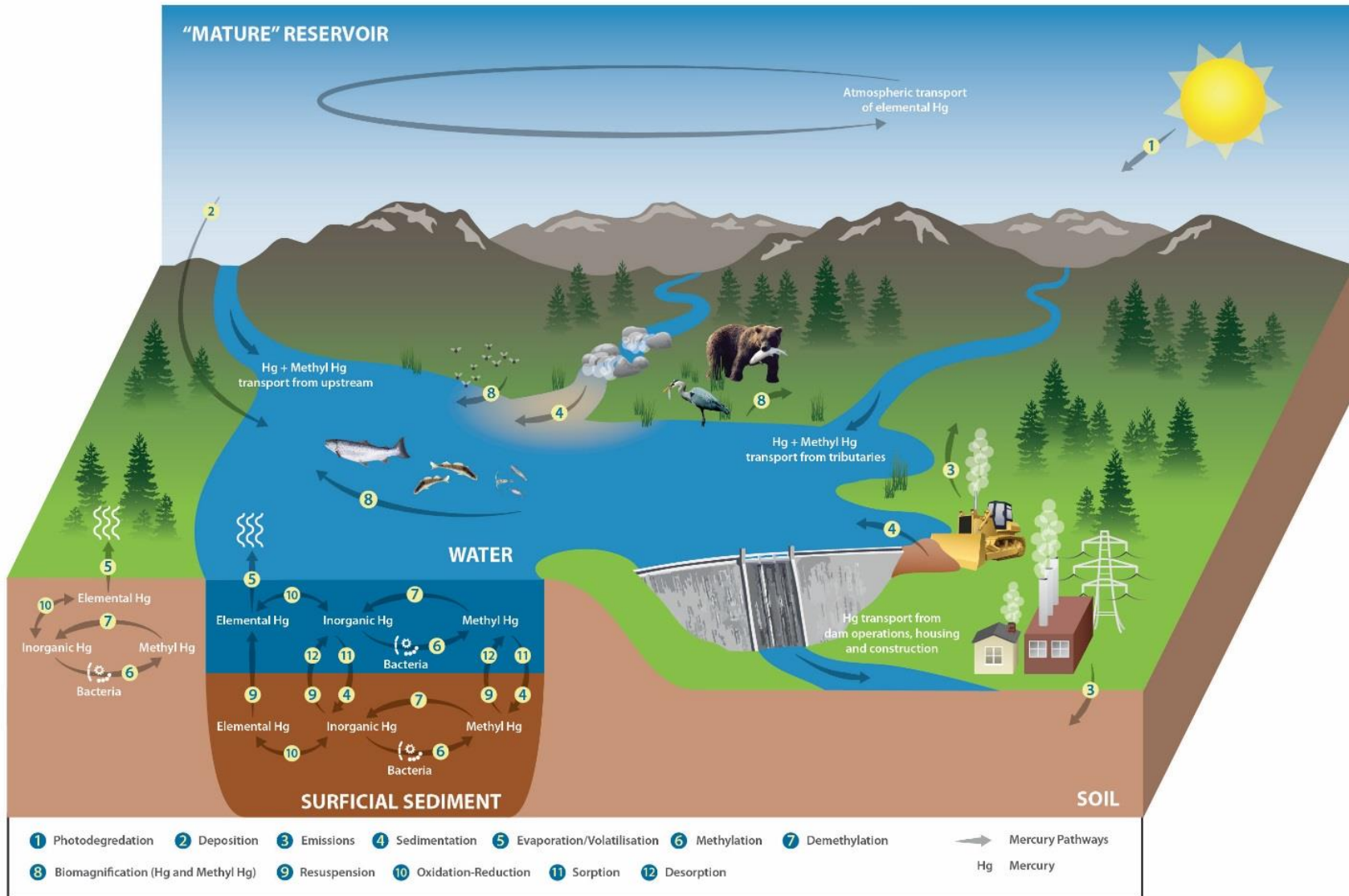
Figure 4-2. The mature reservoir pathway model in existence for 40 or more years of Project operations.

4.2.3   New Reservoir Model

The new reservoir model reflects physical habitat and chemical dynamics of a basin that is 30 or fewer years in existence (Figure 4-3). Based on research by Bodaly et al. (2007), elevated concentrations in fish tissue decline to background levels over 30 years from inception of the new impoundment. Mercury mobilization potential will be predicted in the reservoir immediately after pooling and up to 30 years following impoundment.

Examples of increased fish tissue concentrations and mechanisms of mercury (Hg) transfer in the aquatic environment are provided in several studies. In a study conducted by sampling, increased Hg concentrations in benthivorous lake whitefish from reservoirs of northern Manitoba were described after flooding and formation of the impoundment. Mercury concentrations increased from between 0.06 μg/g and 0.14 μg/g in fish tissue samples when background concentrations in natural lakes of the region ranged between 0.03 μg/g and 0.06 μg/g (Bodaly et al., 2007). The mechanism for increased Hg concentrations in fish tissue from these recently formed reservoirs is bacterial methylation of elemental Hg deposited in flooded soils (Bodaly et al., 2007).

Concentrations of methyl-mercury (MeHg) increase in water, fish, zooplankton, and other invertebrates during active flooding of a new reservoir (Hall et al., 2009). The largest proportion of MeHg is produced and resides in flooded soils and not mobilized into the water column (Hall et al., 2009). Periphyton, zooplankton and fish communities account for the remaining proportion of MeHg produced in flooded reservoirs, accounting for 1% to 10% of the total quantity (Hall et al., 2005). The mechanisms for bioaccumulation of MeHg in higher aquatic vertebrates including fishes, is through direct adsorption from the water column through respiratory tissue like gill filaments (Friedl and Wuest, 2002). Efficiency of adsorption of MeHg from water through respiratory tissues of salmonids is a small percentage of that available in surrounding water. The amount of MeHg adsorption is estimated as 7.1% to 8.3% of the total available in hard water (a hardness of 385 mg/L). The adsorption efficiency increases in soft water (hardness= 30 mg/L) to approximately 25% of the total available in surrounding water (Stokes and Wren, 1987). Modeling of MeHg production and transformation in flooded land demonstrates that 2-5 years of enhanced MeHg production results in elevated MeHg concentrations in predatory fish tissue lasting from between 20-30 years in this condition (Hall et al., 2005). Factors that mediate Hg adsorption from water are: concentration, fish metabolic rate, and efficiency of adsorption based on water quality characteristics like hardness (Stokes and Wren, 1987).

Dissolved organic carbon (DOC) mediates MeHg bioavailability in the aquatic food web, but with equivocal effects. In many cases, DOC concentration is directly related to change in MeHg concentration. Current literature also reports a reduction in accumulation of MeHg from surface water to components of the food web like zooplankton and other biota even though concentrations have increased (Hall et al. 2009). One example demonstrated a post-flooding condition with high DOC concentrations in surface water that coincided with MeHg concentrations in plants and soils that were 5 to 6 times greater than other sites in the reservoir with medium and low DOC concentrations (Hall et al., 2005). Bioaccumulation of MeHg appeared to be sequestered in the existing vegetation and soils and not in the aquatic food web of the newly formed reservoir.

The pH in surface water is another factor that mediates mercury bioavailability when conditions are in the neutral to low range of the pH scale. Anaerobic surface water and pore water conditions are associated with low pH and low dissolved oxygen concentrations that result in an increase of

methylation of mercury when microbial respiration is increased under these conditions. As a consequence, inorganic mercury is methylated forming methyl-mercury (MeHg) as a byproduct of microbial (sulfate-reducing bacteria) respiration. Often times, an increase in microbial respiration will result in an increase in the rate of methylation of inorganic mercury.

Surface water and pore water temperature is a common controlling factor in mediation of biogeochemical transformations. This is also the case for predicting how temperature will affect rates of methylation. The role of temperature as a mediating factor for methylation of inorganic mercury is a consequence of the setting (e.g., shallow portion of reservoirs), the amount of organic-rich soils in the flooded zone, and mercury input (Friedl and Wuest 2002). The potential for bioaccumulation of methylmercury in fishes is then the balance between methylation and demethylation and the magnification factor in the food chain (Friedl and Wuest 2002).

Sequestration of mercury in compartments of the aquatic ecosystem (e.g., sediment compartment) is enhanced by dominance of select minerals and nutrient particles. The high mercury-binding capacity of naturally-occurring materials like iron-rich, laterite soils in older reservoir watersheds is likely to decrease the mobility, methylation, and bioavailability of Hg (Ikingura and Akagi, 2003).
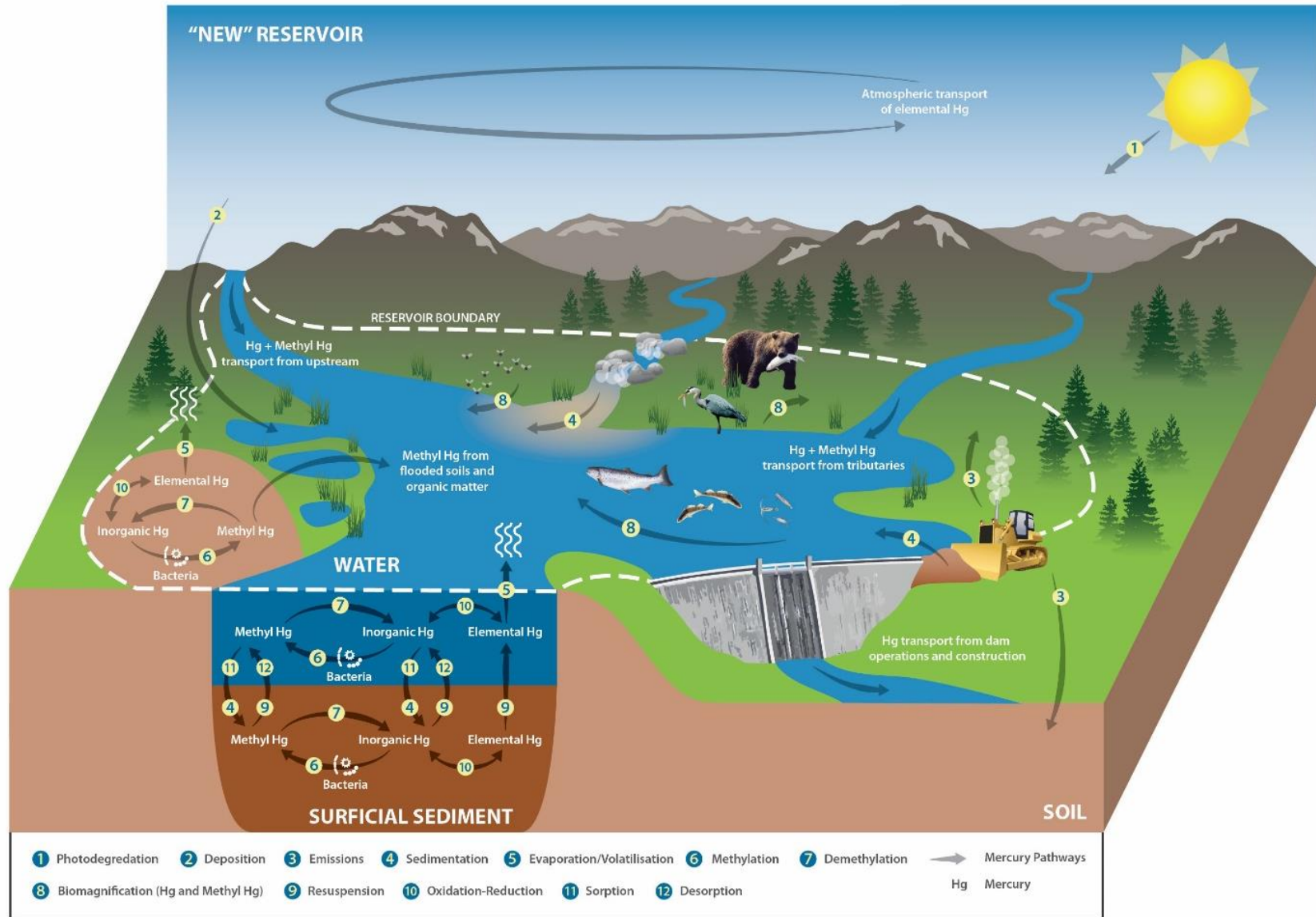
Figure 4-3. A mercury pathway model for a new reservoir following impoundment of water.

4.3   How the Pathway Model is Used

Pathways models for groups of metals (e.g., organometals or divalent metals) are focused on transfer between media while "toxicological models" focus on "factors" that facilitate transfer. Pathways models describing cycling of a metal in the aquatic environment are described for riverine, mature reservoir, and new reservoir conditions (Figure 4-1 through Figure 4-3, respectively). One or more factors can mobilize a metal from a sequestered phase into part of the aquatic ecosystem where exposure by aquatic organisms is likely.

Pathway analysis (use of the pathway model and toxicological model) is conducted by initially examining individual metals concentrations in sediment, pore water, and surface water. Data from three media should be collected from a site so that relative concentrations can be compared and examined for current potential for bioavailability. Harmful effects to aquatic life are determined by identifying media where primary contact is made and if concentrations exceed current water quality or sediment standards, when available.

A secondary part of the analysis is focused on determining future potential for metals mobilization or mercury methylization when factors in surface water conditions promote mobilization from sediment-to-pore water or pore water-to-surface water. These factors are identified as components of the toxicological models. These factors are discussed for each metal in Section 4.6 and are associated with mobilization from: 1) sediment to pore water, or 2) pore water to surface water. Several flow scenarios are possible with the Susitna-Watana Hydroelectric Project in-place and are partitioned based on: wet, dry, and average flow years as well as seasonal release patterns from the reservoir (operational scenarios). Factors that influence mobilization of metals based on the toxicological models may change under one or more of the operational scenarios and so can differ from current conditions in potential for bioavailability. Each of the operational scenarios will be examined in the new reservoir, mature reservoir, and riverine segments of the basin for potential metals mobilization and bioavailability to aquatic life.

4.4   Site Specific Mercury and Methylmercury Predictions

Pathway analysis using mercury data collected from above and below the Susitna-Watana Hydroelectric Project sites are the focus for predicting potential for mobilization and bioavailability of mercury and methylmercury. Areas of the Susitna River that will be inundated following establishment of the hydroelectric project will be on the mainstem and mouths of major tributaries above the dam location and inundation of select locations below the dam site with periodic increase in flows depending on water release patterns from the dam. In areas of the reservoir and river where sediment and pore water data are not available, pathway analysis will be limited to comparison of metals results with ADEC water quality criteria and confirmation that water quality factors (from toxicological models) are responsible for exceedances which likely result in mobilization from pore water and/or sediment.

4.5   Predicting Mercury Bioavailability

The most important factors promoting mercury bioavailability in surface water are neutral to low pH, low dissolved oxygen, low DOC, and increased temperature. One of several factors is necessary to limit transferability of this metal between media (e.g., sediment or surface water) and reduce bioavailability.

4.6   Potential Mobilization of Metals from Various Media: Toxicological Models

Pathway and toxicological models are available for additional metals and used to predict potential for release and exposure of aquatic life to chronic or acute concentrations. These models will be used in the same way as that described for predicting potential bioavailability of mercury and methylmercury. Metals occurring in the Susitna Basin that can affect aquatic life in higher concentrations are categorized as divalent and organometals. Water quality conditions that promote divalent metal bioavailability in either the water column or the sediment, will be analyzed. These factors include hardness, dissolved oxygen, and pH that control toxicity and bioavailability of divalent metals (zinc, lead, and cadmium). Organometals are associated with organic matter in the water column and sediment and have distinct set of conditions that promote bioavailability. Other metals that are commonly found in freshwater aquatic environments may have toxic effects on aquatic life if found in high enough concentrations in sediment or surface water.

Other commonly occurring metals in aquatic ecosystems are found in concentrations high enough to cause effects on aquatic life. Moreover, presence of multiple metals can often impose a cumulative, toxic impact to individual organisms and so are evaluated individually for potential to cause harmful effects. Metals toxicity and potential chronic or acute effects are evaluated individually and then blended together to determine if a synergistic or additive effect is possible. Thresholds identified from background literature that guides the development of criteria used to determine potential effects are generally protective of aquatic life, but do not consider the synergistic or additive effects on target aquatic species.

The following diagrams outline connectivity between media in the aquatic environment and factors that promote transfer of each metal of concern between the media. Description of ranges for those factors that promote transfer are based on existing water quality criteria or standard ranges reported in the literature (e.g., low, medium, or high hardness). Factors present that promote transfer of metals of concern between media represent a potential for exposure of aquatic biota to harmful effects and may not result in measureable or observable influences to aquatic receptors (e.g., fish, invertebrates, amphibians).

4.6.1   Potential for Bioavailability of Zinc

The exposure risk of aquatic biota to zinc and the likelihood of bioaccumulation are greatest in surface water (as opposed to sediment or pore water). Important factors with the potential to promote zinc bioavailability in surface water are low hardness, low DOC, and low suspended material (see the water column portion of Figure 4-4). One or more of these factors can limit bioavailability and control effects to biota. The most important physicochemical factors affecting bioavailability of zinc in water are hardness and pH (EPA 1987; Florence and Batley 1980).

Zinc

Fate Processes Increasing Bioavailability

Transport/ Ecological Compartments

Effects

Low hardness

↓ pH

↑ temperature

↓ **DOC**

↓ **Suspended material**

Water Column → Aquatic Toxicity

(Acute and Chronic)

Bioconcentration

Pore Water

↑ **Fine particle size**

↓ pH

Low oxygen, redox

Sediment

Benthic Uptake

Bioconcentration

Toxicity

Figure 4-4. Generalized toxicological model for zinc in an aquatic system.

4.6.2   Potential for Bioavailability of Cadmium

The exposure risk of aquatic biota to cadmium and the likelihood of bioaccumulation are predicted to be greatest in sediment (the risk of bioaccumulation is moderate in surface water and pore water). Important factors with the potential to promote cadmium bioavailability in surface water are low hardness and low suspended material (Figure 4-5). One or more of these factors can limit bioavailability and control effects to biota.

Cadmium

Fate Processes Increasing Bioavailability

Transport/ Ecological Compartments

Effects

Low hardness

↓ pH

↑ temperature

↓ chloride

↓ **Suspended material**

↑ **Fine particle size**

↓ pH

Low oxygen, redox

Water Column

Pore Water

Sediment

Aquatic Toxicity

(Acute and Chronic)

Bioconcentration

Trophic Transfer

Bioaccumulation

Benthic Uptake

Bioconcentration

Toxicity

Figure 4-5. Generalized toxicological model for cadmium in an aquatic system.

4.6.3   Potential for Bioavailability of Lead

The exposure risk of aquatic biota to lead and the likelihood of bioaccumulation are greatest in sediment (the risk of bioaccumulation is moderate in surface water and pore water). Important factors with the potential to increase lead bioavailability in surface water are low hardness, low DOC, and low suspended material (Figure 4-6). One or more of these factors can limit bioavailability and control harmful effects to biota.
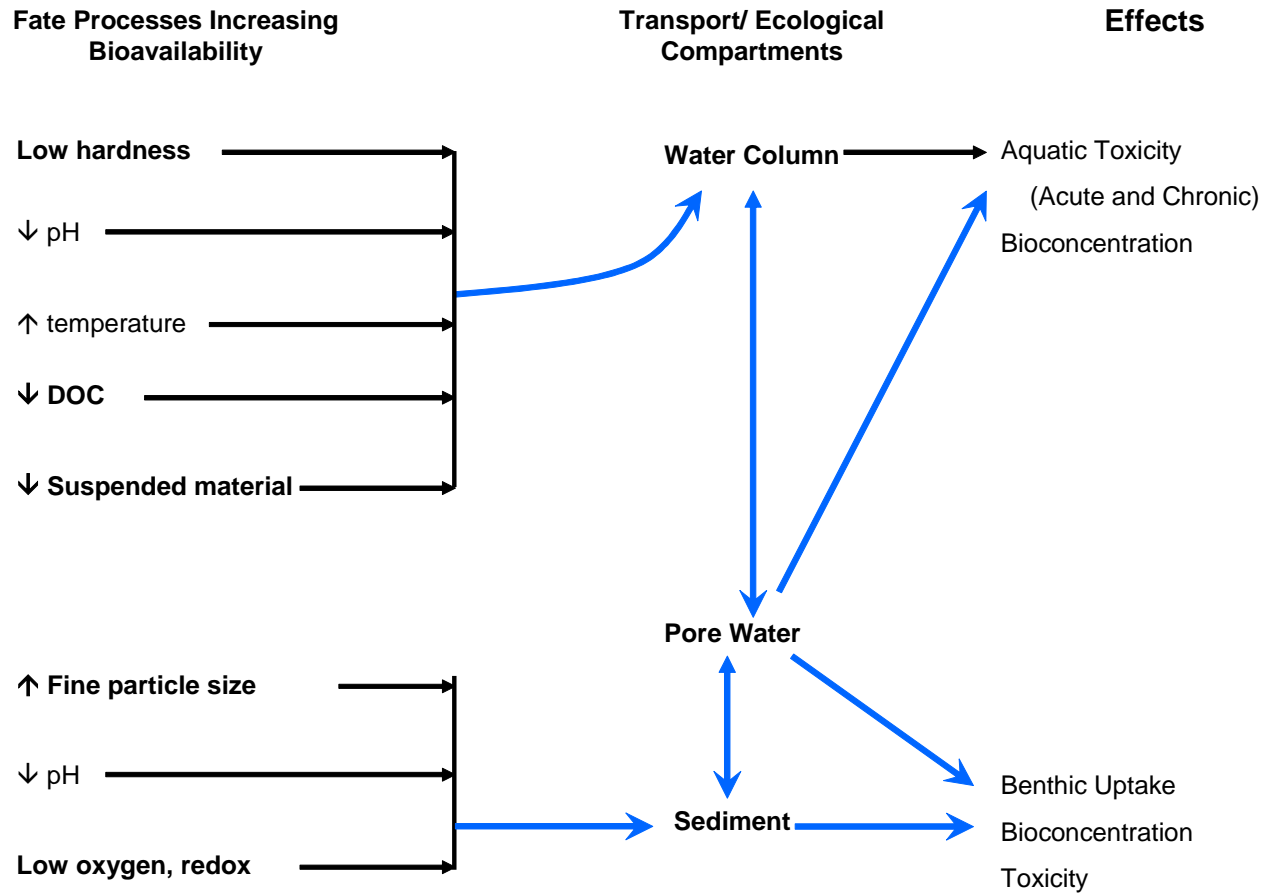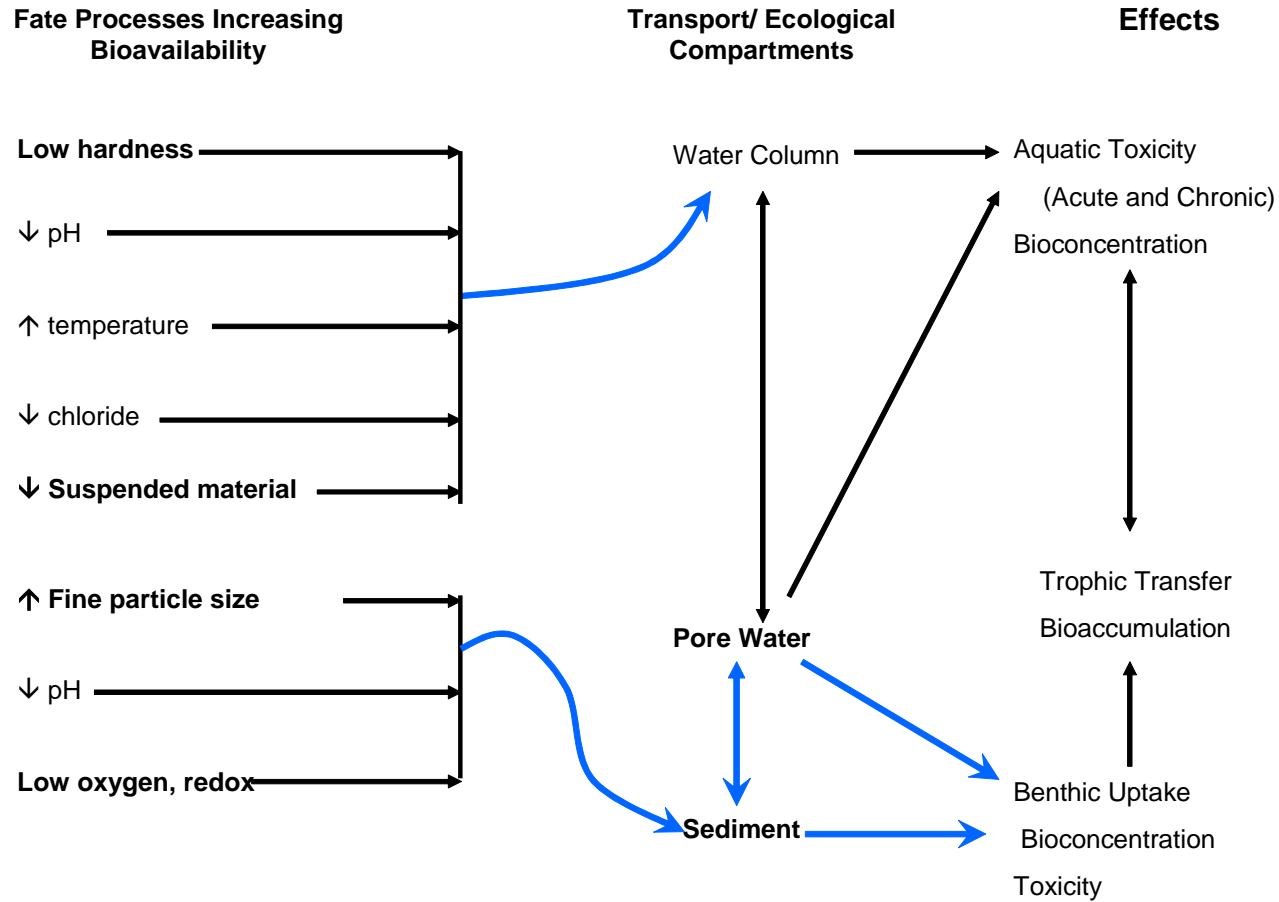
Lead
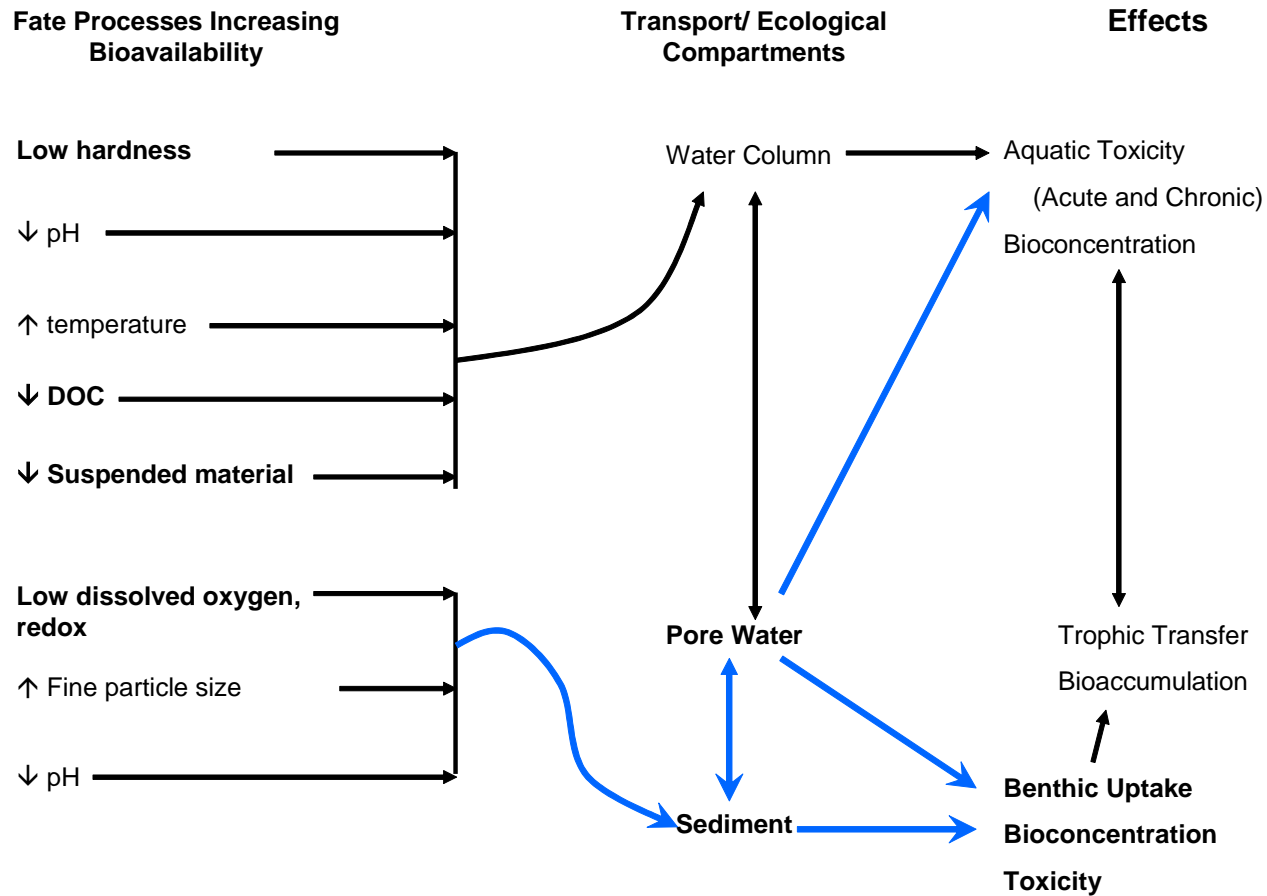
Figure 4-6. Generalized toxicological model for lead in an aquatic system.

4.6.4   Potential for Bioavailability of Arsenic

The exposure risk of aquatic biota to arsenic and the likelihood of bioaccumulation are greatest in quiescent areas of a river or reservoir (e.g., sediment, pore water, and surface water). Arsenic is classified an organometal and associated strongly with organic particulates that form part of the sediment matrix or mobilized in the water column adsorbed to organic particles. Suspension in the water column and associated with organic particles can present a more serious threat of bioaccumulation under some circumstances. An important factor that could promote arsenic bioavailability in surface water is a reducing condition (low dissolved oxygen or anoxic conditions) (Figure 4-7). Suspended particles consumed from the water column by filter-feeders are another pathway for bioaccumulation in body tissue. Arsenic does not have to be in the dissolved form and contacting respiratory tissues when evaluating potential for bioaccumulation.

Arsenic

Fate Processes Increasing Bioavailability

Transport/ Ecological Compartments

Effects

Reducing Conditions

- with increased pH
- with ↓ FeOH concentration
  ↓ Sulfides

↑Arsenite Concentration through dissolution

Water Column

Toxicity (Acute and Chronic)

Bioaccumulation

Bioconcentration

Biomethylation

- with anoxic conditions
- with microorganisms

↑MMA Concentration

Nitrification

↑solubility

Pore Water

MMA = Monomethyl Arsenic Acid

Trophic Transfer

Oxidizing Conditions

- with decreased pH
- with ↑ FeOH concentration
  ↑ Sulfides

↑Arsenate Concentration through precipitation

Sediment

Benthic uptake

(bioaccumulation)

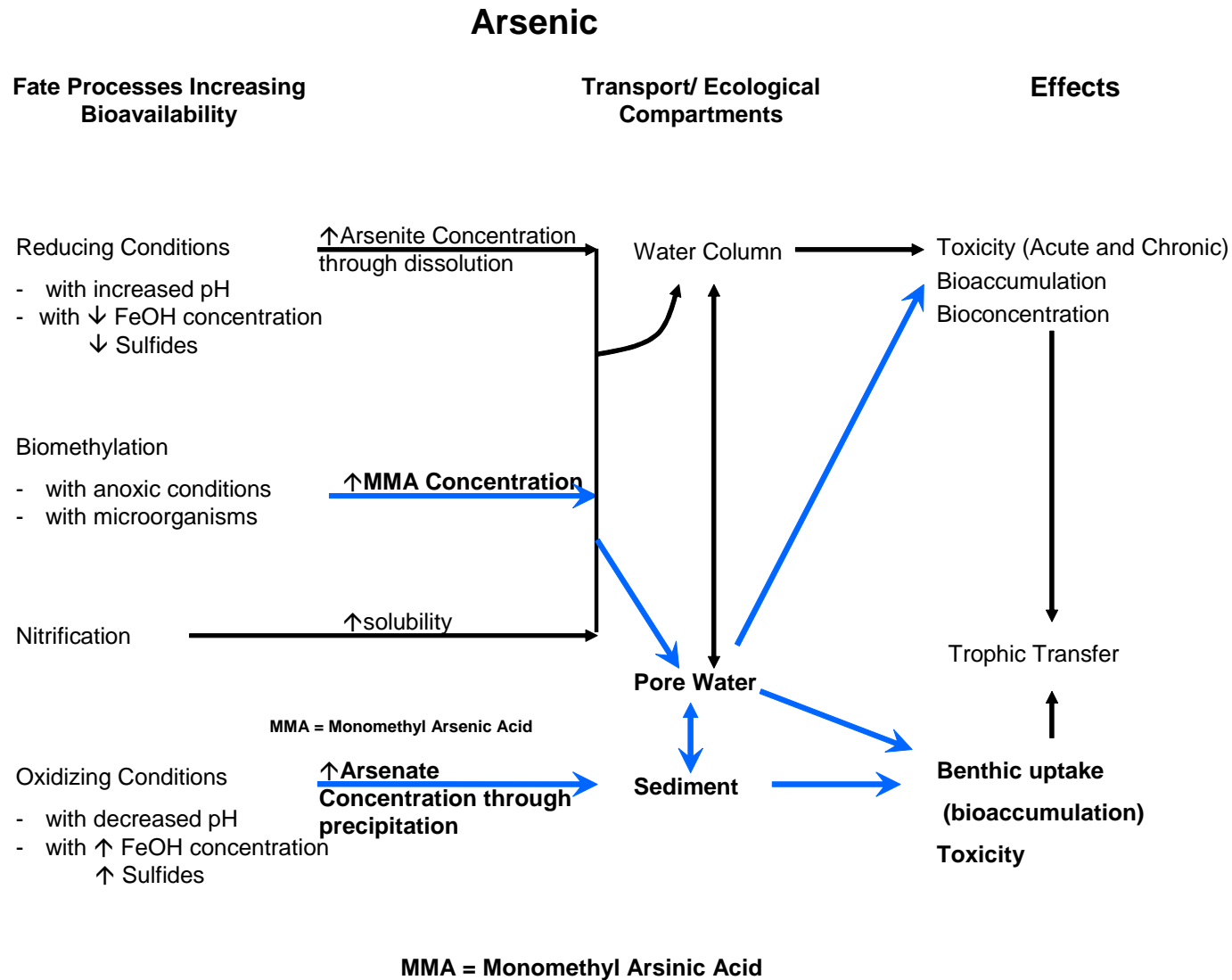**Toxicity**

MMA = Monomethyl Arsinic Acid

Figure 4-7. Generalized toxicological model for arsenic in an aquatic system.

5. DESCRIPTION OF RESULTS FROM PATHWAY ANALYSIS

Pathway analysis for each of the select toxics will initially be completed for each of the sites where sediment, pore water, and surface water samples were collected. These 10 sites are located below and above the proposed Susitna-Watana dam and will be evaluated under existing conditions and later under select reservoir operational scenarios.

Potential for bioaccumulation of mercury and select metals under existing conditions use results collected from the 10 sediment sampling locations below and above the Susitna-Watana dam site. Results were examined for each of the media at a site by determining if the concentration of mercury exceeds a state water quality or sediment criterion, a TRV (toxicity reference value) or a SQuiRT (Screening Quick Reference Table). The thresholds are used to identify the presence of a concentration gradient that could transfer metals through diffusion from a spatial area of higher concentration to one with lower concentration.

Media with a higher concentration of mercury (or concentration of other metals) will initially be compared against applicable thresholds (as those described above) at the ten sediment sampling locations. Concentration of mercury in three media (e.g., sediment, pore water, and surface water) are compared simultaneously to determine if a diffusion gradient exists between any two media. Factors that promote transfer between media are used to explain the potential for transfer and if exposure of aquatic life and effects may occur.

The following series of three graphs are an example of concentrations for zinc in three media (sediment, pore water, and water column) and collected from multiple sites in a reservoir in northeast Washington State (Boundary Reservoir) (Figure 5-1 through Figure 5-3). Metals criteria are displayed in each graph as well as actual results for analysis of zinc. Concentration of zinc is highest in sediment and then diminishes in the direction of surface water.
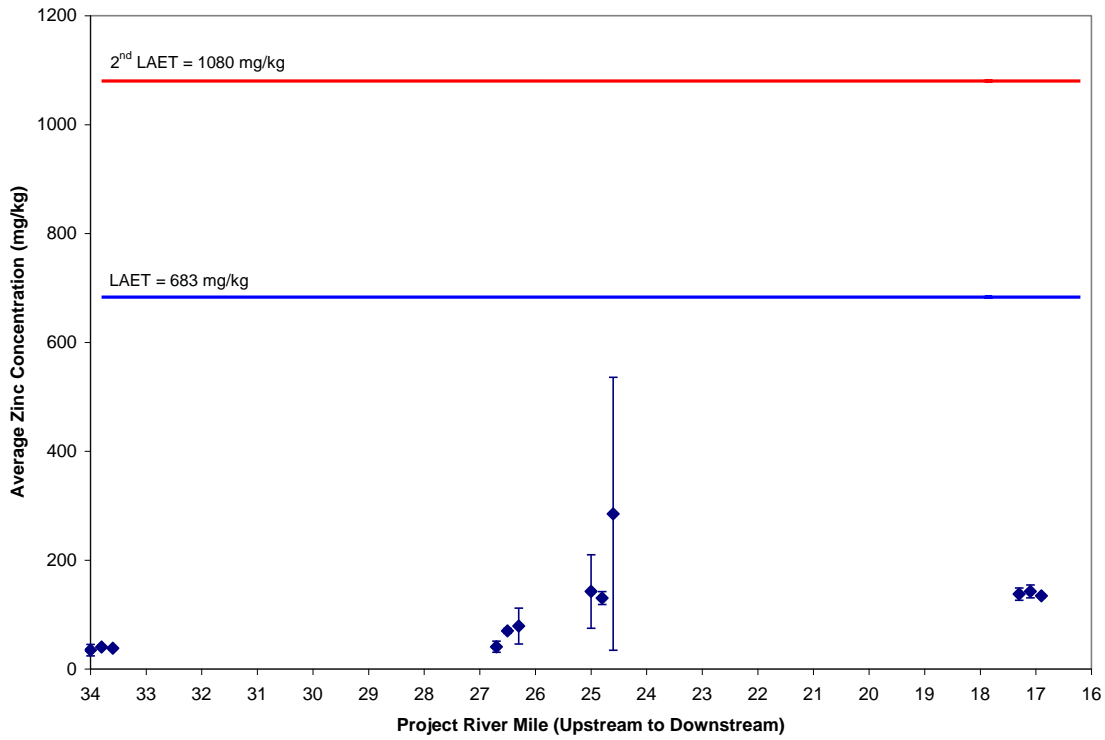
Figure 5-1. Example of sediment samples collected from multiple sediment sampling sites and zinc concentration in each (note the sediment criteria inserted into the graph).
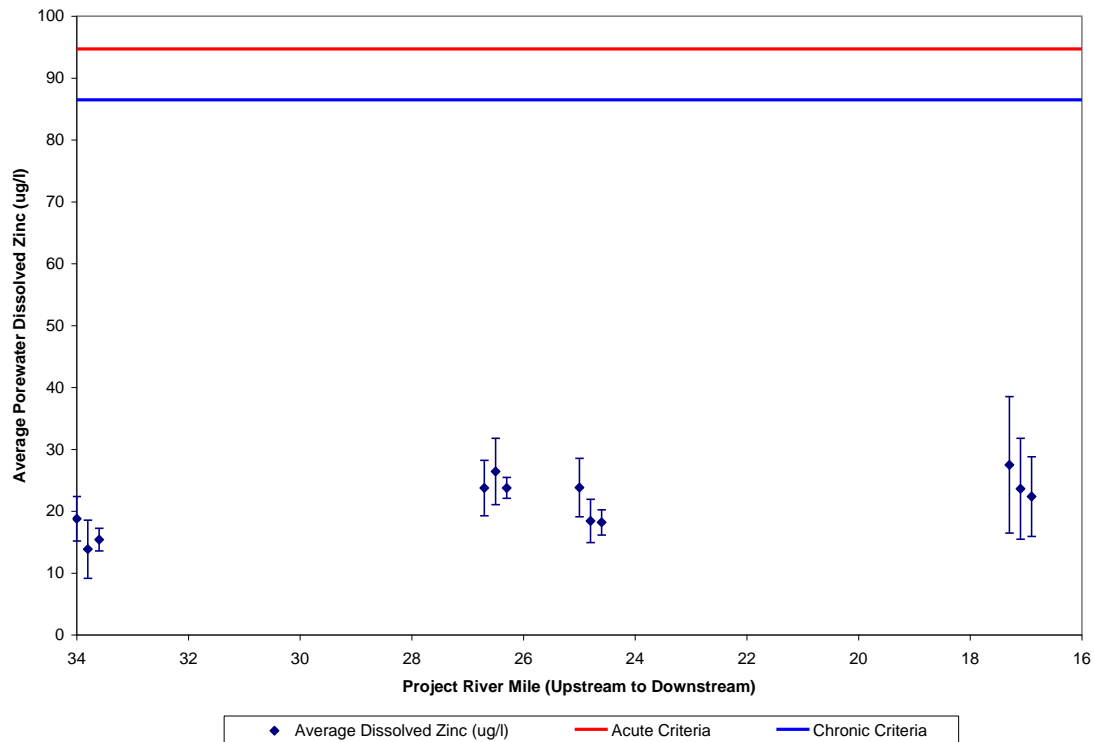

Figure 5-2. Example of pore water samples collected from multiple sediment sampling sites and zinc concentration in each (note the water quality criteria inserted into the graph).

Figure 5-3. Example of water column samples collected from multiple sediment sampling sites and zinc concentration in each (note the water quality criteria inserted into the graph).

The three previous examples of zinc concentrations in media and potential for transfer between media (e.g., sediment - pore water, pore water - surface water) are facilitated by factors listed in the toxicological model for zinc (Figure 5-1). If the fate processes increasing bioavailability are present at a location, then it is likely that zinc may transfer from sediment to pore water; depending on specific factors like presence of fine sediment or low oxygen and redox potential (Figure 5-1). The transfer process exposes aquatic life to toxic effects of the metal like mercury or zinc.

Evaluation of potential for bioaccumulation of mercury (and other metals) will begin with assessment of existing conditions and then assessment of water quality conditions under several operational scenarios. Water quality conditions under operational scenarios are based on model predictions at specific locations in the reservoir where results from multiple media are available. Factors that increase the potential for bioavailability will be predicted by the reservoir model including, but not limited to: pH condition, dissolved oxygen concentrations, total suspended solids concentration, dissolved organic carbon, and redox potential. The predicted water quality condition at points where sediment monitoring had occurred will be identified and a determination made if there is a potential for mercury mobilization between media. The determination for potential mobility is made by comparing mercury (and other select metals) concentration with the state criteria and other sediment standards (e.g., TRV's or SQuiRTs).

6.   DISCUSSION OF SIGNIFICANCE OF RESULTS

Comparison of results from sediment, pore water, and surface water with thresholds or state water quality criteria indicates exposure risk to aquatic life in the new reservoir. The potential for mobilization of mercury and select metals from parent media (e.g., sediment) and transfer to pore water and/or surface water represents water quality conditions in the reservoir influenced by reservoir operations. Susitna river flow and water quality conditions entering the reservoir represent initial drivers for conditions at the upper end of the reservoir. Changes to these water quality conditions will be mediated by several factors including tributaries to the reservoir, large-scale wind fetch, and volume of flow into the basin.

The reservoir water quality model will predict water quality conditions (parameters that influence mobilization of mercury and other metals) under several reservoir operational scenarios. Water quality conditions may differ when the reservoir is operated during dry, wet, and average runoff years. These differences in water quality conditions may represent periods of time during the year when mobilization of mercury or other metals may occur and could affect condition of aquatic life when high concentrations are present in sediments.

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APPENDIX A: SUSITNA-WATANA HYDROELECTRIC PROJECT: MERCURY PATHWAYS LITERATURE REVIEW & SUMMARY

Literature Source	Summary Points
Nilsson C. and K. Berggren. 2000. Alterations of Riparian Ecosystems Caused by River Regulation. BioScience. 50:783-792.	• In addition to modifying the environment at the dam site proper, a dam affects riparian communities upstream by rising water levels and modifying water-level fluctuations and downstream by altering flow regimes • Converting running waters to reservoirs lead to permanent loss of habitat; especially profound where reservoirs are close to mountains or in far north where river valleys are usually the most productive landscape element • Initial effect of inundation on plants is through the root system; waterlogged soil becomes anoxic and this lead to oxygen stress and elimination of the primary root system • When flooded soils and vegetation decompose they release greenhouse gases (CO_2 and CH_4) which contribute to global warming and methylmercury, which accumulates in predatory fish (Rosenberg et al 1997) • Riparian wetlands, deltas and estuaries are usually highly productive and have high species numbers but may degrade following river regulation
Bodaly R. A. et al. 2007. Postimpoundment Time Course of Increased Mercury Concentrations in Fish in Hydroelectric Reservoirs of Northern Manitoba, Canada. Arch. Environ. Contam. Toxicol. 53:379-389	• Mercury (Hg) concentrations in fish in boreal reservoirs have been shown to be increased for up to 3 decades after impoundment. • In the benthivorous lake whitefish Hg concentrations increased after flooding to between 0.2 and 0.4 ug/g wet weight compared with pre-impoundment concentrations between 0.06 and 0.14 ug/g and concentrations in natural lakes between 0.03 and 0.06 ug/g • Concentrations in lake whitefish were usually highest within 6 years after impoundment and took 10 to 20 years after impoundment to decreased to background concentrations • Hg concentrations in predatory northern pike and walleye were highest 2 to 8 years after flooding at 0.7 and 2.6 ug/g compared with pre-impoundment concentrations of 0.19 to 0.47 ug/s and natural lake concentrations of 0.35 to 0.47 ug/g • Hg concentrations in predatory species decreased consistently in subsequent years and required 10 to 23 years to return to background levels • Bodaly and Hecky (1979) and Bodaly et al. (1984a) initially hypothesized that increased Hg concentrations in fish in newly flooded reservoirs was caused by the bacterial methylation of Hg found in flooded soils. This hypothesis has been confirmed by experimental studies in which terrestrial materials were experimentally flooded (Hecky et al. 1991; Therien & Morrison 1999), in studies of experimental reservoirs • Bodaly et al 1997 reviewed published evidence and concluded that new methyl mercury was likely produced by flooding • Amount of flooding appears to be an important factor influencing post-impoundment Hg concentrations • Upstream flooding tended to increase Hg concentrations in fish in downstream reservoirs but effect was quite variable • Increased in Hg concentrations took place in northern Manitoba reservoirs in all fish species examined; peak values observed within 10 years • Observed increased of Hg concentrations in fish from hydroelectric reservoir are consistent with observations on the production of significant amount of new MeHg in the flooded zones of new boreal reservoirs. Increased Hg concentrations in the food chains of boreal reservoirs have been related to increased production of MeHg stimulated by the decomposition of flooded organic matter. • Hg concentrations in fish reached an asymptote at approximately 100% flooding. May be related to the fact that once a reservoir if flooded extensively, the littoral zone, with its higher temperatures and consequently higher rates of organic carbon decomposition and Hg methylation, would be compared entirely of flooded terrestrial area, and MeHg production would be at a maximum for these systems; therefore further flooding may not result in higher Hg concentrations in fish

	• Although peak production of new MeHg in boreal reservoirs is reached within a few years of flooding Hg concentration in predatory fish will take up to 10 years to reach peak levels and up to 3 decades to return to background
Hall, B.D. et al. 2009. Changes in methyl mercury concentrations in zooplankton from four experimental reservoirs with differing amounts of carbon in the flooded catchments. Can. J. Fish. Aquat.Sci. 66:1910-1919	• Overall results suggest that reservoir designs that minimize the amount of flooded terrestrial C should result in shorter periods of elevated MeHg in the food web • Flooding following creation of new reservoirs stimulates decomposition of inundated terrestrial organic matter, which in turns stimulates the activity of bacteria that convert inorganic Hg to MeHg • Increases in MeHg concentrations in flooded environments occur typically in water, fish, zooplankton and other invertebrates • Because Hg methylation is a microbial process linked to C decomposition it is reasonable to expect that the amount of stored C in flooded areas will have a positive relationship with MeHg production in newly formed reservoirs • St. Louis et al (1994, 1996) found greater MeHg concentrations in outflow from catchments with wetlands (high C storage) versus uplands (lower C storage) • Although MeHg concentrations in zooplankton were similar among reservoirs in the first two years of impoundment, the amount of terrestrial C flooded in each reservoir influenced the length of time that MeHg concentrations remained elevated • MeHg concentrations in zooplankton from the flooded wetland remain high elevated even after 14 years • Changes in MeHg concentrations in zooplankton were highly correlated with changes in MeHg concentrations in unfiltered water • Although MeHg production rates were correlated with the amount of C stored in the reservoirs prior to flooding, the majority of Mehg was produced in the flooded soils and was not transferred to the water column. Suggest that the majority of MeHg produced in reservoirs did not enter the water column and was therefore not available to organisms in pelagic food webs • Flooding not only affected concentrations of MeHg but also modified many other aspects of water chemistry and food chain structure in the experimental reservoirs. In the years following flooding, concentrations of major nutrients and food web productivity increased considerably as a result of the decomposition of flooded terrestrial organic matter. • Changes in MeHg concentrations in unfiltered water explained by far the largest proportion of variation in MeHg concentrations in zooplankton (60-80%) however other factors also affected the magnitude of response. Results suggest that variations in DOC or pH among reservoirs altered the relationship between MeHg in unfiltered water and zooplankton • Increased MeHg concentrations in waters with increasing DOC likely due to increased solubility of MeHg facilitated by the formation of DOC-MeHg complexes • Results highlight the dual role of DOC in affecting MeHg transfer to aquatic food webs. DOC may increase MeHg availability because DOC and MeHg concentration are typically correlated but transfer from water to zooplankton and other biota may also be reduce with increases in DOC • Study found that initial increases in MeHg concentrations in zooplankton were not correlated with the amount of flooded terrestrial C in each catchment but the duration of elevated MeHg increased with C stores.
Friedl G. and A. Wuest. 2002. Disrupting biogeochemical cycles – consequences of damming. Aquat. Sci. 64:55-65	• Potential consequence of the transition from a river to a lake is the depletion of oxygen • Within the reservoir the depletion of oxygen triggers reduction of nitrate, manganese (hydr)oxides, iron hydroxides and sulfate • Under anoxic conditions microbial methanogenesis and denitrification lead to the production of potential emission of greenhouse gases • Hg present in all soils; Elevated Hg concentrations partly due to the geological underground and partly due to atmospheric deposition of Hg prior to damming

	• In aquatic systems inorganic mercury is transformed into MeHg. Concentration of MeHg is a result of the balance between production of the compound and degradation by microorganisms. Production within and remobilization from the sediment is especially intense under anoxic conditions often encountered in young reservoirs • Believed that sulfate-reducing bacteria, active under anoxic conditions, trigger the conversion of inorganic Hg to MeHg • MeHg enters the food chain and accumulates in higher organisms and fishes or it is directly adsorbed from water in the gills of fish • Final MeHg concentration in the fishes is determined by Hg input, the net balance between methylation and demethylation and the magnification factor in the food chain • Hecky et al 1991 found that the methylation/demethylation balance rather than the total mercury concentration in the substrate determines MeHg concentrations in fish • Methylation seems to be favored in the presence of terrestrial material • "Flooding of areas with terrestrial organic matter and occurring sulfate reduction seem to be the trigger for enhanced methylation. The highest methylation rates are therefore to be expected in shallow reservoirs, where anoxic waters cover organic rich soils."
Zhong, Y. and G. Power. 1996. Some Environmental Impacts of Hydroelectric Projects on Fish in Canada. Impact Assessment. 14:3 285-308.	• Mercury concentration in fish has been identified as a serious impact in number of newly impounded reservoirs in Canada since the late 1970s • Increase in fish Hg Levels generally believed to be consequence of bacterial methylation stimulated by decomposition of flooded organic materials • Louchouarn et al 1993 suggested that long distance atmospheric transport of Hg and suspension of humic horizon from flooded soils important for Hg cycling • MeHg can be absorbed directly form water across gills or be obtained from food; 10 times toxic than inorganic Hg • In Southern Indian Lake and the Churchill River diversion area, Hg levels in several fish species were correlated with the area of land flooded and increase in water level • Residence time related to biological production and Hg export rate and is corrected with Hg levels • Duration of reservoir fills is corrected to fish Hg Level; significant delay in the rise in Hg concentration in fish in La Grande 3 Reservoir which took 3 year and 4 months to fill • Hg levels were markedly higher in 5 species of fish in downstream rivers where the discharge had greatly increased following impoundment • Hg accumulation might be restrained in sea water. Migratory populations of Cisco and lake whitefish exhibited much lower Hg levels than resident populations of the same species in La Grande River, although both resident and anadromous populations of lake whitefish showed significantly higher Hg levels after construction of the hydro project compare to pre-impoundment levels • High temperature important factor that stimulated methylation but retarded demethylation in lab experiments and in lakes; rates of methyl Hg demethylation in lakes and reservoirs were inversely related to temperature • Hg concentration in 4 species of fishes were significantly and positively correlated with mean epilimnetic water temperature • Fish generally concentration Hg more quickly in the early period of impoundment and reach max levels 3 to 9 years after impoundment • Once max level reached, Hg concentrations in fish tend to decrease with increased age of the reservoir • Heavy bank erosion contributing new organic materials may lengthen the duration of higher Hg concentrations
Hall, B.E. et al 2005. Impacts of Reservoir Creation on the Biogeochemical Cycling of Methyl Mercury and Total Mercury in Boreal Upland Forests. Ecosystems. 8:3, 248-266	• Flooded three upland forest sites with varied organic carbon stores to test hypothesis the MeHg production in reservoirs I related to amount of flooded organic matter • Within 5 weeks of flooding MeHg concentrations in the reservoir outflows exceeded inflows and remained elevated for the duration of the experiment, peaking at 1.6 ng/L in the Medium Carbon reservoir

	• There was an initial pulse of MeHg production in all reservoirs that lasted for 2 years after which time net demethylation began to reduce the pools of MeHg but not back to level found prior to flooding • Large increased in MeHg stores in soils compared to those in water and biota indicate that flooded soils were main sites of MeHg production • Determined MeHg and Total Hg stored in foliage, shrubs, ground cover, wood, and soils prior to flooding of reservoirs • Prior to flooding average MeHg concentrations in plants and soils ranged from 0.12 to 1.13 ng/g, average Total Hg concentrations were 3.6 to 96.0 ng/g; MeHg stores prior to flooding in the High Carbon site were 5 to 6 fold greater than in the medium and low carbon sites • Total Hg stored in vegetation and soils in the High C and Medium carbon sites were similar and about 2 fold greater than in the low carbon sites • For all sites, MeHg and total Hg were predominately stored in soils (81-95% and 95-98%, respectively) • Large increases in MeHg stores in soils postflood suggest that flooded soils were the main sites of MeHg production • Periphyton, zooplankton and fish communities represented the smallest MeHg pools in the upland reservoirs at the end of each flooding season accounting for 1 to 10% of total MeHg • Pools of MeHg in food web organisms generally did not differ among reservoirs • Results support hypothesis that the reservoir with the highest amount of stored organic carbon would have the highest amount of MeHg production; greenhouse gas production did not differ among reservoirs indicating that amount of easily decomposable organic carbon was similar among the upland reservoir However, results suggest that once flooded, newer more labile organic carbon stored in upland forests promotes relatively higher rates of MeHg production compared to lder, more recalcitrant organic carbon stored in peatlands • Majority of MeHg was produced in the soils and peat and was not transferred to the water column; unless other processes that enhance the movement of MeHg associated with flooded soils and peat particles to the water column are present, flooding wetland may not necessarily result in a worse-case scenarios for MeHg contamination of reservoir fisheries because majority of MeHg does not enter water column and therefore the food web • After two years of flooding there was net demethylation in the soils of the reservoirs • However modeling exercises have shown that 2-5 years of enhanced MeHg production can result in 20-30 years of elevated MeHg concentrations in predatory fish (author cites R. Harris, Tetra Tech, Inc, Oakville, ON, personal communications!) •
Rosenberg, D.M. et al 1997. Large scale impacts of hydroelectric development. Environ. Rev. 5:27-54.	• MeHg problems in fish are confined to the reservoirs themselves and short (<100km) distances downstream • MeHg can reach very high levels in predatory fish; i.e. predatory fish in La Grande 2 Reservoir in Quebec reached approximately 6 times background levels • MeHg levels in predatory fish usually remain elevated for 2 to 3 decades following impoundment whereas levels in water and zooplankton remain elevated for 10 and 10-15 years, respectively • MeHg can be elevated in biota downstream of reservoirs; i.e. fish downstream of dams have higher MeHg concentrations than fish in the reservoir upstream, because downstream fish feed on fish than are injured passing through the turbines • A higher proportion of land flooded to the final surface area of the reservoir produces higher MeHg levels than when a low proportion of the surface area is flooded land • Study done on reference Lake 240 (ELA) showed that food was the dominant pathway of MeHg uptake by fish at natural levels of MeHg
Ikingura, J.R. and H. Akagi. 2003. Total mercury and methylmercury levels in fish from hydroelectric reservoirs in Tanzania. The Science of the Total Environment. 304:355-368	• Important factors limiting MeHg production and bioavailability include low total mercury concentrations in the inundated soils and sediments, rapid oxidation and decay of organic matter leading to low total organic carbon in

	• reservoir sediments and water column, and possibly rapid photo-degradation of MeHg under intense sunlight in the relatively shallow and clear water reservoirs • High Hg binding capacity of iron-rich laterite soil in the reservoir watersheds also likely to decrease the mobility, methylation, and bioavailability of Hg

Stokes, P.M. and C.D. Wren. 1987. Bioaccumulation of Mercury by Aquatic Biota in Hydroelectric Reservoirs: A Review and Consideration of Mechanisms. Lead, Mercury, Cadmium and Arsenic in the Environment. John Wiley and Sons, Ltd. Pp. 255-277	• Fish can accumulate Hg either through food or directly from the water
	• Efficiency of Hg assimilation from food appears to vary among species; experimental studies shown that 68-80% of Hg ingested is assimilated by rainbow trout, 20% by northern pike
	• Hg uptake form water will be determined by water concentration, fish metabolic rate and efficiency of update (bioavailability) as determined by ambient water characteristics
	• Biotic and abiotic variables affecting fish metabolic rate and Hg uptake include water temperature and fish body size
	• Uptake efficiency of MeHg from water by salmonids has been estimated at 7.1% and 8.3% (hardness 385 mg/L); uptake efficiency increased to 25% in soft water (hardness 30 mg/L); increased uptake efficiency may partially explain elevated Hg levels in fish from low pH lakes
	• From various studies, can conclude that is it clear that fish Hg is frequently unacceptably high in impoundments remote from major point sources and that the phenomenon has been described for a variety of geographic regions
	• Studies on La Grande river reservoirs pre and after impoundment; after impoundment Hg in fish increased and for all fish species there was a correlation between age and Hg, or between length and Hg; authors considered a major controlling factor for methylation was a decrease in pH of surface water and subsurface water, inundation of vegetation and concentrations of nutrients which could enhance methylation of mercury
	• Reasonable to assume source of Hg is either materials already in the lake/river prior to flooding or the flooded soils and vegetation and that this mercury is either natural or at least background even if not pre-industrial levels. No immediate atmospheric source in these situation. Questions of mechanism then becomes one of mobilization and methylation of existing Hg results from factors which change between pre and post-impoundment
	• From the review in the paper, author reaches a consensus that soils and vegetation in the flooded areas are the source of Hg
	• Experimental studies at Churchill River diversion (Manitoba) indicate best source of Hg and promoter of methylation is Sphagnum moss; addition of inorganic subsoil to experimental enclosures did not have same increase in Hg
	• Sweden study review Hg issues in remote lakes and fish Hg levels, concluded that major route of Hg for fish is transport from surrounding soils and vegetation (which in Southern Sweden are already contaminated by increased atmospheric fallout). If this is true for unflooded systems then flooding would probably further enhance this tendency
	• Non-microbial methylation (probably via free radical reaction) is also important in systems, stimulated by organic matter and certain metals such as Fe, Mn, and Cu
	• Assuming elevated Hg is sufficiently serious and long-lived and decreasing fish Hg realistic only 4 management approaches appear to be even remotely appropriate
	    o Removal of vegetation and possibly organic soil horizon from area to be inundated, prior to flooding
	    o Addition of selenium to water
	    o Deliberate addition of suspended sediment, assuming that the sediment itself is not contaminated (not acceptable in reservoir situation where methylation rates are limiting rather than Hg concentrations)
	    o Intense fishing can decrease levels of Hg in fish; alteration of the "biological flow of Hg"
	• Author believes only the first options is even remotely possible

Bodaly, R.A., R.E. Hecky, and R.J.P. Fudge. 1984. Increase in Fish Mercury Levels in Lakes Flooded by the Churchill River Diversion, Northern Manitoba. 1984. Can. J. Fish. Aquatic. Sci. 41:682-691	• Increases in fish muscle Hg levels occurred coincidentally with flooding at three lakes affected by the Churchill River diversion • Post-impoundment Hg levels in predatory fish appeared to be related to the flooded terrestrial area compared with pre-impoundment lake area • Hypothesize that observed fish Hg level increases due to bacterial methylation of naturally occurring mercury found in flooded soils • Hg levels in predatory fish became elevated within 2-3 years of impoundment and not indication of declines from peak levels within 5 to 8 years • Increase in Hg in the lakes flooded for the Churchill River diversion not due to atmospheric fallout since over 30 lakes in northern Manitoba show no trends in increasing fish Hg levels • Sediment core from Southern Indian Lake showed a slow constant increase in Hg concentration from the base of the core to the top resulting in a 2X top to bottom differential in Hg concentration but there is no evidence of a dramatic increase in Hg deposition prior to flooding • Appears that reservoir formation and associated inundation of land led to higher fish Hg concentration • Hypothesis that elevated fish Hg Levels were due to bacterial methylation of naturally occurring mercury found in flooded soils; primary source of Hg was probably upper, organic soil horizon because Hg levels in this soil layer were much higher than in inorganic subsoil layers • Water Hg levels throughout the Churchill River diversion system were very low
Tjerngren, I., T. Karlsson, E. Bjorn, and U. Skyllberg. 2012. Potential Hg methylation and MeHg demethylation rates related to the nutrient status of different boreal wetlands. Biogeochemistry. 108:335-350	• Study reports potential Hg methylation (Km) and MeHg demethylation (Kd) rate constants in boreal wetland soils • The Km/Kd ratio generally followed %MeHg in soil and both measures were highest at the fen site with intermediate nutrient status • Molybdate addition experiments suggest that net MeHg production was mainly caused by the activity of sulfate reducing bacteria • Comparison of other studies showed that Km and % MeHg in boreal freshwater wetlands in general are higher than in other environments • Results support previous work that suggest highest MeHg production in boreal landscapes is to be found in fens with an intermediate nutrient status • Seasonal variation in Km revealed the highest numbers in September; probably due to fairly high temps, availability of newly deposited above-and belowground litter and dead microbial material potentially available as electron donors for methylating bacteria • Several studies have shown that organic matter quantity and quality is one of the major factors controlling net MeHg production in soils and sediments • MeHg net production optimal not at the poorest or richest nutrient sites but at sites with an intermediate nutrient status • Addition of Mo during incubation did not reveal any clear differences among the wetlands regarding which group of microorganisms are responsible for methylation of Hg; however experiment did clearly illustrate that most Hg methylation in wetlands in this study was conducted by sulfate reducing bacteria • Low pH stimulates methylation and high concentrations of sulfide hamper the activity of sulfate reducing bacteria • Some studies suggest the iron reducing bacteria contribute to methylation of Hg • "In this study, we show that boreal wetlands with low to intermediate nutrient status have the highest net production of MeHg, as reflected by potential methylation and demethylation rates and %MeHg in soil. We suggest that an improved quality of organic matter as electron donors for bacteria and nutrient status in fens, as compared to ombrotrophic bog-type of wetlands favors methylation over demethylation, whereas a further increase in nutrient status and the concurrent change in alkalinity (increased pH) favors demethylation over methylation reactions."

| Tremblay, A. and M. Lucotte. 1997. Accumulation of total mercury and methyl mercury in insect larvae of hydroelectric reservoirs. Can. J. Fish. Aquati. Sci. 54:832-841 | • Mean total Hg and MeHg concentrations in insect larvae from HE reservoirs were 3 to 5 times higher (up to 10 times) than in their counterparts from natural lakes
• Results suggest that suspended particulate matter eroded from flooded soils by wave and ice action and bacterial activity enhanced by the release of labile carbon and nutrients from the flooded soils may indirectly transfer MeHg from flooded soils to insect larvae
• Aquatic insect larvae closely associated with sediment and represent a major proportion of the diet of many fish species, they may constitute an important pathway for the transfer of sedimentary Hg to the food web
• Tremblay et al 1996 reported positive correlation between MeHg in sediments and those in insect larvae in study of 11 natural Quebec lakes
• Highest total Hg and MeHg concentrations were found in Heteropterans and the lowest values generally observed in dipterans for both natural lakes and reservoir
• Mean overall MeHg concentrations in predators were 3 to 4 times greater than in detrivores-grazers and the proportion of MeHg to total Hg ranged from 22% in some dipterans to 85% in odonates
• Despite wide range mean overall total Hg and MeHg concentrations were 3 to 5 times higher in insects from reservoirs than in their counterparts from natural lakes
• Upon flooding, forest soils are subjected to physical modifications such as saturation of interstitial spaces and undergo numerous biogeochemical changes that may affect the metal-binding capacities of soil components
• Enhanced bacterial productivity in reservoir may represent an important pathway for the trophic transfer of both total Hg and MeHg from flooded soils to the insects
• Suspended particles which are rich in MeHg and total Hg settle to the bottom where they are mixed with algae and bacteria present at the soil-water interface. Rapid accumulation of total Hg and MeHg in benthic insects after flooding indicates that these animals may feed at the soil-water interface rather than in the soils themselves; authors propose that sedimented suspended particles represents another pathway that may, along with bacteria and the soils themselves, account for the observed patter of MeHg accumulation in insects over time |
| Hammerschmidt, C.R. et al. 2006. Biogeochemical Cycling of Methylmercury in Lakes and Tundra Watersheds of Arctic Alaska. Environ. Sci. Technol. 40:1204-1211 | • Important sources of the monomethylmercury (MMHg) aquatic cycling include MMHg production in lacustrine and wetland sediments where sulfate reducing bacteria are presumed primary methylators of Hg
• In temperate lakes in situ sedimentary production and mobilization is a major source of MMHg, watersheds can also contribute modest amounts depending upon physicochemical characteristics and relative area of wetlands they contain
• Characterization of major MMHg fluxes in arctic ecosystems critical for assessment of anticipated clime change on the cycling of MMHg
• Study lakes near Toolik Field Station above arctic circle; lakes oligotrophic and contain low levels of sulfate
• Watershed production accounted for relatively higher levels of MMHg during low flow and the asymptotic concentration at greater flow rates may reflect runoff of atmospherically derived MMHg
• Net production of MMHg in Alaskan tundra low compared to temperate watersheds, watershed MMHg estimated net production about 0.005 µg MMHg/m2-year. This rate is lower range for temperature watershed (0.01-0.44 µg MMHg/m2-year) but 5 fold greater than in watershed of Canadian High Arctic
• MMHg deposited directly to lake surface via precipitation; mean concentration of MMHg in July rain was 0.025 ng/L. Comparable to concentration found in precipitation at temperate North American locations but greater than that in oceanic rain
• There was no consistent relationship between either sediment organic content and water depth or Hg and organic matter in surface deposits.
• Was relationship between watershed/lake area ratio and Hg in surface sediments suggesting unweathered soils contribute major fraction of Hg in sediment of the study lakes
• Sedimentary distribution of MMHg in contract to Hg appears to be governed primarily by organic matter |

	• Potential gross rates of Hg methylation in surface sediments related positively to concentration of Hg in filtered pore water; relationship suggests that availability of Hg is an important factor influencing MMHg production in arctic lake sediments • Average sediment-water flux from arctic lake sediments was 3.1 ng/m2-day; comparable to estimates from budget for temperate lakes (2.8-8.5 ng/m2-day) • Temperature important factor influencing bacterial MMHg production in sediments; presumed little seasonal variation in benthic production and efflux of MMHg in arctic lakes because temp of most sediments in summer (4-7°C) not much greater than winter (1-4°C) • Estimated depth-integrated photodecomposition fluxes (±50%) were 0.89, 0.46, 0.51, and 1.31 µg/m2-year for E1, E5, F2, and Toolik lake respectively • Biomagnification results in more than a 10^2 increase in MMHg concentration between sedimentary organic matter/epilithon and fish muscle • Estimated bioaccumulation of MMHg by Arctic char in E5 and F2 is 0.01 and 0.06 µg/m2-year, respectively • Estimated bioaccumulation of MMHg by Arctic grayling Toolik Lake is 0.08 µg/m2-year • Estimated bioaccumulation of MMHg by slimy sculpin about 0.02 µg/m2-year • In-lake process dominate cycling of MMHg; benthic flux of MMHg accounts for 80-91% total inputs; Catchment runoff, including both precip and production in tundra less than 20% total inputs • Lake photodecomposition major removal process; during 100 day ice free period account for destruction of 80-96% MMHg mobilized from sediments and 66-88% of total annual inputs • Photodecomposition major role in cycling of MMHg in lakes and appears to reduction significantly pool of MMHg available for biological uptake • Warming of arctic may increase MMHg bioaccumulation by enhancing Hg methylation and reducing role of photodecomposition; temp enhances Hg methylation • Enhanced weathering of watershed have potential to liberate sulfate from mineral phase with can increase methylation by increasing sulfate in otherwise sulfate limiting systems
Hammerschmidt, C.R. and W. F. Fitzgerald. 2010. Iron-Mediated Photochemical Decomposition of methylmercury in an Arctic Alaskan Lake. Environ. Sci. Technol. 44:6138-6143	• Sunlight-induced decomposition is the principal sink for methylmercury (CH3Hg+) in arctic Alaskan lakes and reduces its availability for accumulation in aquatic food webs • Results from in situ incubation tests indicate that CH3Hg+ is not decomposed principally by either direct photolysis (i.e., no degradation in reagent-grade water) or primary photochemical reactions with dissolved organic material • Results demonstrate that CH3Hg+ decomposed in natural surface water by oxidants, apparently hydroxyl radical, generated from the photo-Fenton reaction • Paper shows photodecomposition of CH3Hg+ in arctic lake water is 1) by an indirect pathway, 2) independent of nitrate, 3)dependent on labile Iron, 4) inhibited by ●OH scavenging molecules, and 5) mediated primarily by sunlight between 320 and 480 nm • Results are consistent with ●OH, produced by the photo-Fenton reaction, being the principal agent of CH3Hg+ decomposition in natural surface water • Photochemical degraded of CH3Hg+ pronounced in oligotrophic arctic lakes of the Alaskan tundra
Hall, B. D., V. L. St. Louis, and R.A. Bodaly. 2004. The stimulation of methylmercury production by decompositions of flooded birch leaves and jack pine needles. Biogeochemistry. 68:107-129	• Birch leaves decomposed approx. 2.4 times faster than jack pine needles; however net MeHg production in enclosures containing birch leaves was 5 times lower than in enclosures contain jack pine needles • Results showed that MeHg production were related to rates of organic matter decomposition and that increases in MeHg associated with flooded birch leaves and jack pine needles resulted from the production of new MeHg as opposed to leaching of MeHg in plant tissue • Number of studies have shown that inundation of plant tissue results in increased MeHg concentrations in surrounding water and biota

| | Although Total Hg and MeHg concentrations in boreal plants is typically very low; litterfall has been shown to be an important input of MeHg and THg to forest floors Percent dry weight and carbon content was greater in fresh jack pine needles than fresh birch leaves Concentrations of sulfate in water with jack pine needles were lower than enclosure with birch leaves at end of experiment possibly suggesting greater rates of sulfate reduction MeHg concentrations in fresh birch leaves (0.36 ng/g) were 3.6 times higher than in jack pine needles (0.10 ng/g). THg concentrations in fresh birch leaves (9.31 ng/g) were 1.3 times lower than in jack pine needles (12.26 ng/g). Average concentrations of MeHg in water were significantly higher in enclosures with jack pine needles than in enclosures with birch leaves at end of experiment Average total net increase of MeHg mass in the jack pine needles treatment exceeded that in the birch leaves treatment by over 8-fold, despite greater initial MeHg mass in the birch treatment and higher rates of decomposition Data support hypothesis that there was production of NEW MeHg associated with decomposition of flooded plant tissues as opposed to just leaching of MeHg already present; Data did not support 2nd hypothesis that rates of Hg methylation are directly proportional to rates of organic carbon mineralization Results consistent with other studies that examined MeHg increases in coniferous needles compared to deciduous leaves and grasses; Studies in South Indian Lake in Northern Manitoba demonstrated when spruce boughs were added to enclosures with perch, THg concentrations in these perch were greater than in those held in enclosures to which prairie sod and moss-peat were added Black spruce needed sampled from litterbags planed in an experimentally flooded wetland at ELA exhibited increase of 800% original MeHg mass, compared to increases of 630% of original mass in Sphagnum fuscum moss and 50% of original mass in sedge grass stalks At end of experiment there was 1.5 times more DOC in enclosures with birch leaves than jack pine needles; which may have resulted in more inhibition of methylation in the birch leaves Stimulation of MeHg production has been found in environments with low pH, increased temperature, low redox potential and increased sulfate concentrations In this study, pH nor water temperature were different between enclosures and Se concentrations are generally extremely low at the ELA and unlikely to suppress methylation Despite the aerobic water column, anoxia could have developed in micro-zones surrounding plant tissues while the enclosures sat undisturbed; jack pine needles do not break up into small pieces and float like birch leaves and therefore anaerobic micro-zones more likely to occur among jack pine needles sitting on the bottom of the enclosures Lower sulfate concentrations and more active sulfate reduction in the enclosures with jack pine needles and hence Hg methylation support hypothesis that anaerobic micro-zones may have formed with the pine needles Study suggest that amount of organic carbon stored in a reservoir prior to flooding is not a good predictor of the extent of future MeHg increases. Reservoirs created by flooding upland forest that contain relatively less organic carbon stores may result in contamination of reservoir fishers equal to or exceeding reservoir created over wetland areas with very large organic carbon stores |
| Kasper D et al. 2014. Reservoir Stratification Affects Methylmercury levels in River water, plankton and Fish downstream from Balbina Hydroelectric Dam, Amazonas, Brazil. Environ. Sci. Technol. Online | Investigated seasonal variation of MeHg levels in the Balbina reservoir and how they correlated with the levels encountered downstream of the dam Variations in thermal stratification of the reservoir influenced MeHg levels in the reservoir and the river downstream Uniform depth distributions of MeHg and DO in the poorly stratified reservoir during rainy season coincided with uniformly low MeHg levels along the river downstream During the dry season, reservoir was strongly stratified and anoxic hypolimnion water with high MeHg levels was exported downstream; MeHg levels declined gradually to 200 km downstream MeHg dynamics in water and plankton of the Uatuma River near the dam is driven by the seasonal stratification while MeHg dynamics in the lower Uatuma is controlled by seasonal flood pulse and/or tributary inputs |

	• Conclude that higher Hg Levels in fish form the Uatuma River immediately downstream of the reservoirs are mainly due to mercury export from the dam.