Quality Assurance Project Plan

Wenatchee and Mid-Columbia Basins: Impact of Copper Use on Receiving Waters

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November 2007

Publication Number 07-03-112

This plan is available on the Department of Ecology's website at
www.ecy.wa.gov/biblio/0703112.html.

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303(d) Listings Addressed in this Study: none

Waterbody Numbers: WA-45-1010, WA-CR-1030, WA-CR-1040

Project Code: 08-049

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November 2007

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Abstract

The Washington State Department of Ecology regulates irrigation discharge of copper herbicides through a National Pollutant Discharge Elimination System permit. The permit requires the irrigation discharger to monitor copper in surface water where the discharge enters natural waters.

This study will conduct surface water and sediment monitoring to measure background copper concentrations above the Wenatchee and Columbia Irrigation Project areas, downstream of major discharges (near outfall of Shop Spillway and PE16.4), and downstream of the irrigation project area. Sample timing is structured to maximize information gained from irrigation operations. This involves sampling at the end of the irrigation season (October/November 2007), at the beginning of irrigation operations (March 2008), and two times during the maximum copper herbicide-use season (June and August 2008). Results will be compared to Washington State water quality standards and sediment toxicity screening criteria.

Background

Issue

Uncovered irrigation canals, especially returns draining water from agricultural fields, provide an optimum growing environment for aquatic plants and algae. Sunlight is accessible, water is maintained during the growing season, and nutrients are available to facilitate growth. Aquatic vegetation may clog irrigation canals, causing inefficient water delivery and drainage.

Keeping the irrigation canals clear of excessive plant growth is the result of varied management actions including (but not limited to):

1. Limit sunlight to canal.
    a. Artificial cover (piped water).
    b. Riparian growth (shade from natural species).
2. Limit nutrient entry to canal (source reduction and riparian filter).
3. Stock biological harvesters (grass carp).
4. Use mechanical harvesting.
5. Use aquatic herbicides.

Ideally, an integrated vegetation management plan will incorporate more than one practice to limit excessive aquatic plant growth.

Copper is one of three active ingredients permitted as herbicides used in irrigation canals (Ecology, 2002). Other permitted herbicides include acrolein and xylene. Copper products are generally inexpensive, easy to apply, effective, and have been used in vegetation management for over 100 years (CropLife, 2007). Copper is an essential micronutrient for plants, does not break down beyond its inorganic base (Cu^{+}, Cu^{2+}), and is likely to build up in sediments.

In excess, copper is toxic to fish, invertebrates, and plants. Approximately 160,000 pounds of copper-based herbicides are applied to irrigation canals in Washington State each year (Kelly McLain, personal communication). Dissolved copper is regulated through a surface water discharge permit, requiring a maximum daily concentration of 25 µg/L at the point of discharge release to natural waters (Ecology, 2002). The maximum daily concentration is equal to the Washington State acute standard for the protection of aquatic life for copper at 150 mg/L hardness ($mgCaCO_3/L$ – see following section). The maximum daily limitation is defined as the highest allowable daily discharge. Daily discharge means the discharge of a pollutant measured during a calendar day, and the maximum daily discharge is the average measurement of the pollutant over the day (Ecology 2002).

Toxicity

Copper toxicity is expressed through several modes of action. Most mechanisms are dependent on copper availability as a free ion (Cu^{+} or Cu^{2+}), although copper complexes (e.g., copper sulfate ($CuSO_4$)) are toxic in their own right. The predominant acute toxicity mechanism involves ionic copper blocking the uptake of sodium through fish gills, causing sodium/potassium-ATPase inhibition and osmoregulation imbalance, leading to necrosis (localized cell death).

Sorption of copper to solid materials, humic acids, anions, and competition with other cations reduces its availability as an aquatic toxicant. Copper may be sampled in the dissolved phase to eliminate fractions which are sorbed to larger materials and biologically unavailable. Hardness (mg/L $CaCO_3$) and dissolved organic carbon (DOC) measurements provide cationic/anionic and humic acid binding estimates.

Hardness is frequently tested in Washington State surface waters, while DOC is less common. A cumulative distribution of Washington State hardness results illustrates the difference in susceptibility of major watercourses to dissolved copper toxicity (Figure 1). Of 147 hardness measurements in the Wenatchee River, 10% are below 14.7 mg/L, 50% below 26 mg/L and 90% below 36 mg/L. The corresponding results in the Mid-Columbia River are 59, 66.2 and 80 mg/L. All results were obtained from the Washington State Department of Ecology's (Ecology's) Environmental Information Management (EIM) System (www.ecy.wa.gov/eim/).

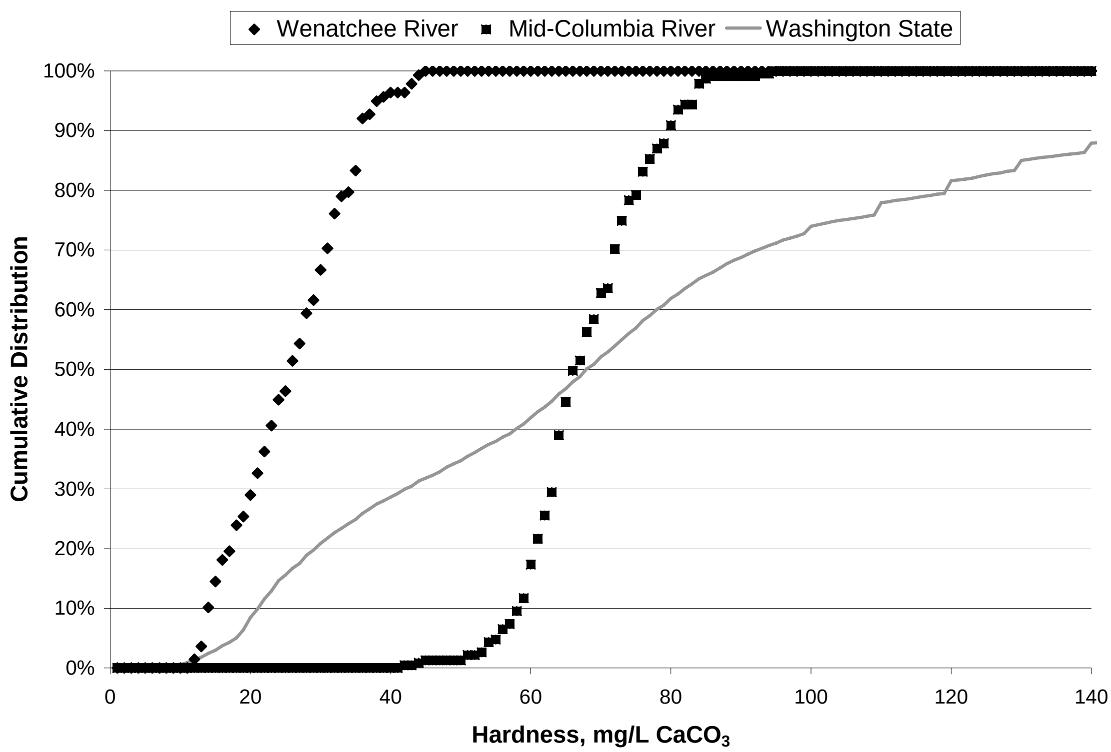

Figure 1. Cumulative distribution of hardness results in Washington State waters.

The state of Washington, under the federal Clean Water Act, promulgated standards to evaluate dissolved copper toxicity (Figure 2).

- Acute standard violation if sample concentration is > (0.960)($e^{(0.9422[\ln(\text{hardness})] - 1.464)}$).
- Chronic standard violation if sample concentration is > (0.960)($e^{(0.8545[\ln(\text{hardness})] - 1.465)}$) (WAC 173-201A, 2006).

The acute standard is based on a one-hour concentration not to be exceeded more than once every three years on average. Similarly, the chronic standard is based on a four-day average concentration not to be exceeded more than once every three years on average. For the purposes of impaired waters assessment, a grab sample (no averaging) is sufficient to meet the acute and chronic temporal criteria as long as:

- A minimum of three excursions exist from all data considered.
- At least ten percent of single grab sample values in a given year exceed the standard. (Ecology, 2006).

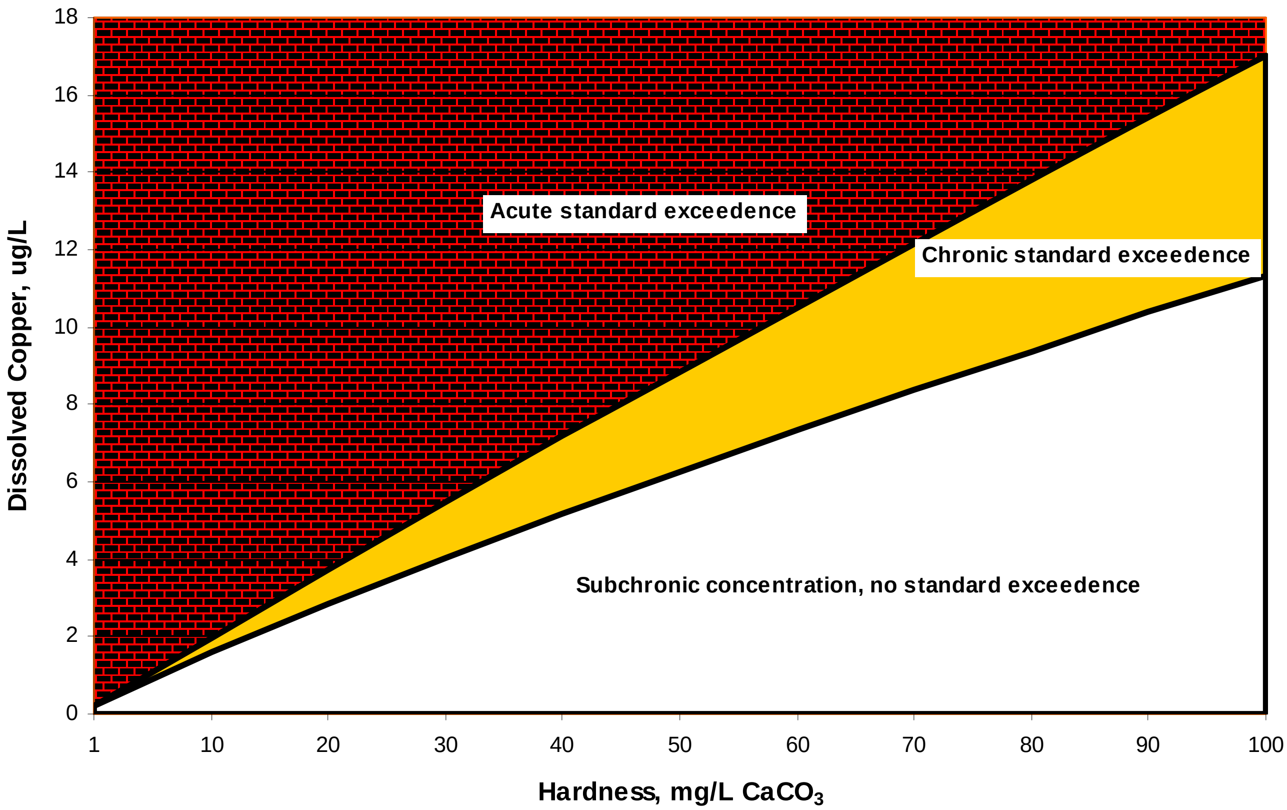

Figure 2. Acute and chronic water quality standards for dissolved copper.

Ten percent of hardness samples taken from the Wenatchee River are below 14.7 mg calcium carbonate ($CaCO_3$)/L. This corresponds to a dissolved copper chronic standard of 2.21 µg/L. The 10% Mid-Columbia River exceedence value is 59 mg/L $CaCO_3$, corresponding to a chronic dissolved copper standard of 7.23 µg/L. The 90% exceedence (upper 10% of values) of dissolved copper results from the Wenatchee River is 0.26 µg/L and 1.18 µg/L in the Mid-Columbia River. All results were obtained from ambient monitoring stations and did not target irrigation discharge receiving waters.

Copper entering receiving waters may accumulate in sediments, resulting in impacts to the benthic organisms (Buchman, 2004; EPA, 2005). Standards have not been established for freshwater sediments in Washington. WAC 173-204-340, Freshwater Sediment Standards, states that Ecology "will determine on a case-by-case basis the criteria, methods, and procedures necessary to meet the intent of this chapter." Avocet Consulting (2003) proposed a set of sediment quality standards (SQS) and cleanup screening levels (CSL) as part of Ecology's effort to develop freshwater sediment criteria for Washington. The proposed SQS is 80 mg/Kg, and the CSL is 830 mg/Kg (Avocet, 2003). Additionally, the Environment Canada Interim Sediment Quality guideline is 35.7 mg/Kg (CCME, 2001). Nationally, background sediment copper concentrations range from 10 to 25 mg/Kg (Buchman, 2004) and will be evaluated in this study through upstream stations.

Authority

Ecology permits use of aquatic herbicides in irrigation returns through a joint state/federal National Pollutant Discharge Elimination System (NPDES) permit. The NPDES is a point-source control measure authorized by the federal Clean Water Act, governed by the United States Environmental Protection Agency (EPA) Office of Water, and administered by Washington State within state boundaries.

Project Description

The goal of this study is to monitor surface water concentrations of total and dissolved copper to:

- Determine if use of copper in irrigation returns is causing a potential for adverse impacts in receiving water and sediments.
- Assist NPEDS permit writers in meeting the objectives of the NPDES: limiting degradation to aquatic life.

The Columbia and Wenatchee Irrigation Projects were selected for the study (Figure 3). The Columbia Irrigation Project was chosen due to the intensity and extent of irrigated agriculture in that area. The Wenatchee Irrigation Project was chosen due to the low hardness of receiving waters and increased susceptibility to dissolved copper toxicity.

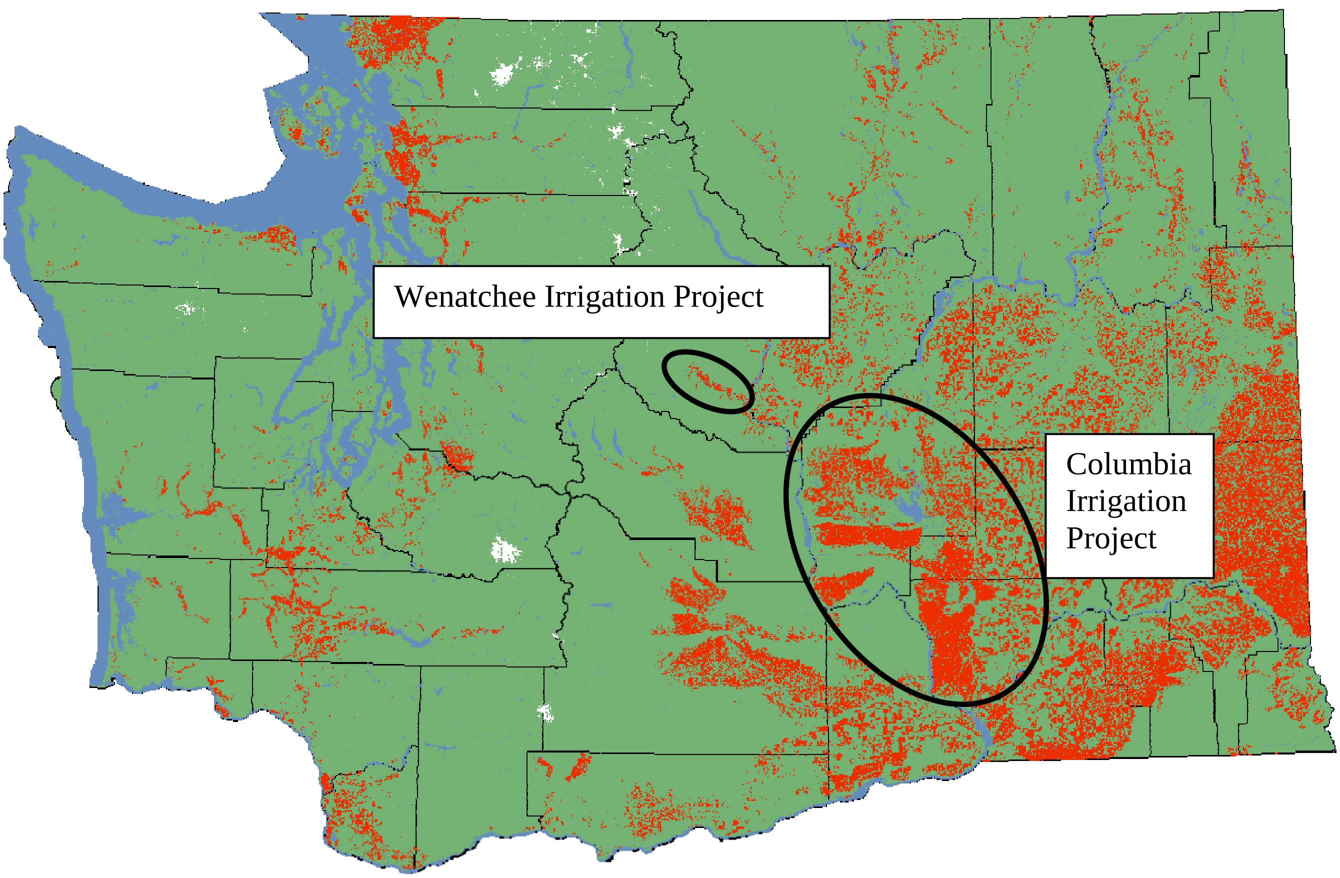

Figure 3. Density of Agriculture in Washington State (dot representation).

Total recoverable and dissolved copper will be measured in surface water, and total recoverable copper will be measured in sediment. Dissolved surface water and total recoverable copper in sediment have standards or criteria for comparison. Total recoverable copper in surface water is measured to determine the quantity of copper which may settle to the sediments or become biologically available (dissolve). Additional water quality parameters will be collected to indicate source, transport, fate, and variables influencing toxicity to aquatic life.

Hardness, dissolved organic carbon (DOC), total suspended solids (TSS), temperature, pH and conductivity are collected in surface water. Hardness and DOC are indicators of chemical and humic components which may limit toxic effects of dissolved copper to aquatic organisms. Temperature influences the reaction rate of the toxic mechanisms, and pH influences the dominant form of copper available (Cu^{+}, Cu^{2+}). Conductivity and TSS provide an indicator of contaminant source.

Grain size, percent solids, and total organic carbon (TOC) accompany the total recoverable copper sediment sampling. These tests are indicators of contaminant sources and availability of copper to benthic (sediment-dwelling) organisms.

Objectives of this study include:

Spatial-Temporal Influence

- Assess background copper concentrations upstream of selected irrigation projects.
- Evaluate the difference (if any) between background and receiving water downstream of the irrigation project area.
- Evaluate localized concentrations within the sediment deposition zone of two irrigation discharges.
- Evaluate seasonal variation due to irrigation operations.

Potential Toxicity

- Investigate surface water toxicity through Washington State Surface Water Quality Standards.
- Assess potential sediment toxicity according to local and national guidelines.
- Assess the influence of ancillary parameters on copper distribution and toxicity.

Organization and Schedule

Organization

Name	Organization	Phone Number	Role
Paul Anderson	EAP-SCS-SAU	360.407.7548	Project Manager, EIM
Chris Burke	EAP-SCS-SAU	360.407.6139	QAPP Author
Kelly McLain	WQ-PDS	360.407.6938	Client
Andrew Kolosseus	WQ-WMU	360.407.7543	Client Assistance
Dan Dugger	EAP-EOS-DSU	509.454.4183	Field Assistance
Jerry Jorden	EAP-EOS-DSU	509.454.7865	Field Assistance
Dale Norton	EAP-SCS-SAU	360.407.6765	Unit Supervisor
Dean Momohara	Manchester Laboratory	360.871.8808	Unit Supervisor
Stuart Magoon	Manchester Laboratory	360.871.8801	Lab Director
Bill Kammin	Ecology	360.407.6964	QA Officer

EAP = Environmental Assessment Program.
SCS = Statewide Coordination Section.
SAU = Statewide Assessment Unit.
WQ = Water Quality Program.
PDS = Program Development Services.
WMU = Watershed Management Section.
EOS = Eastern Operations Section.
DSU = Directed Studies Unit.

Schedule

Sampling and Analysis	
Field Work	Oct/Nov 2007; March, June, August 2008
Laboratory Analysis Completed	October 2008
Environmental Information System (EIM) Data Set	
EIM Data Engineer	Paul Anderson
EIM User Study ID	CBUR0007
EIM Study Name	A Study of Copper Discharge from Irrigation Canals
EIM Completion Due	February 2009
Final Report	
Author	Paul Anderson
Schedule	
Draft Due to Supervisor	December 2008
Draft Due to Client/Peer Reviewer	January 2009
Final Report Due	February 2009

Quality Objectives

Table 1 presents project targets for accuracy and precision. Sources of error from sample collection, transportation, and storage will be minimized by adherence to:

- EPA Method 1669 Low Level Metals Sampling in Surface Water (EPA, 1995).
- Puget Sound Estuary Program (PSEP) Sediment Protocols (EPA, 1996).
- EPA sediment technical guidance (EPA, 2001).
- Requirements of Ecology Sediment Management Standards (Ecology, 2003).

Table 1. Quality objectives for surface water samples.

Parameter	Accuracy - % recovery		Precision –RPD	
	Check Standard LCS	Matrix Spike MS Duplicate	Replicate	MS/MSD Pair
Surface Water				
Total recoverable copper	85-115	75-125	±15	±20
Dissolved copper	85-115	75-125	±15	±20
Hardness	85-115	75-125	±15	±20
DOC	85-115	NA	±15	NA
TSS	NA	NA	±15	NA
Sediment				
Total recoverable copper	75-125	70-130	±25	±30
TOC	75-125	NA	±15	NA
Percent solids	NA	NA	±15	NA
Grain size	NA	NA	±15	NA

RPD = Relative Percent Difference is the difference between samples and their mean value, expressed as a percentage.
LCS = Laboratory Control Sample.
MS = Matrix Spike.
MSD = Matrix Spike Duplicate.

Sampling Process (Experimental) Design

Timing

The irrigation season in Eastern Washington extends from March through mid-October, and the maximum use period of irrigation herbicides extends from June through mid-September (Kolosseus, personal communication). Four sample events are assigned to maximize information gained from irrigation operations:

1. End of irrigation season. Surface water and sediment samples collected in late October or early November 2007 to evaluate the residual copper concentrations following the irrigation season.
2. Initiation of irrigation. Initiation of irrigation is characterized by a 3 times or greater increase in baseflow of canals or diversion of water into canals if dry. Surface water and sediment samples will be collected in March 2008.
3. Maximum copper use season. Surface water samples will be collected in June 2008.
4. Maximum copper use season. Surface water samples will be collected in August 2008.

Sample Sites

Six sample sites, three each, are proposed for the Wenatchee and Columbia Irrigation Project areas (Table 2, Figures 4 and 5 respectively). One sample will be collected at each location for each sampling event.

Table 2. Purpose and location of monitoring sites.

Site	Purpose	Wenatchee River	Mid-Columbia River
Upstream	Provide assessment of background conditions prior to entering major irrigation project drainages	Upstream of Leavenworth	Downstream of Rocky Reach Dam tailrace
Near outfall	Evaluate first sediment deposition area downstream of outfall for potential maximum impacts to aquatic life in receiving waters	400 feet downstream of Shop Spillway	200 feet downstream of PE16.4 wasteway located in Ringold
Downstream	Evaluate overall contribution of copper (from all sources), compared to near outfall and upstream background. Located in mid-channel sediment deposition area at downstream extent of irrigation project boundaries.	Downstream of major irrigation discharges, in vicinity of the passenger bridge located at Wenatchee Confluence State Park	Downstream of major irrigation discharges, tail end of island 1.7 miles downstream of Potholes canal discharge.

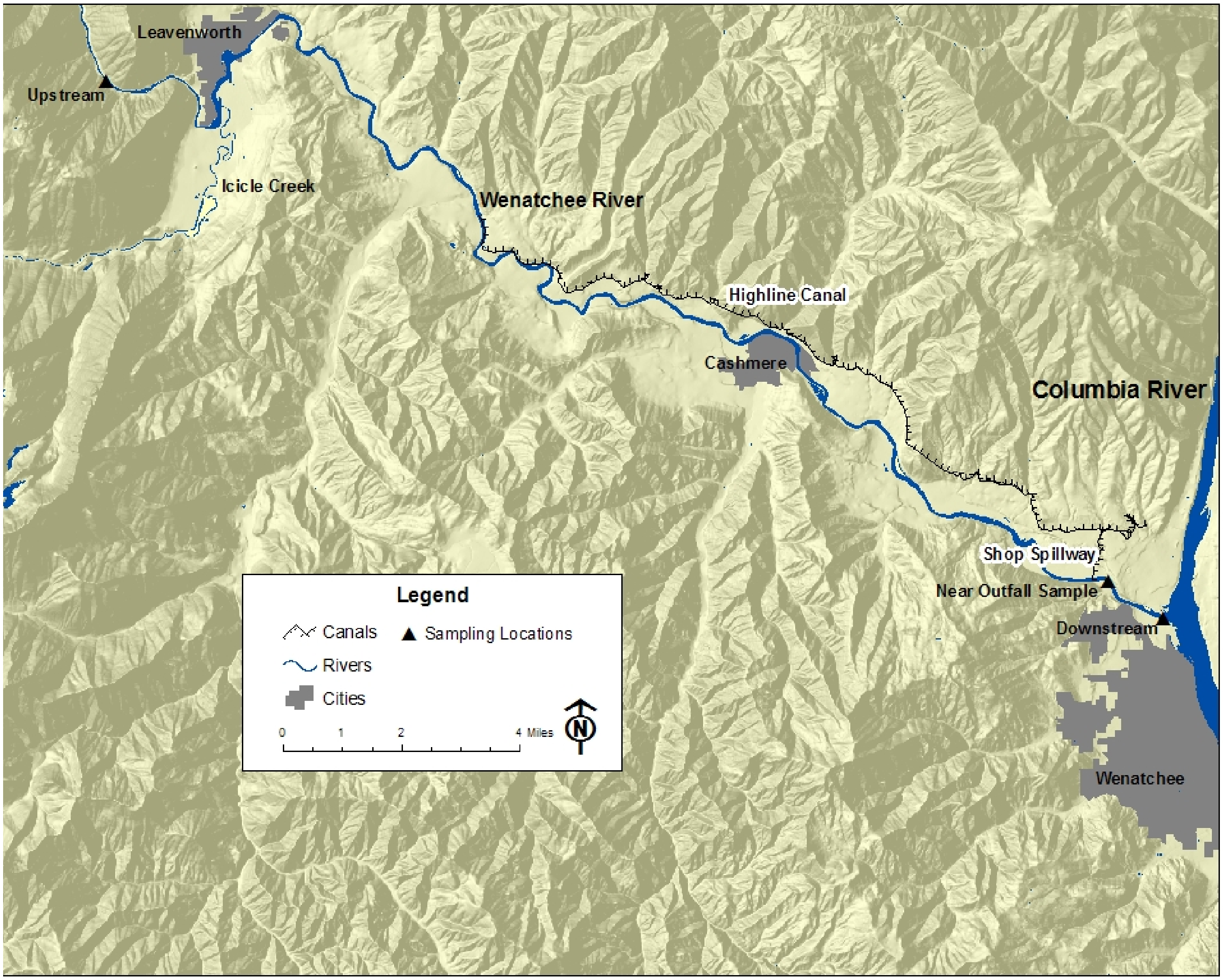

Figure 4. Wenatchee watershed sampling stations.

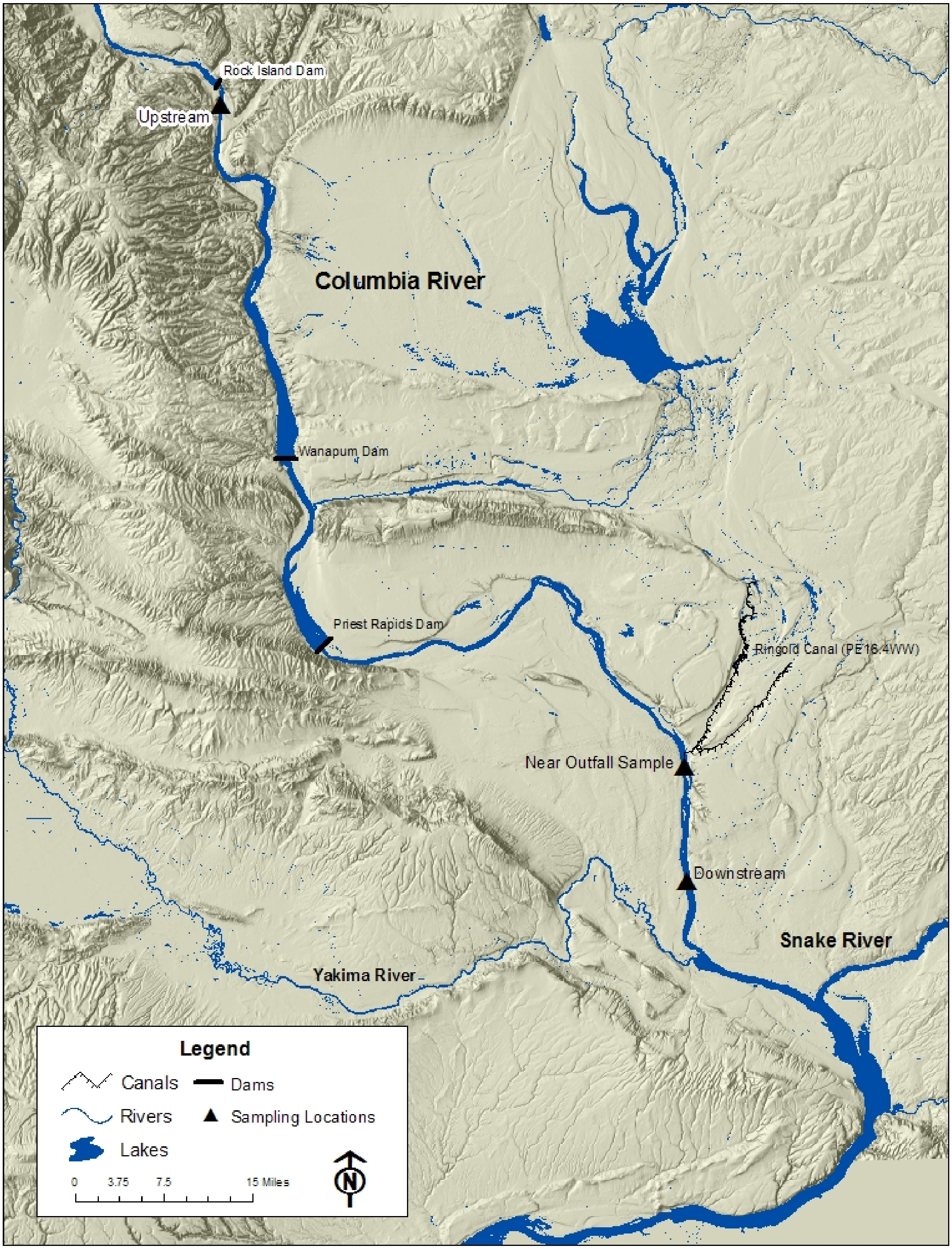

Figure 5. Mid-Columbia watershed sampling stations.

Sampling Procedures

Table 3 lists the sample size, container, preservation and holding time for each parameter. Sample containers will be obtained from Manchester Environmental Laboratory (MEL).

Table 3. Sample size, container, preservation, and holding time.

Parameter	Sample size	Container	*Preservation	Holding time
Surface Water				
Total recoverable copper	500 mL	Teflon bottle	HNO_3 to pH<2	6 months
Dissolved copper	500 mL	Teflon bottle	Filter-0.45µm, HNO_3 to pH<2	6 months
Hardness	100 mL	125 poly bottle	H_2SO_4 to pH<2	6 months
Dissolved organic carbon	50 mL	60 poly bottle	Filter-0.45µm, HCl to pH<2	28 days
Total suspended solids	1000 mL	1000 poly bottle	Cool to 4^oC	7 days
Sediment				
Total recoverable copper	50 grams	Glass/Teflon lid	Cool to 4^oC/Freeze	6 months
Total organic carbon	25 grams	Glass/Teflon lid	Cool to 4^oC/Freeze	14 days/ 6 months
[1]Grain size	100 grams	Glass/Teflon lid	Cool to 4^oC	6 months
Percent solids	25 grams	Glass/Teflon lid	Cool to 4^oC	7 days

*All samples are cooled to 4^oC
[1]Grain size is the percent gravel, sand, silt and clay.

All samples will be located and positions recorded using a hand held global positioning system (GPS) following Ecology standard operating procedures (EAP SOP 013; Janisch, 2006). Where appropriate, positions relative to fixed stream bank structures will also be recorded.

Surface Water

Surface water sampling procedures will be consistent with EPA Method 1669 (Low Level Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels; EPA, 2005) and Ecology standard operating procedures. Clean techniques and low-level metals procedures will be employed for surface water samples according to Ecology's Environmental Assessment Program (EAP) standard operating procedures:

- EAP 015 Manually Obtaining Surface Water Samples (Joy, 2006).
- EAP 029 Collection and Field Processing Of Metals Samples (Ward, 2007).

Field measurement of temperature, conductivity, and pH will be performed according to

- EAP 010 Field measurement of Conductivity (Draft).
- EAP 011 Instantaneous Measurement of Temperature in Water (Draft).
- EAP 031 Measurement of pH in Fresh Water (Draft).
- EAP 033 Hydrolab DataSonde and MiniSonde Multiprobes (Swanson, 2007).

EAP standard operations procedures are available online at www.ecy.wa.gov/programs/eap/quality.html. Conductivity, temperature, and pH standard operating procedures will be publicly available prior to sampling in October/November 2007.

An agency (Ecology) standard operating procedure has not been established for freshwater sediment sampling; thus, the procedure is reviewed in detail.

Sediment

Sampling methods for sediment will be consistent with (1) Puget Sound Estuary Program protocols (EPA, 1996); (2) Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual (EPA, 2001), and (3) guidance for meeting requirements of the Ecology Sediment Management Standards (Ecology, 2003).

Sediment samples will be collected with a 0.02 square meter stainless steel petite ponar grab sampler. The sampler will be lowered by hand or winch wire from a boat or bridge to collect a sample at each designated site. Where the use of a bridge or boat is not practical or possible, samples will be collected by wading with the grab sampler. When wading or operating a boat in shallow water, the sampler must take care not to contaminate the sample location with disturbed sediment. Samplers will wear non-talc, disposable nitrile gloves while manipulating any sediments samples.

At each sediment site, a sample will consist of one to three individual grabs. The top 2 centimeters (cm) of sediment will be removed at each location to reflect recently deposited material. A grab will be considered acceptable if it is not over-filled with sediment, overlying water is present and not excessively turbid, the sediment surface is relatively flat, and the desired depth penetration has been achieved.

Upon retrieving a successful grab, overlying water will be siphoned off, and the top 2-cm layer of sediment will be removed with a stainless steel spoon. Any sediment in contact with the side of the grab sampler will not be used. Sediment will be spooned into a stainless steel bowl and homogenized by stirring to a uniform color and consistency. Sub-samples will be removed from the homogenate and placed in sample containers.

Sample containers will be labeled with unique sample identification numbers and placed in polyethylene bags. Glass sampling containers will be protected from breakage by wrapping each in bubble-wrap or similar material. Sample containers will be kept in an iced cooler or refrigerator at 4°C until transport to the laboratory.

All sample containers will be pre-cleaned to EPA quality assurance/quality control (QA/QC) specifications (EPA, 1990) and have Teflon lid liners. A 4-oz glass container will be used for total copper, separate 2-oz glass containers will be used for total organic carbon and percent solids, and an 8-oz plastic container will be used for grain size. Chain-of-custody will be maintained.

Back-up sampling equipment, sample containers, positioning instruments, and spare parts will be carried during field sampling to minimize the loss of any samples.

Decontamination Procedures

Stainless steel spoons and bowls used to manipulate the sediments for analysis will be pre-cleaned by washing with Liquinox detergent in hot tap water, followed by sequential rinses with tap water, 10% nitric acid, and deionized water. The equipment will then be air-dried and wrapped with aluminum foil until used in the field. The same procedure will be used to pre-clean the grab before going into the field. Between stations in the same waterbody, cleaning of the grab will consist of thorough brushing with on-site water. Cleaning of the grab between waterbodies will follow the same procedure used for pre-cleaning.

Measurement Procedures

Field and laboratory measurement procedures are presented in Table 4. Methods were chosen to provide (1) reporting limits less than the lowest concentration of interest, and (2) precision appropriate to evaluate differences in results between sites and sample seasons. Manchester Environmental Laboratory (MEL) will analyze all laboratory samples, except grain size. MEL and their contractor may use other methods after consulting with the project lead.

Table 4. Measurement methods.

Analysis	Expected Range of Results	Lowest Concentration of Interest	Reporting Limit	Analysis Method
Surface Water Field Measurements				
Temperature	2-20°C		0.2°C	EAP011
pH	7-8.8 units		0.1 units	EPA150.1
Conductivity	30-160 µs/cm		1 µS/cm	SM2510B
Surface Water Laboratory Measurements				
Total recoverable copper	0.4-15 µg/L		0.1 µg/L	EPA200.8
Dissolved copper	0.3-15 µg/L	2.2 µg/L	0.1 µg/L	EPA200.8
Hardness	10-100 mg/L	12 mg/L	1 mg/L	SM2340B
Dissolved organic carbon	<1-5 mg/L		1 mg/L	EPA415.1
Total suspended solids	<1-12 mg/L		1 mg/L	SM2540
Sediment Laboratory Measurements				
Total recoverable copper	<1-40 mg/Kg	35.7 mg/Kg	0.1 mg/Kg	EPA200.8
Grain size	NA		NA	ASTM-D422 /PSEP1996
Total organic carbon	<1-5 mg/Kb		1 mg/Kg	PSEP1997
Percent solids	9-99%		1%	EPA160.3

PSEP references are presented at the end of this document.

The lowest concentrations of interest are presented for parameters which are evaluated as a regulatory component of copper toxicity. These include:

- Chronic surface water standard (dissolved copper) corresponding to the lower 10% of hardness values in the Wenatchee and Mid-Columbia Rivers.
- Lower 10% of hardness values in the Wenatchee and Mid-Columbia Rivers.
- Interim Sediment Quality Guideline (CCME, 2001) for total recoverable copper.

The reporting limits are based on past performance of MEL, their contractors, and the analysis methods selected for this project. The lower detection level for key analyses is at least ten times below the concentrations of interest, minimizing error when comparing data to environmental criteria.

Quality Control Procedures

Field

Field quality control will consist of surface water blanks and replicates (Table 5). Transfer blanks evaluate potential for contamination while sampling is being conducted and during transport to the laboratory. Filter blanks are transfer blanks which have been passed through a dissolved copper or dissolved organic carbon (DOC) filter. Paired with the transfer blank, filter blanks isolate potential contamination from the filter. Blanks are prepared using organic-free water by the analyzing laboratory. A portion of laboratory water is transferred to a new bottle during grab sampling of surface water at a particular site. A transfer blank will accompany each sample event.

Table 5. Field quality control procedures.

Analysis	Transfer Blank	Filter Blank	Replicate	MS/MSD
Surface Water				
Total recoverable copper	4/project	NA	2/project	2/project
Dissolved copper	4/project	1/project	2/project	2/project
Hardness	4/project	NA	2/project	
Dissolved organic carbon	4/project	1/project	2/project	
Total suspended solids	4/project	NA	2/project	
Sediment				
Total recoverable copper	NA	NA	2/project	2/project
Grain size	NA	NA	2/project	
Total organic carbon	NA	NA	2/project	
Percent solids	NA	NA	2/project	

MS/MSD = Matrix Spike/Matrix Spike Duplicate.

The environmental variability of metals and conventional water quality data for this project will be assessed by collecting selected samples in replicate. The replicates will consist of separate sets of samples collected five-to-ten minutes apart. As part of the regular sampling regime, a replicate sample will be taken during each sampling event at Wenatchee and Mid-Columbia River near-outfall locations. Results will be averaged. This is due to the expected variability within the mixing zone. Two additional replicates will be collected at either the upstream background site or the downstream receiving water site.

A matrix spike/duplicate (MS/MSD) is a replicate sample which is spiked with a known amount of analyte (e.g., dissolved copper). The MS/MSD evaluates analyte recovery (accuracy) and precision in terms of sample and recovery replication. Two MS/MSD pairs are scheduled for dissolved and total recoverable copper.

Laboratory

Total and dissolved copper quality control samples to be analyzed with each set of water samples will include a laboratory control sample (LCS) and a method blank. The LCS is comprised of standard reference material, a known concentration of copper, obtained from an external supplier.

Laboratory quality control samples for metals in sediment will include replicate sample analysis (lab splits), matrix spike and spike duplicates (lab split), method blanks, and LCS. MEL will purchase and analyze total copper Standard Reference Material (SRM) with each batch of samples. Field MS/MSD pairs constitute both field and laboratory quality control.

Laboratory quality control samples for all other analytes will follow routine MEL practice.

The laboratory costs are estimated to be $14,194 (Table 6) and represent a 50% discount by MEL.

Table 6. Cost Estimate. Price reflects 50% MEL discount.

Analysis	Samples			Price per Sample ($)	Total ($)
	*Regular	QC	Total		
Surface Water					
Copper, total LL analysis	32	10	42	35	1470
Container, preservative	32	10	42	24	1008
Clean room prep per sample	32	10	42	24	1008
Copper, dissolved LL analysis	32	11	43	35	1505
Container, filter, preservative	32	11	43	48	2064
Clean room prep per sample	32	11	43	24	1032
Hardness	32	6	38	20	760
Dissolved organic carbon	32	7	39	32	1248
Total suspended solids	32	6	38	10	380
Subtotal Surface Water					*10475*
Sediment					
Copper, total recoverable	16	6	22	42	924
Grain size – (contract laboratory)	16	2	18	85	1530
Data review of GS (25% lab cost)	16	2	18	21.25	382.5
Total organic carbon	16	2	18	39	702
Percent solids	16	2	18	10	180
Subtotal Sediment					*3718.5*
Project Total					**14193.5**

*Near-outfall sites are replicated as part of the regular sample regime. The results are averaged.
GS = grain size
QC = quality control.

Data Management Procedures

Field data will be written in permanent marker and recorded in a bound notebook of waterproof paper.

The data packages from MEL will include a case narrative discussing any problems with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. The data package should also include all associated quality control results. This information is needed to evaluate the accuracy of the data and to determine whether the quality objectives were met. This should include results for all blanks, check standards/LCS samples, matrix spikes, and duplicates included in the sample batch.

All project data will be entered into Excel spreadsheets. All entries will be independently verified for accuracy by another individual of the unit.

All project data will be entered into EIM. Data entered into EIM follow a formal Data Validation Review Procedure where data are reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

Audits and Reports

MEL participates in performance and system audits of their routine procedures. Results of these audits are available on request. Audits of contracting laboratories will be reviewed by MEL.

Following the August 2008 sampling event, a draft report will be prepared for the client in January 2009. A final report is expected in February 2009. Project data will be entered into EIM on or before February 2009. The staff member responsible for the report and EIM entry is Paul Anderson.

Data Verification

Field notes will be verified by reviewing calibration, check standard, and results prior to leaving the field. MEL will conduct a review of all laboratory data and case narratives, including those submitted by outside contractors. MEL will verify that (1) methods and protocols specified in this Quality Assurance Project Plan were followed; (2) all calibrations, checks on quality control, and intermediate calculations were performed for all samples; and (3) the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, laboratory control sample analyses, and appropriateness of data qualifiers assigned. MEL will prepare written data verification reports based on the results of their data review. A case summary can meet the requirements for a data verification report.

To determine if project quality objectives have been met, results for check standards/LCS, duplicate samples, and matrix spikes will be compared to quality control limits. The method blank results will be examined to verify there was no significant contamination of the samples. To evaluate whether the targets for reporting limits have been met, the results will be examined for non-detects and to determine if any values exceed the lowest concentration of interest.

The project lead will review the laboratory data packages and MEL's data verification report. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

Data Quality (Usability) Assessment

The project lead will determine if data quality supports use in calculations, determinations, and decisions for which the project was conducted.

1. Compare data collected against available water quality standards and sediment quality guidelines to assess potential for adverse environmental impacts.
2. Assess seasonal and spatial influence on copper concentrations.

The scoping design of this assessment restricts statistical comparison of data points.

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