



Irrigation Canal Effects on Copper Levels in Water and Sediment of the Mid-Columbia and Wenatchee Rivers



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Irrigation Canal Effects on Copper Levels in Water and Sediment of the Mid-Columbia and Wenatchee Rivers

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Abstract

The Washington State Department of Ecology (Ecology) regulates the use of copper herbicides in irrigation canals through a National Pollutant Discharge Elimination System (NPDES) permit. In order to evaluate the effectiveness of discharge limits set in the permit, Ecology conducted surface water and sediment monitoring to measure copper concentrations in two irrigation project areas during 2007-08.

The Mid-Columbia Irrigation and Wenatchee Reclamation project areas were sampled in three types of locations: above irrigation project inputs, near a major outfall (Shop Spillway and Ringold Canal), and downstream of irrigation project inputs.

In each irrigation project area, samples were collected in rivers that receive discharge from irrigation canals. Surface water samples were collected in the Mid-Columbia River and the Wenatchee River before and after irrigation operations and two times during the maximum use period for copper. Sediment samples were collected in both rivers before and after irrigation operations.

None of the water samples were found to be above Washington State Water Quality Standards. In the majority of the samples, copper was found to be in the dissolved form which makes it biologically available.

No Washington State standards have been established for freshwater sediments. Therefore, the data were compared to proposed sediment quality values and a Canada interim sediment quality guideline. None of the sediment samples contained copper concentrations above these guidelines. Conventional parameters for sediment showed that there was not much fine-grained sediment available for copper to adsorb to.

Data collected showed that there is little potential for adverse impacts to aquatic and sediment-dwelling organisms in the areas sampled.

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Background

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. This aquatic vegetation may clog irrigation canals, causing inefficient water delivery and drainage.

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

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

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

Copper is one of six herbicides permitted for use in irrigation canals (Ecology, 2008). Other permitted herbicides include acrolein, xylene, sodium carbonate peroxyhydrate, fluridone, and imazapyr.

Copper products are generally inexpensive, easy to apply, effective, and have been used in vegetation management for over 100 years (CropLife, 2008). Approximately 160,000 pounds of copper-based herbicides are applied to irrigation canals in Washington State each year (Burke, 2007). Copper sulfate is the main active ingredient being used throughout the state. There is some minor use of chelated copper.

In 2007, the Columbia Irrigation and Wenatchee Reclamation projects used 2,300 and 1,647 lbs of copper sulfate, respectively. These two irrigation projects are using small amounts of copper sulfate compared to other users in the state (Table 1).

Table 1. 2007 Copper Sulfate Use for the State of Washington (pounds).

Irrigation Project	Usage (lbs)
QCBID	26,254
Cascade	850
Wenatchee RD	1,647
ECBID	85,246
SCBID	36,975
Columbia	2,300
Kittitas	1,867

QCBID – Quincy-Columbia Basin Irrigation District.

RD – Recreation District.

ECBID – East Columbia Basin Irrigation District.

SCBID – South Columbia Basin Irrigation District.

Copper used in irrigation systems is regulated through a surface water discharge permit, requiring a maximum instantaneous concentration of 25 µg/L of dissolved copper at the point of discharge to natural waters (Ecology, 2008). The maximum instantaneous concentration is defined as the highest allowable discharge at any time.

Washington State, under the federal Clean Water Act, issued standards to evaluate dissolved copper toxicity (WAC 173-201A, 2006).

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

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.

Introduction

The Washington State Department of Ecology (Ecology) regulates the use of copper herbicides in irrigation canals through a National Pollutant Discharge Elimination System (NPDES) permit. In order to evaluate the effectiveness of discharge limits set in the NPDES permits to prevent adverse impacts on aquatic life, Ecology monitored surface water and sediment for copper in two rivers receiving discharge from irrigation canals. The goals of the sampling were to:

- Determine copper levels in river receiving water and sediment near two irrigation returns.
- Evaluate the potential for adverse impacts to aquatic life from the use of copper herbicides in irrigations canals.

The Columbia Irrigation and Wenatchee Reclamation projects were selected for study (Figure 1). The Columbia Irrigation project was chosen due to the intensity and extent of irrigated agriculture in that area. The Wenatchee Reclamation project was chosen due to the low hardness of receiving waters which increases the toxicity of copper. Water volumes in the receiving waters (Mid-Columbia River and Wenatchee River) are variable over the year and could impact copper concentrations through dilution. Hydrographs for the Mid-Columbia and Wenatchee Rivers are shown in Figures 2 and 3, respectively. The Mid-Columbia River hydrograph shows oscillations throughout the year due to the dam operations.

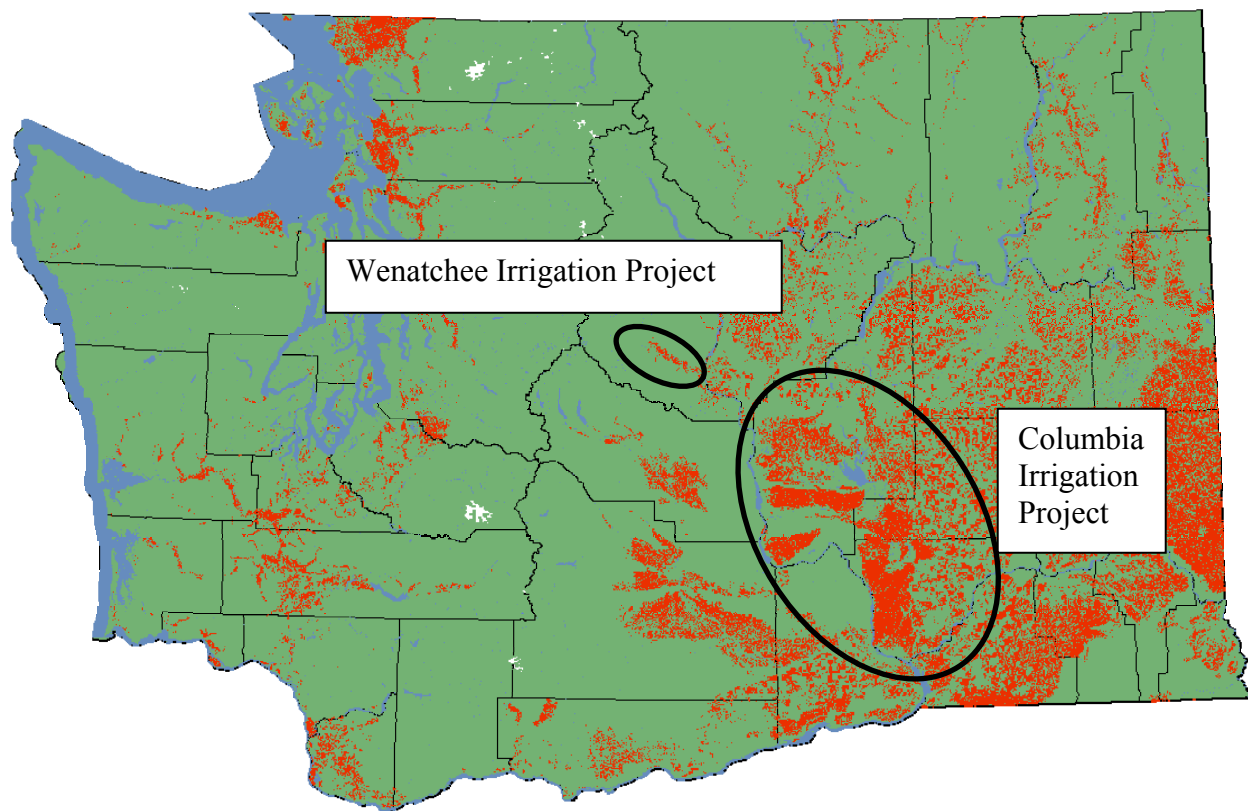


Figure 1. Locations of the Columbia Irrigation Project and the Wenatchee Reclamation Project in Relation to Washington State.

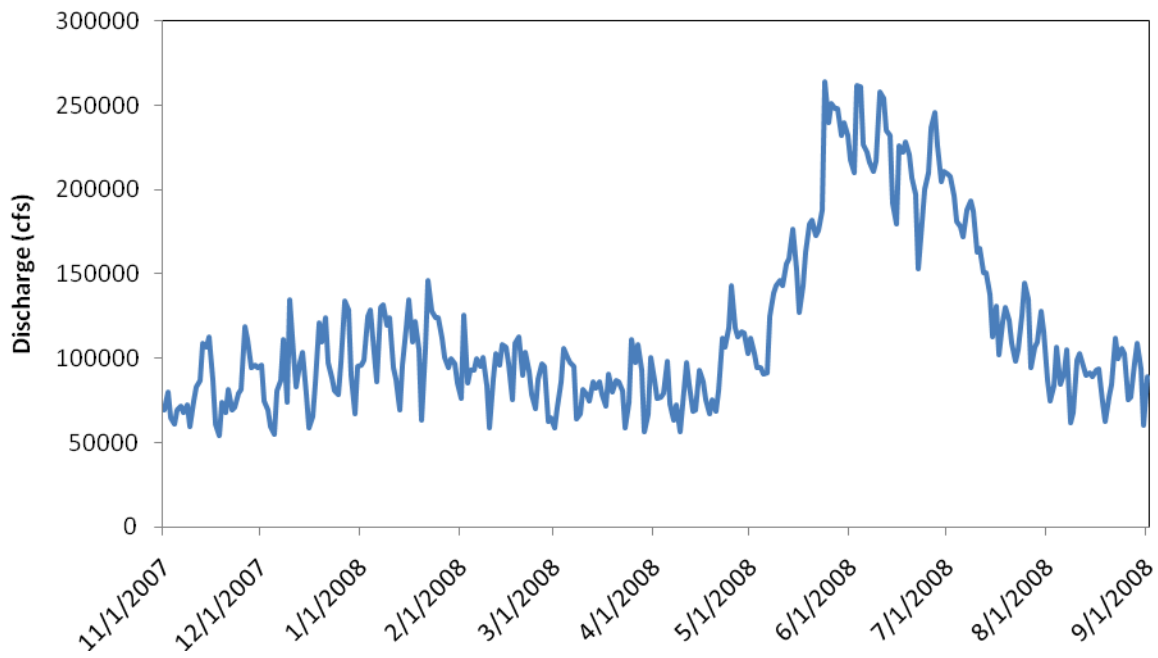


Figure 2. Columbia River Discharge at Priest Rapids.

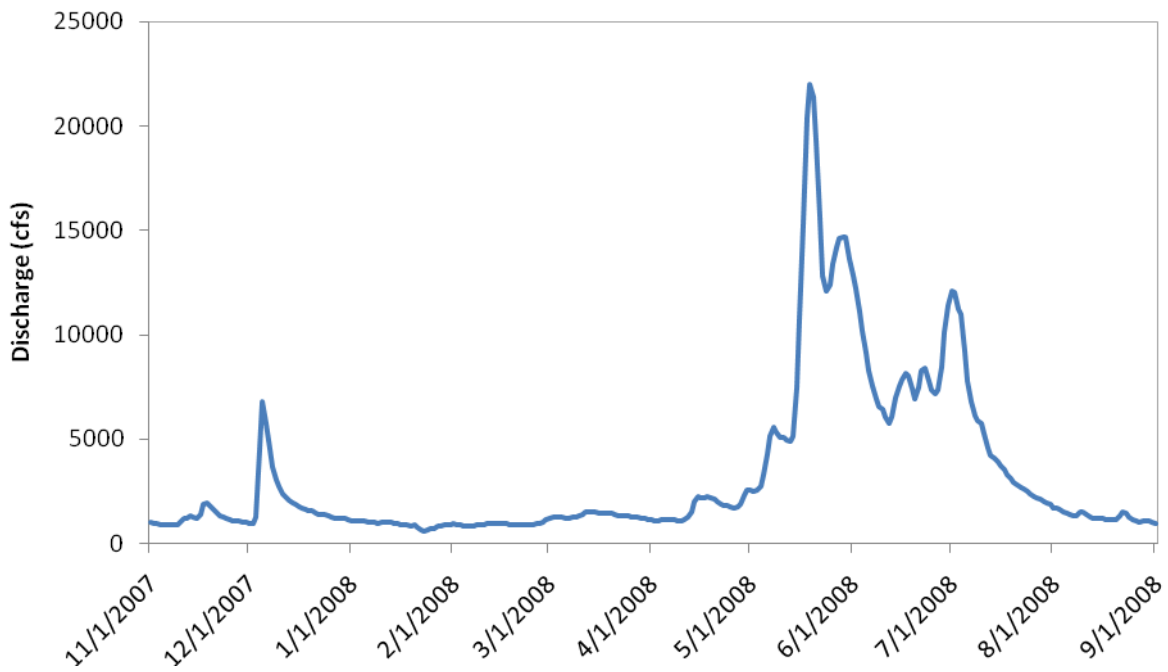


Figure 3. Wenatchee River Discharge at Monitor.

Toxicity

At concentrations above Washington State water quality criteria, copper is toxic to fish, invertebrates, and plants. 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. Free copper (Cu^+ , Cu^{2+}) is considered to be the form of copper that is most toxic and biologically available. 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 localized cell death (Sorensen, 1991; EPA, 2005).

A large part of free copper availability is influenced by pH. The abundance of free copper increases with increasing pH until a threshold pH of 8.5 is reached. At this point, free copper becomes less abundant, but the toxicity does not decrease (EPA, 2007). Therefore, at sites where the water is more basic ($\text{pH} > 7$), biologically available copper is more toxic than at sites that have neutral or acidic water ($\text{pH} \leq 7$) (EPA, 2007; Sorensen, 1991).

Adsorption of copper to solid materials, humic acids, anions, and competition with other cations reduces its availability as an aquatic toxicant (EPA, 2005). Copper may be sampled in the dissolved phase to eliminate fractions which are adsorbed to larger materials and are biologically unavailable.

Dissolved organic carbon (DOC) measurements provide a humic acid binding estimate. Copper forms organic complexes with DOC, making it unavailable to aquatic organisms (EPA, 2007).

Hardness measurements provide cationic/anionic binding estimates. Hardness, as mg/L calcium carbonate (CaCO_3), is an indicator of the amount of cation competition and anion complexation (Sorensen, 1991). Copper, a cation, will have competition from other cations (calcium, magnesium, and sodium) at binding sites in aquatic organisms. Therefore, when hardness is elevated, higher concentrations of copper will be needed to cause a toxic effect (EPA, 2007). Conversely, when hardness is low, copper becomes more toxic at lower concentrations.

Temperature influences the reaction rate of toxic mechanisms. As temperature increases, the metabolic rate of aquatic organisms increases, which consequently increases the uptake of biologically available copper. This increase in the uptake of copper can cause an increase in mortality (Sorensen, 1991).

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Methods

Sampling Design

The irrigation season in Eastern Washington extends from March through mid-October, and the maximum period of herbicide use in irrigation canals extends from June through mid-September (Burke, 2007). Sampling was conducted during four events.

These sampling events occurred at:

- The end of the irrigation season. Surface water and sediment samples were collected to evaluate the residual copper concentrations following the irrigation season.
- The initiation of irrigation. Dramatic increases in water volumes or addition of water to dry canals likely will deliver deposited copper to receiving waters. Surface water and sediment samples were collected to assess copper concentrations coinciding with the start of water delivery.
- The maximum use period of copper (two sample events). Only surface water was collected during this period.

Total and dissolved copper were measured in surface water, and total copper was measured in sediment. Total copper in surface water was measured to determine the quantity of copper which may be attached to particulate matter. Additional water quality parameters were collected to indicate source, transport, fate, and variables influencing toxicity to aquatic life.

Hardness, DOC, total suspended solids (TSS), temperature, pH, and conductivity were collected in surface water. Grain size, percent solids, and total organic carbon (TOC) accompanied the total copper sediment sampling.

Sampling Sites

One major irrigation return in each of the Columbia Irrigation project and Wenatchee Reclamation project was selected for evaluation. Ringold Canal (PE16.4) was selected for the Columbia Irrigation project and Shop Spillway was selected for the Wenatchee Reclamation project.

Samples were collected from the mainstem Mid-Columbia and Wenatchee Rivers above the Columbia Irrigation project and the Wenatchee Reclamation project areas (background), downstream of the selected irrigation returns, and downstream of the irrigation project area (Figure 4 and 5, respectively). One sample was collected at each location for each sampling event.

Exact locations and descriptions of each site can be found in Appendix A, Table A-1.



Figure 4. Mid-Columbia River Sampling Locations.

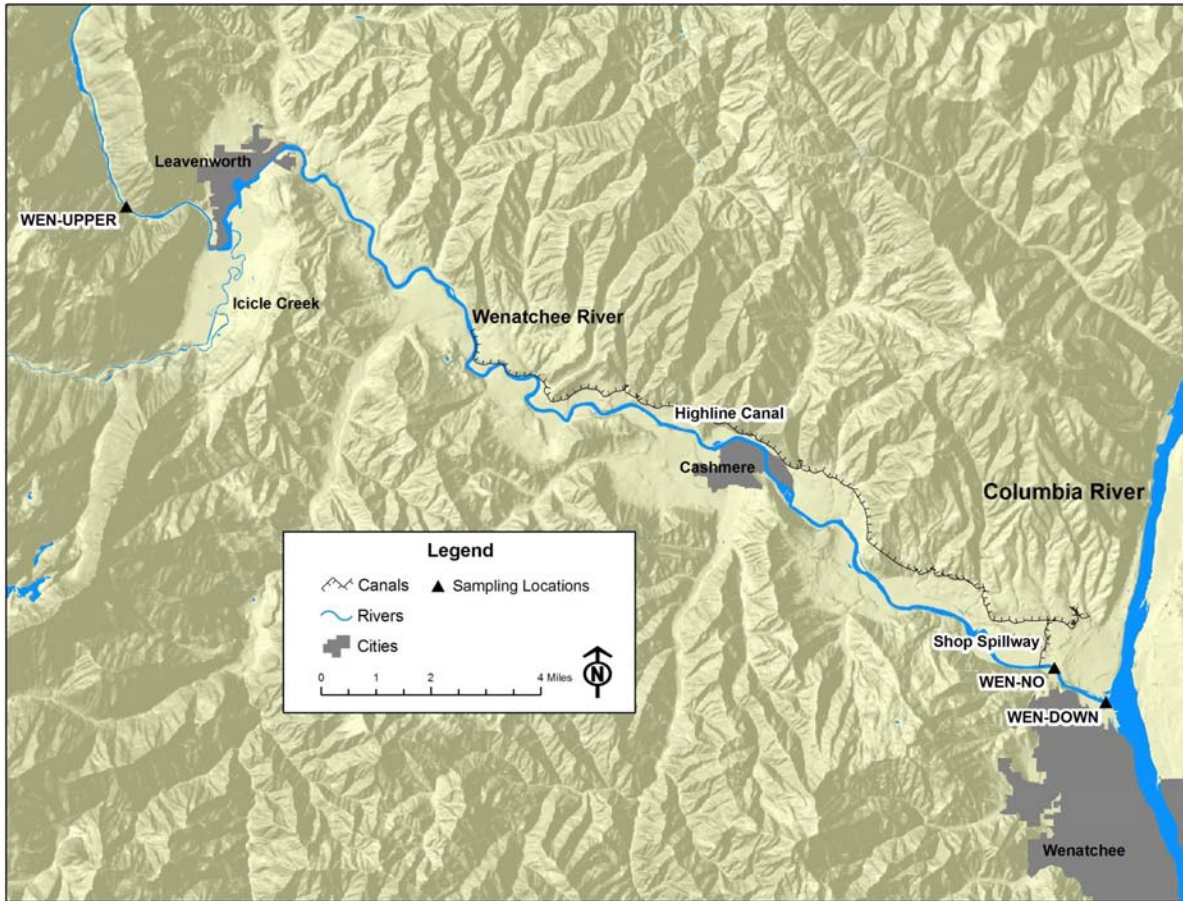


Figure 5. Wenatchee River Sampling Locations.

Field Procedures

Surface Water

Samples were collected using clean sampling techniques based on Environmental Protection Agency (EPA) Method 1669 (EPA, 1995) and Ecology standard operating procedures (SOP) (Joy, 2006 and Ward, 2007a). Surface water samples were collected using a 1.2 L acrylic Kemmerer water sampler. The Kemmerer sampler was cleaned prior to use in the field and between waterbodies by washing with Liquinox® detergent in tap water, followed by sequential rinses with tap water, 10% nitric acid, and deionized water. After cleaning, the sampler was transported closed to prevent contamination. Between sampling sites, within the same waterbody, the Kemmerer sampler was rinsed with on-site water before collection of samples. Metal samples were collected directly into pre-cleaned 500 mL Teflon bottles.

Samples for dissolved metals were filtered in the field through a pre-cleaned 0.45 µm Nalgene filter unit using procedures from Ecology SOP EAP029 (Ward, 2007a). The filtrate was transferred to a pre-cleaned 500 mL Teflon bottle. Whole and filtered water samples were preserved to pH<2 with sub-boiled 1:1 nitric acid, carried in small Teflon vials, one per sample. Teflon sample bottles, Nalgene filters, and Teflon acid vials were cleaned at Manchester Laboratory, as described in Kammin et al. (1995), and sealed in plastic bags. Non-talc nitrile gloves were worn by personnel filtering the samples. Filtering was done in a glove box constructed of a PVC frame and polyethylene cover.

Field measurement of temperature, conductivity, and pH were performed according to Ecology SOPs (Nipp, 2006; Ahmed, 2006; Ward, 2007b).

Sediment

Sediment samples were collected using a 0.02 m² stainless steel petite Ponar grab and techniques from Ecology's SOP for collection of freshwater sediment (Blakley, 2008). All equipment used for collecting and compositing grab samples was cleaned using the Ecology SOP referenced above.

All sample containers were supplied by the laboratory, pre-cleaned to EPA quality assurance/quality control (QA/QC) specifications (EPA, 1990), and had Teflon lid liners. A 4-oz glass container was used for total copper, separate 2-oz glass containers were used for TOC and percent solids, and an 8-oz plastic container was used for grain size.

Laboratory Procedures

All samples were analyzed at Manchester Environmental Laboratory (MEL) with the exception of grain size which was analyzed by Columbia Analytical Services, Inc. Table 2 contains information on the analytical methods used to perform laboratory analysis and reporting limits for each analyte.

Table 2. Analytes and Analytical Methods by Matrix.

Analyte	Method	Reporting Limit
Water		
Total Copper	ICPMS, EPA 200.8*	0.1 µg/L
Dissolved Copper	ICPMS, EPA 200.8*	0.1 µg/L
Dissolved Organic Carbon	EPA 415.1*	1 mg/L
Hardness	ICP, EPA 200.7/SM2340B*	1 mg/L
Total Suspended Solids	SM2540D*	1 mg/L
Sediment		
Copper	EPA 3050B/ICPMS, EPA 200.8*	0.1 mg/Kg
Grain Size	PSEP, Sieve and Pipette*	NA
Total Organic Carbon	PSEP, TOC*	1 mg/Kg
Percent Solids	SM2540G*	1%

ICPMS = Inductively Coupled Plasma/Mass Spectrometer.

PSEP = Puget Sound Estuary Program.

EPA = Environmental Protection Agency.

SM = Standard Methods.

*References: APHA, 1998; EPA, 1994a; EPA, 1994b; EPA, 1996; PSEP, 1986; PSEP, 1997.

Data Quality Assessment

Results from MEL included case narratives describing Quality Assurance/Quality Control (QA/QC) procedures used during analysis. These QA/QC results included: holding times, instrument calibrations, method blanks, matrix spikes, laboratory duplicates, laboratory control samples, and standard reference materials (SRMs). The SRM used for water was SLRS 4, River Water Reference Material for Trace Metals, from the National Research Council of Canada. The SRM used for sediment was ERA 247, Metals in Soil, from Environmental Research Associates. Case narratives describing the quality of the data are available upon request. QA/QC results can be found in Appendix B.

Surface Water

No difficulties were encountered in the analysis of water samples, and all QC analyses were within acceptance limits.

Two types of field replicate samples were used to assess sampling and environmental variability.

1. Split replicates were analyzed to provide an estimate of sampling and laboratory variability for the project.
2. The replicates were prepared by filling two separate sample containers from the same grab sample. Sequential replicates were analyzed at the near-outfall sample sites to assess environmental variability. These replicates were prepared by filling two separate sample containers from grab samples collected approximately 15 minutes apart.

Most split replicate samples agreed within $\pm 15\%$ relative percent difference (RPD). Six sets of split replicate samples for various parameters had replicate RPD values outside of the acceptable range. The failure of these samples to fall within the acceptable range is most likely due to the high amount of variability in detections near the minimum reporting limit (Mathieu, 2006; Martin, 2002). These small values can have a low mean which creates a high RPD.

Transfer and filter blanks were analyzed to evaluate the potential for contamination. Transfer and filter blanks were prepared using blank water from MEL. For transfer blanks, laboratory water was transferred from its container to a new sample container. Filter blanks were prepared in a similar manner with the difference being that the blank water was passed through a filter before being transferred to a sample container. All transfer and filter blanks had no detections, with the exception of a single sample for total copper that was reported as $0.11 \mu\text{g/L}$ (reporting limit = $0.10 \mu\text{g/L}$).

The data quality assessment indicated most water data met measurement quality objectives outlined by the project plan (Burke, 2007). The data outside of the quality objectives were determined not to have an effect on the usability of the data set. This determination was based on the explanation given for the issues with replicates.

Sediment

No difficulties were encountered in the analysis of sediment samples, and all laboratory QC analyses were within acceptable limits except for one sample. The laboratory duplicate RPD for copper in sediment was greater than the acceptance limit. The sample and duplicate were qualified as estimates.

Two types of field replicate samples were used to assess sampling and environmental variability. Split replicates were analyzed to provide an estimate of sampling and laboratory variability for the project. The replicates were prepared by filling two separate sample containers from the same grab sample. A second set of samples were collected and analyzed as replicates at the near outfall sample sites to assess environmental variability. These replicates were prepared by filling sample containers from separate sets of grab samples that were collected in close proximity to each other.

Most split replicate samples agreed within $\pm 15\%$ RPD. Two sets of replicate sediment samples analyzed for grain size had RPD values, for the gravel particle size, that fell outside of the acceptable range. This failure is due to the high variability found in the gravel particle size range, especially with the sand particle size making up greater than 94% of the samples.

The data quality assessment indicated most sediment data met measurement quality objectives outlined by the project plan (Burke, 2007). The data outside of the quality objectives were determined not to have an effect on the usability of the data set. This determination was based on qualification of data and the explanation given for the issues with replicates.

Results

Surface Water

Conventional Parameters

Results for conventional analysis of surface water samples are presented in Table 3. Any parameter collected in replicate is reported as an average.

pH at all sample sites shows little variation over the four sample events with the exception of August. At all sites pH values were lowest during August. Elevated pH values were measured at the downstream Wenatchee River site.

Temperature data collected appears to follow typical seasonal variations with the highest measurements in August. Conductivity measurements in the Mid-Columbia River ranged from 77 to 173 $\mu\text{mhos/cm}$ and in the Wenatchee River from 22 to 77 $\mu\text{mhos/cm}$. Hardness measurements in the Mid-Columbia River ranged from 51.3 to 88.6 mg/L CaCO_3 and in the Wenatchee River from 11.5 to 34.9 mg/L CaCO_3 . Total suspended solids measurements in the Mid-Columbia River ranged from 1 to 15 mg/L and in the Wenatchee River from 1 to 4.5 mg/L. Dissolved organic carbon measurements in the Mid-Columbia River ranged from 1.0 to 2.3 mg/L and in the Wenatchee River from 1.0 to 1.9 mg/L.

Copper

Total and dissolved copper results for surface water samples collected at all six sites are presented in Table 4. Total copper concentrations ranged from 0.34 to 2.97 $\mu\text{g/L}$, and dissolved copper ranged from 0.30 to 1.13 $\mu\text{g/L}$. For all sites except for the upstream Mid-Columbia River, copper results were highest during the June sampling event. The upstream mid-Columbia River site had the highest total copper concentration during the November sampling event. Mean dissolved copper percentages for all sites were found to be greater than 67%. Dissolved copper concentrations were greater than 50% for all sample events except for the November sample collected at the upstream Mid-Columbia River site.

Table 3. Conventional Parameter Results for Water Samples from the Mid-Columbia and Wenatchee Rivers.

Site	Date	pH	Temperature (°C)	Conductivity (µmhos/cm)	Hardness (mg/L CaCO ₃)	TSS (mg/L)	DOC (mg/L)
Mid-Columbia River							
MCOL-UPPER	11/6/2007	8.1	13.2	159	62.6	1	1.0
	4/16/2008	8.5	6.4	92	75.3	2	1.1
	6/11/2008	7.9	12.2	86	51.3	5	2.1
	8/6/2008	7.6	18.7	110	62.0	1	1.5
MCOL-NO*	11/5/2007	8.1	13.0	114	66.0	1.5	1.0 U
	4/15/2008	8.3	7.5	144	77.1	4.5	1.0
	6/10/2008	8.3	12.7	77	51.4	7.5	2.3
	8/5/2008	7.8	19.8	122	64.5	3	1.6
MCOL-DOWN	11/5/2007	8.6	12.6	168	88.6	3	1.3
	4/15/2008	8.4	8.0	173	85.3	6	1.2
	6/10/2008	8.2	12.7	86	56.5	15	2.2
	8/5/2008	8.2	20.3	147	84.6	4	1.8
Wenatchee River							
WEN-UPPER	11/7/2007	7.6	6.2	27	16.3	1 U	1.0 U
	4/17/2008	7.6	5.6	46	18.6	2.5	1.3
	6/11/2008	7.6	10.2	22	11.5	4	1.2
	8/6/2008	6.7	18.2	41	13.2	1	1.0 U
WEN-NO*	11/7/2007	8.1	5.7	53	32.9	2 U	1.0 U
	4/16/2008	9.0	9.3	51	34.9	4.5	1.8
	6/11/2008	8.0	10.3	30	16.9	5	1.3
	8/6/2008	7.8	20.1	59	23.9	2	1.0 U
WEN-DOWN	11/6/2007	9.2	6.4	77	32.1	1	1.0 U
	4/16/2008	9.2	8.6	51	36.2	4	1.9
	6/11/2008	8.9	10.2	31	17.0	4	1.3
	8/6/2008	7.4	19.8	58	23.6	2	1.0 U

*MCOL-NO and WEN-NO values are derived from an average of two measurements collected as replicates.

U – The analyte was not detected at or above the reported result.

TSS – Total Suspended Solids.

DOC – Dissolved Organic Carbon.

Table 4. Copper Results for Water Samples Collected from the Mid-Columbia and Wenatchee Rivers ($\mu\text{g/L}$).

Site	Date	Total Copper	Dissolved Copper	Percent Dissolved
Mid-Columbia River				
MCOL-UPPER	11/6/2007	2.97	0.73	25
	4/16/2008	0.70	0.70	100
	6/11/2008	1.95	1.43	73
	8/6/2008	0.89	0.78	88
mean		1.63	0.91	71
MCOL-NO*	11/5/2007	0.62	0.55	89
	4/15/2008	0.85	0.64	75
	6/10/2008	1.66	1.16	70
	8/5/2008	0.96	0.93	97
mean		1.02	0.82	83
MCOL-DOWN	11/5/2007	1.49	0.87	58
	4/15/2008	1.14	0.75	66
	6/10/2008	2.18	1.31	60
	8/5/2008	1.25	1.03	82
mean		1.52	0.99	67
Wenatchee River				
WEN-UPPER	11/7/2007	0.34	0.30	88
	4/17/2008	0.65	0.50	77
	6/11/2008	0.91	0.74	81
	8/6/2008	0.41	0.34	83
mean		0.58	0.47	82
WEN-NO*	11/7/2007	0.54	0.32	59
	4/16/2008	0.78	0.53	68
	6/11/2008	0.88	0.62	70
	8/6/2008	0.55	0.43	78
mean		0.69	0.48	69
WEN-DOWN	11/6/2007	0.73	0.49	67
	4/16/2008	0.65	0.51	78
	6/11/2008	1.46	0.99	68
	8/6/2008	0.74	0.52	70
mean		0.90	0.63	71

*MCOL-NO and WEN-NO values are derived from an average of two measurements collected as replicates.

Information on water and sample depths can be found in Appendix A, Table A-2.

Spatial and Temporal Evaluation

Data were collected at three sites in two rivers over four sampling events. The four sampling events were spread out over the year to capture seasonal variations in copper concentrations due to irrigation operations. To aid in assessing the data for seasonal variation, a Kruskal-Wallis H test was performed on both the Mid-Columbia and Wenatchee Rivers using a significance level of 0.05. Results from the Kruskal-Wallis H test showed that there was a statistically significant difference between samples collected over the sampling period in both rivers.

In the Mid-Columbia River, the data show that samples collected in April and November had lower dissolved copper concentrations than samples collected during the maximum copper use season. The highest dissolved copper concentrations were seen in June and August (Figure 6). This pattern of detection fits with what would be expected given the timing of the maximum copper use period. The June samples correspond to a high-flow period in the river, and the August samples correspond to a low-flow period in the river (Figure 2).

The Wenatchee River data showed a different pattern than the Mid-Columbia River. Highest dissolved copper concentrations were seen in April and June, and lowest concentrations were seen in August and November (Figure 7). The April dissolved copper concentrations may be explained by the first flush of the irrigation system after initial delivery of water. Copper adsorbed to suspended sediment may have settled to the bottom of the canals over the course of the maximum copper use season, and when the water was shut off for the year the copper was left behind. When water was re-introduced into the irrigation system, the water volumes and velocities likely re-suspend deposited sediment. When the sediment was re-suspended, copper was returned to the water column and in turn was delivered to the receiving water.

In addition to evaluating seasonal variations, the three sampling sites in each river were located to assess variation in copper concentrations between background (above outfall), near outfall, and downstream sampling sites. To determine if there was a difference between the three sites, a Kruskal-Wallis H test was run on the data. The results of the Kruskal-Wallis H test showed that for both rivers there is no significant difference between the three sites at a significance level of 0.05. Due to the small sample size, the test is not considered to be robust. Even with a larger sample size, it is not likely that there would be a detectable significant difference between sites.

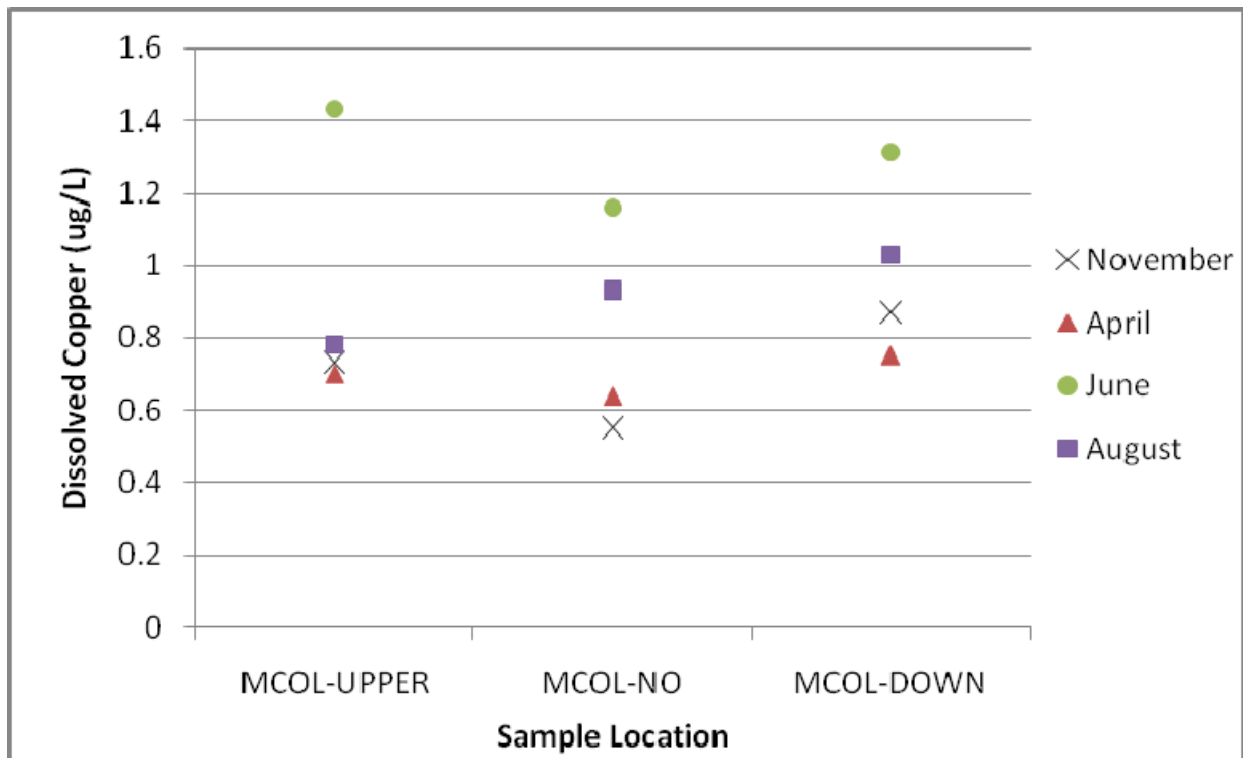


Figure 6. Mid-Columbia River Dissolved Copper Concentrations (µg/L).

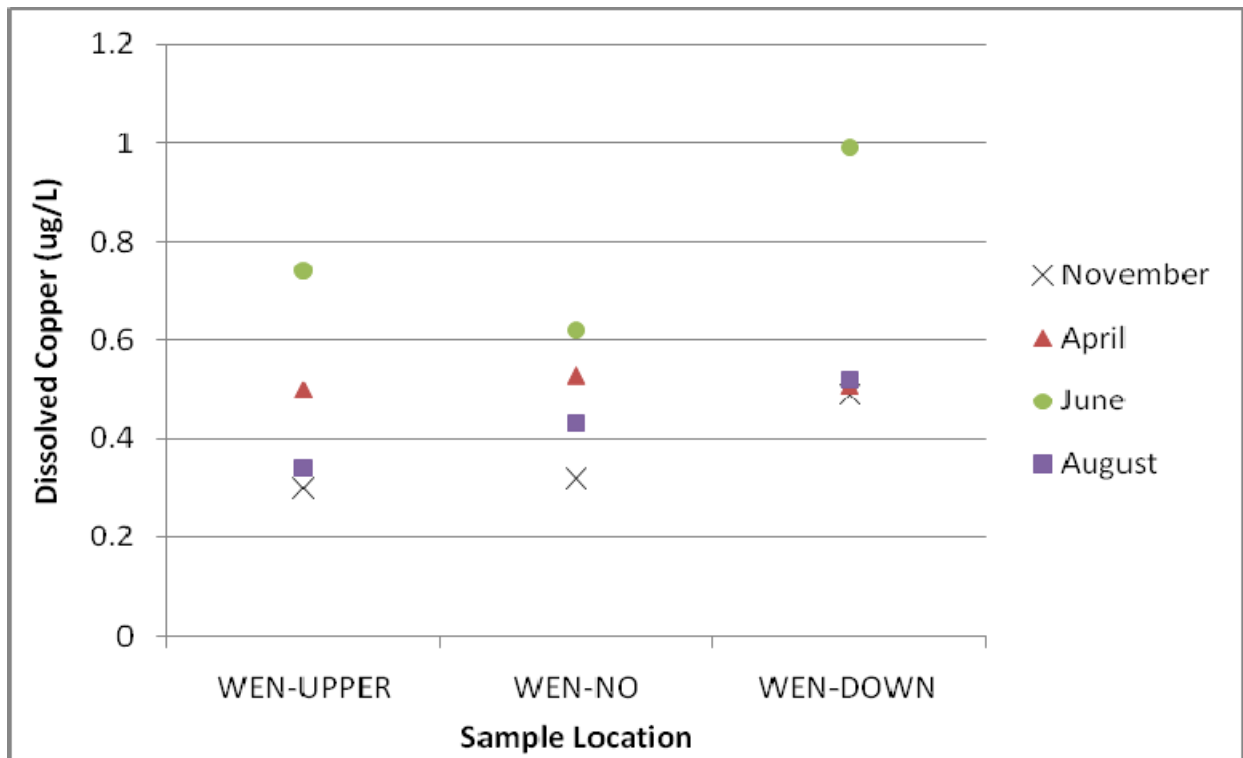


Figure 7. Wenatchee River Dissolved Copper Concentrations (µg/L).

Sediment

Conventional Parameters

Table 5 summarizes results for percent solids, TOC, and grain size in sediment samples collected from the Mid-Columbia and Wenatchee Rivers. Parameters collected in replicate are reported as averages. Total organic carbon measurements in the Mid-Columbia River were low, ranging from 0.12 to 0.28%. In the Wenatchee River, TOC ranged from 0.11 to 0.63%. Grain size analysis showed that the percentage of sand was greater than 85% in all but one sample. Most of the remaining portions of the samples were made up of silt and very small amounts of clay.

Table 5. Physical, Chemical, and Copper Results for Sediment Samples from the Mid-Columbia and Wenatchee Rivers.

Site	Date	Solids (%)	TOC (%)	Grain Size (%)				Copper (mg/Kg dw)
				Gravel	Sand	Silt	Clay	
Mid-Columbia River								
MCOL-UPPER	11/6/2007	73.1	0.12	0.03	99.19	0.59 J	0.11	18.0
	4/16/2008	77.8	0.10 U	0.02	99.91	0.10 J	0.00	24.1
MCOL-NO*	11/5/2007	64.6	0.28	0.22	86.58	11.7	4.75	13.2
	4/15/2008	65.8	0.20	0.24	85.43	7.95	3.35	14.6
MCOL-DOWN	11/5/2007	67.6	0.17	0.18	97.05	4.25 J	1.15	10.4
	4/15/2008	71.7	0.14	0.05	81.74	11.4	0.82	10.5
Wenatchee River								
WEN-UPPER	11/7/2007	80.3	0.11	11.7	86.61	0.83 J	0.03	8.19
	4/17/2008	72.2	0.15	2.93	94.92	1.25 J	0.00	9.34 J
WEN-NO*	11/7/2007	70.3	0.63	5.27	96.61	2.59 J	0.43	12.1
	4/16/2008	66.6	0.55	1.45	92.23	4.47 J	0.00	15.5
WEN-DOWN	11/6/2007	72.1	0.15	0.54	97.29	2.40 J	0.15	11.4
	4/16/2008	78.7	0.11	0.76	98.48	0.52 J	0.00	12.5

*MCOL-NO and WEN-NO values are derived from an average of two measurements collected as replicates.

TOC – Total Organic Carbon.

U – The analyte was not detected at or above the reported result.

J – The analyte was positively identified. The associated numerical value is the approximate concentration of the analyte in the sample.

Detailed descriptions of surface sediment sample physical characteristics for each site can be found in Appendix A, Table A-3.

Copper

Copper results for sediment samples collected at all six sample sites are presented in Table 5. Copper in sediment ranged from 8.2 to 24.1 mg/Kg dry weight (dw). The highest copper concentrations were measured during the April sampling event at the upstream Mid-Columbia River site.

Spatial and Temporal Evaluation

The data show that copper concentrations were higher in April than in November in both rivers (Table 5). The largest difference was found at the upstream Mid-Columbia River site. The April copper concentration was 6.1 mg/Kg dw higher than the concentration in November (Table 5). To assess differences seasonally in the Mid-Columbia and Wenatchee Rivers, a Kruskal-Wallis H test was used. The results of the test showed that at a significance level of 0.1, there is no significant seasonal difference.

To assess differences between sites, a Kruskal-Wallis H test was run on the data using a significance level of 0.1. The results of the test showed that there is no statistical difference between the three sites in both rivers. Due to the small sample size, the test is not considered to be robust. Even with a larger sample size, it is not likely that there would be a significant difference between the sites. Despite the lack of significant differences between the sites, there seems to be a pattern in the Mid-Columbia River. Copper concentrations in the sediment decreased moving downstream. There is no apparent pattern for the Wenatchee River. These results probably reflect differences in depositional patterns in the two rivers, or the results may be due to random chance.

In addition to evaluating seasonal variation and differences between sampling sites, data were compared to national background copper concentrations. All data fell within the national background copper concentration range of 10 to 25 mg/Kg (Buchman, 2004).

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Discussion

Surface Water

Comparison to Water Quality Standards

Dissolved copper results are compared to Washington State Water Quality Criteria (WAC 173-201A, 2006) in Table 6. The water quality standards are for dissolved copper and are calculated using hardness. None of the dissolved copper samples are above any calculated chronic or acute water quality criteria. Most values are 1-2 orders of magnitude below water quality criteria.

Table 6. Chronic and Acute Water Quality Criteria for Dissolved Copper Calculated Using Hardness.

Site	Date	Hardness (mg/L CaCO ₃)	Dissolved Copper (µg/L)	Acute Standard ¹ (µg/L)	Chronic Standard ² (µg/L)
Mid-Columbia River					
MCOL-UPPER	11/6/2007	62.6	0.73	10.9	7.6
	4/16/2008	75.3	0.70	13.0	8.9
	6/11/2008	51.3	1.43	9.1	6.4
	8/6/2008	62.0	0.78	10.8	7.5
MCOL-NO*	11/5/2007	66.0	0.55	11.5	8.0
	4/15/2008	77.1	0.64	13.3	9.1
	6/10/2008	51.4	1.16	9.1	6.4
	8/5/2008	64.5	0.93	11.3	7.8
MCOL-DOWN	11/5/2007	88.6	0.87	15.2	10.2
	4/15/2008	85.3	0.75	14.6	9.9
	6/10/2008	56.5	1.31	9.9	7.0
	8/5/2008	84.6	1.03	14.5	9.8
Wenatchee River					
WEN-UPPER	11/7/2007	16.3	0.30	3.1	2.4
	4/17/2008	18.6	0.50	3.5	2.7
	6/11/2008	11.5	0.74	2.2	1.8
	8/6/2008	13.2	0.34	2.5	2.0
WEN-NO*	11/7/2007	32.9	0.32	6.0	4.4
	4/16/2008	34.9	0.53	6.3	4.6
	6/11/2008	16.9	0.62	3.2	2.5
	8/6/2008	23.9	0.43	4.4	3.3
WEN-DOWN	11/6/2007	32.1	0.49	5.8	4.3
	4/16/2008	36.2	0.51	6.5	4.8
	6/11/2008	17.0	1.32	3.2	2.5
	8/6/2008	23.6	0.52	4.4	3.3

*MCOL-NO and WEN-NO values are derived from an average of two measurements collected as replicates.

¹Acute copper standard is derived from the following hardness based equation $(0.960)(e^{(0.9422[\ln(\text{hardness})]-1.464)})$.

²Chronic copper standard is derived from the following hardness based equation $(0.960)(e^{(0.8545[\ln(\text{hardness})]-1.465)})$.

Comparison to Historical Data

Dissolved and total copper results are compared to historical data from Ecology’s Environmental Information Management System (EIM) in Table 7. Historical data from EIM were filtered to eliminate bias from results directly related to studies conducted in areas known to have metals contamination. A comparison was conducted to see how the data collected for this study compared to data collected in rivers and streams around the state. Concentrations of dissolved and total copper for this study fell within the range of the statewide data from EIM (Table 7). Median values for dissolved and total copper (0.67 and 0.87 µg/L) were lower than the statewide median of 0.72 and 1.7 µg/L, respectively (Table 7). Maximum dissolved and total copper concentrations for this study were found to be much lower than those found in other rivers and streams throughout the state.

Table 7. Comparison of This Study Data to Historical River and Stream Data for Dissolved and Total Copper in Water (µg/L).

Form of Copper	Cu in Irrigation Project				Statewide Historical Data			
	n	min	median	max	n	min	median	max
Dissolved Copper	24	0.3	0.67	1.43	970	0.017	0.72	16.3
Total Copper	24	0.34	0.87	2.97	982	0.01	1.7	232

Statewide data from Ecology’s Environmental Information Management system (EIM).

Relationship of Conventional Parameters to Copper Availability and Toxicity

Many of the conventional parameters measured for this project influence the bioavailability and toxicity of copper to aquatic organisms.

Hardness measurements in the Mid-Columbia River show that there may be some mitigation of copper availability through cation competition or anion complexation. Low hardness measurements in the Wenatchee River indicate that there would be little potential for reduction of copper availability. Low DOC measurements at all sites indicate that there would be little potential for mitigation of free copper concentrations from complexation with organic matter.

All pH measurements, with one exception, show that the sampled waters range from slightly basic to basic. This indicates that copper toxicity would be increased at these sites, most notably at the downstream Mid-Columbia River site, the near outfall Wenatchee River site, and the downstream Wenatchee River site where pH was the highest.

Samples analyzed for total and dissolved copper showed that during all of the sample events, except one, dissolved copper made up the majority of the sample fraction (Table 4). The one sample that had a majority of total copper was collected in November at the upstream Mid-Columbia River site. With all of the sites having dissolved copper as the major form in the water column over the sampling period, it is highly likely that this is the case throughout the year. These data also show that most of the copper at these sites is biologically available because copper is in the dissolved form.

Sediment

Comparison to Sediment Quality Values

In the State of Washington, standards have not been established for freshwater sediments. Washington Administrative Code 173-204-340, Freshwater Sediments 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 SQS is used to evaluate a potential no-effects impact level for sediment-dwelling organisms and CSL is used to evaluate potential cleanup sites. Proposed freshwater sediment quality values and Canadian Interim Sediment Quality Guidelines (ISQG) for copper are shown in Table 8.

Table 8. Freshwater Sediment Quality Values for Copper.

Freshwater Sediment Quality Values	Copper Concentration mg/Kg dw	Description
Sediment Quality Value (SQS)	80	Level below which adverse effects are not observed
Cleanup screening Level (CSL)	830	Level below which only minor adverse effects would occur
Canadian Interim Sediment Quality Guideline (ISQG)	35.7	Concentration below which adverse biological effects are expected to occur rarely

None of the sediment sample concentrations presented in Table 5 were above the proposed SQS or the CSL. Additionally, none of the sediment samples were above the Environment Canada ISQG for copper (CCME, 2002).

Comparison to Historical Data

In Table 9 total copper results are compared to historical data from Ecology’s EIM. Historical data were filtered to eliminate bias from results directly related to studies conducted in areas known to have metals contamination. Concentrations of total copper for the study fell within the range of the statewide data from EIM. Median values for total copper (12.3 mg/Kg dw) were lower than the statewide median of 22.2 mg/Kg dw. Maximum total copper concentrations for the study were found to be much lower than those found in other rivers and streams throughout the state.

Table 9. Comparison of This Study Data to Historical River and Stream Data for Total Copper in Sediment (µg/L).

Irrigation Project				Historical - EIM			
n	min	median	max	n	min	median	max
12	8.19	12.3	24.1	39	3.3	22.2	72.3

Statewide data from Ecology’s Environmental Information Management system (EIM).

Relationship of Conventional Parameters to Copper Availability

Accumulation of copper in sediments can result in adverse impacts to benthic organisms (Buchman, 2004; EPA, 2005). Similar to water, conventional parameters, such as TOC and grain size, influence the availability of copper in sediment. Organic matter and other deposited material with large surface areas can collect copper by adsorption (Horowitz, 1985). Copper can form complexes with organic matter which makes the copper unavailable to sediment-dwelling organisms and dissolution into the water column.

Grain size influences how copper partitions in the sediment. Grain size is considered to be one of the most important factors influencing metals partitioning into sediments (Horowitz, 1985). As grain size decreases, there is a corresponding increase in adsorbed metal concentrations. This has much to do with the large increase in available surface area as particle size decreases.

All of the sample sites in both rivers had low amounts of TOC and fine grain sediments (Table 4). Most of the samples were made up of sand. This means that there was not a lot of surface area for copper to adsorb. Thus, most of the copper in these rivers will stay in the water column, and will not be deposited to sediment. With most of the copper staying in the water column there is not much potential for toxicity to sediment-dwelling organisms.

Conclusions and Recommendations

Conclusions

Copper concentrations in water from the Mid-Columbia and Wenatchee Rivers were found to be low and comparable to concentrations found elsewhere in Washington State. Measured dissolved copper concentrations were 1 to 2 orders of magnitude below Washington State water quality criteria. Low copper concentrations found in water could be a result of dilution in the receiving waters. The Columbia and Wenatchee Rivers are large bodies of water which can have flows from ten to hundreds of thousands of cubic feet of water per second.

Copper concentrations in sediment were below all available sediment quality values and were within the national background concentration range of 10 to 25 mg/Kg (Buchman, 2004). Sediment data for copper were also comparable to concentrations found in other rivers and streams in Washington State. Copper concentrations in sediments in the sampled areas are probably low due to the lack of fine-grain sediment deposition.

This study did not detect any concentrations of copper in water or sediment that would adversely impact aquatic organisms based on comparison with available criteria and guidelines.

Recommendations

Based on the data collected and analyzed for this study, the following recommendations are made:

- If further sampling is conducted, it should focus on verification of compliance with the NPDES permit for application of aquatic herbicides in irrigation canals.
- Future studies should evaluate the impacts on aquatic organisms from irrigation systems that use large amounts of copper and discharge to small receiving waters.

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Appendices

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Appendix A. Sampling Information

Table A-1. Locations and Descriptions of Sampling Sites

Table A-2. Water and Sample Depths for Surface Water Samples

Table A-3. Field Log Descriptions of Surface Sediments

Table A-1. Locations and Descriptions of Sampling Sites.

Site	Latitude	Longitude	Location Description
Mid-Columbia River			
MCOL-UPPER	47.33349	120.08540	Inside corner of channel on west side of Columbia River in an eddy adjacent to a sandbar.
MCOL-NO	46.47393	119.25995	Behind gravel arm of island (island located near left bank) in calm and shallow water.
MCOL-DOWN	46.35760	119.25917	In eddy behind rock outcrop on left bank. Just downstream of Esquatzel Diversion Channel.
Wenatchee River			
WEN-UPPER	47.58679	120.70757	Sandy beach that extends into the water to the edge of high velocity flow. Site located at Old Pipeline trailhead.
WEN-NO	47.45988	120.34019	Left bank of river under and slightly downstream of Wenatchee Irrigation District pipe crossing bridge.
WEN-DOWN	47.45616	120.32880	Center of channel approximately 90 meters from mouth of Wenatchee River.

Datum = NAD 83.

Table A-2. Water and Sample Depths for Surface Water Samples.

Site	Date	Sample Depth (m)	Water Depth (m)
Mid-Columbia River			
MCOL-UPPER	11/6/2007	1.5	4.0
	4/16/2008	2.1	2.7
	6/11/2008	1.5	2.4
	8/6/2008	0.91	1.5
MCOL-NO*	11/5/2007	0.30	1.2
	4/15/2008	0.61	0.91
	6/10/2008	1.8	3.7
	8/5/2008	0.91	1.5
MCOL-DOWN	11/5/2007	3.0	4.0
	4/15/2008	0.76	0.91
	6/10/2008	1.5	4.6
	8/5/2008	4.6	6.4
Wenatchee River			
WEN-UPPER	11/7/2007	0.46	0.91
	4/17/2008	0.61	1.2
	6/11/2008	0.61	1.5
	8/6/2008	0.76	1.2
WEN-NO*	11/7/2007	0.30	0.76
	4/16/2008	0.45	0.91
	6/11/2008	1.2	2.7
	8/6/2008	0.91	1.2
WEN-DOWN	11/6/2007	0.91	2.4
	4/16/2008	0.61	1.2
	6/11/2008	2.1	4.3
	8/6/2008	0.91	2.1

*MCOL-NO and WEN_NO values are derived from an average of two samples collected as replicates.

Table A-3. Field Log Descriptions of Surface Sediments.

Site	Collection Date	Water Depth (m)	Mean Penetration Depth (cm)	No. of Grabs	Sediment Quality Description
Mid-Columbia River					
MCOL-UPPER	11/6/2007	4.0	4	3	Homogeneous gray sand with shell fragments. Several clams present in sediment.
	4/16/2008	2.7	6.7	3	Homogeneous gray-brown sand with wood, shell, and plant fragments. No odor.
MCOL-NO*	11/5/2007	1.2	7	4	Homogeneous olive-gray sand with a thin (<1cm) top layer of gray silt-clay. Strong odor of hydrogen sulfide.
	4/15/2008	0.91	5.3	6	Homogeneous black-gray sand with a thin (<2mm) top layer of olive-gray silt-clay. Wood, shell, and plant fragments. Worms. No odor.
MCOL-DOWN	11/5/2007	4.0	5	5	Homogeneous gray sand. One live clam present in the sediment.
	4/15/2008	0.91	7.3	3	Heterogeneous mix of olive-brown sand and silt-clay. Wood and plant fragments. No odor.
Wenatchee River					
WEN-UPPER	11/7/2007	0.91	6	3	Heterogeneous mix of gray-black gravel, sand, and silt-clay. Sparse amounts of small wood fragments in sediment.
	4/17/2008	1.2	6.5	3	Homogeneous gray-brown coarse sand with a thin (<1mm) top layer of tan silt-clay. Plant fragments. No odor.
WEN-NO*	11/7/2007	0.76	5	4	Heterogeneous mix of gray gravel and sand with a thin (<1cm) top layer of olive silt-clay. Strong odor of hydrogen sulfide.
	4/16/2008	0.91	4.3	4	Homogeneous gray-brown sand with a thin (<1mm) top layer of brown silt-clay. Wood and plant fragments. Worms. No odor.
WEN-DOWN	11/6/2007	2.4	6	3	Homogeneous gray-brown sand with small wood fragments present throughout. Moderate odor of hydrogen sulfide.
	4/16/2008	1.2	6.3	3	Homogeneous gray sand with a thin (<2mm) top layer of green-brown silt-clay. Plant fragments and settled algae. No odor.

*MCOl-NO and WEN-NO values and descriptions are derived from an average of two samples collected as replicate.

Appendix B. Quality Assurance /Quality Control Data

Table B-1. Field and Filter Blanks for Water Samples.

Table B-2. Field Replicate Results for Water.

Table B-3. Field Replicate Results for Sediment.

Table B-4. Matrix Spike/Matrix Spike Duplicates Results for Water and Sediment.

Table B-5. Standard Reference Material Recoveries for Water and Sediment.

Table B-1. Field and Filter Blanks for Water Samples.

Location	Sample Type	Date	Total Copper (mg/L)	Dissolved Copper (mg/L)	Hardness (mg/L CaCO ₃)	DOC (%)	TSS (mg/L)
Wen-NO	Field Blank	11/6/2007	0.11	0.10 U	0.30 U	1.0 U	1 U
MCol-NO	Field Blank	8/5/2008	0.10 U	0.10 U	0.30 U	1.0 U	1 U
MCol-NO	Filter Blank	11/5/2007	-	-	-	1.0 U	-
Wen-NO	Filter Blank	8/6/2008	-	0.10 U	-	-	-

U – Analyte not detected at or above the reported result.

DOC – Dissolved Organic Carbon.

TSS – Total Suspended Solids.

Table B-2. Field Replicate Results for Water.

Location	Date	Sample Type	Total Copper (mg/L)	Dissolved Copper (mg/L)	Hardness (mg/L CaCO ₃)	DOC (%)	TSS (mg/L)
Wen-Upper	4/17/2008	Sample	0.71	0.54	18.8	1.3	3
	4/17/2008	Replicate	0.59	0.45	18.4	1.3	2
	RPD =		18.46	18.18	2.15	0.00	40.00
Wen-Down	6/11/2008	Sample	1.46	0.99	16.9	1.3	4
	6/11/2008	Replicate	1.05	1.65	17.1	1.3	4
	RPD =		32.67	50.00	1.18	0.00	0.00
MCol-Down	8/5/2008	Sample	1.35	0.99	86.7	1.8	4
	8/5/2008	Replicate	1.15	1.07	82.5	1.7	4
	RPD =		16.00	7.77	4.96	5.71	0.00

RPD – Relative Percent Difference.

DOC – Dissolved Organic Carbon.

TSS – Total Suspended Solids.

Table B-3. Field Replicate Results for Sediment.

Location	Date	Sample Type	Total Copper (mg/Kg)	Grain Size (%)				TOC (%)	Solids (%)
				Gravel	Sand	Silt	Clay		
MCol-Down	11/5/2007	Sample	10.6	0.26	96.36	4.19J	1.16	0.17	68.1
	11/5/2007	Replicate	10.2	0.10	97.73	4.31 J	1.13	0.17	67.9
	RPD =		3.85	88.89	1.41	2.82	2.62	0.00	0.29
Wen-Upper	4/17/2008	Sample	9.09	2.44	94.53	1.19 J	0.00	0.14	73.2
	4/17/2008	Replicate	9.58	3.42	95.31	1.31 J	0.00	0.15	71.2
	RPD =		5.25	33.45	0.82	9.60	0.00	6.90	2.77

RPD – Relative Percent Difference.

TOC – Total Organic Carbon.

J – The analyte was positively identified and the associated numerical value is an approximate concentration of the analyte in the sample.

Table B-4. Matrix Spike/Matrix Spike Duplicates Results for Water and Sediment (%).

Location	Date	Matrix	Parameter	MS	MSD	RPD
Wen-Down	11/6/2007	Water	Dis. Copper	117	111	5.26
Wen-NO	4/16/2008	Water	Dis. Copper	110	111	0.90
MCol-NO	6/10/2008	Water	Dis. Copper	105	106	0.95
MCol-Down	8/5/2008	Water	Dis. Copper	97	98	1.03
mean =						2.04
Wen-Down	11/6/2007	Water	Total Copper	98	98	0.00
Wen-NO	4/16/2008	Water	Total Copper	101	119	16.36
MCol-NO	6/10/2008	Water	Total Copper	104	107	2.84
MCol-NO	8/5/2008	Water	Total Copper	99	96	3.08
mean =						5.57
MCol-NO	11/5/2007	Sediment	Total Copper	89	88	1.13
Wen-Down	4/16/2008	Sediment	Total Copper	96	89	7.57
mean =						4.35

MS – Matrix Spike.

MSD – Matrix Spike Duplicate.

RPD – Relative Percent Difference.

Table B-5. Standard Reference Material Recoveries for Water and Sediment.

Date	Matrix	Parameter	SRM	Recovery (%)
11/2007	water	Dis. Copper	SLRS-4	110
4/2008	water	Dis. Copper	SLRS-4	110
6/2008	water	Dis. Copper	SLRS-4	114
8/2008	water	Dis. Copper	SLRS-4	105
mean =				110
11/2007	water	Total Copper	SLRS-4	108
4/2008	water	Total Copper	SLRS-4	91
6/2008	water	Total Copper	SLRS-4	113
8/2008	water	Total Copper	SLRS-4	104
mean =				104
11/2007	sediment	Total Copper	ERAS 247	105
4/2008	sediment	Total Copper	ERAS 247	113
mean =				109

SRM – Standard Reference Material.

SLRS-4 – Water reference material for trace metals, National Research Council of Canada.

ERAS 247 – Metals in Soil, Environmental Research Associates.