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DEPARTMENT OF
ECOLOGY

Concentrations of 303(d) Listed Metals in the Upper Yakima River

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Concentrations of 303(d) Listed Metals in the Upper Yakima River

by
Art Johnson

Environmental Assessment Program
Olympia, Washington 98504-7710

June 2000

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Abstract

Copper, cadmium, mercury, and silver were analyzed in the Yakima River at Cle Elum and at Umtanum to verify 303(d) listings for violations of state water quality standards, based on historical U.S. Geological Survey data. Zinc and lead were also analyzed. Water sampling included three tributaries – Crystal, Swauk, and Wilson creeks – considered to be potential metals sources to the river.

Results showed metals concentrations were generally low. Zinc and copper were routinely detected at all locations in concentrations ranging from <0.4 - 2.1 ug/L and 0.12 - 2.3 ug/L, respectively. In the main stem, there was a significant downstream increase in copper, partly attributable to Wilson Creek. Lead, cadmium, and mercury were less frequently detected and almost exclusively limited to the three tributaries. All samples analyzed were well within state standards for aquatic toxicity.

It is recommended that the upper Yakima River be removed from the 303(d) list for historically reported metals violations in the water column.

Acknowledgements

- The efforts of Greg Fuhrer in reviewing USGS historical data on the Yakima River are very much appreciated.
- The good work of the Ecology Manchester Environmental Laboratory is acknowledged, especially Jim Ross, Randy Knox, and Sally Cull of the metals group.
- This report benefited from review by Greg Fuhrer, Will Kendra, Joe Joy, Chris Coffin, Bob Raforth, and Phelps Freeborn.
- Dave Rogowski collected the September and November samples for this project.
- The final report was edited and formatted by Dorothy McIntyre and Joan LeTourneau.

Introduction

The Washington State Department of Ecology (Ecology) is required under Section 303(d) of the federal Clean Water Act to prepare a list every two years of waterbodies not expected to meet state surface water quality standards after implementation of technology-based controls. The state must complete a Total Maximum Daily Load (TMDL) study for waters on the list.

The upper Yakima River was placed on the 1998 303(d) list for multiple violations of the state standards for cadmium, copper, mercury, and silver, as shown below. A minimum of two exceedances is required for listing.

Sampling Location	Metals Exceeding Standards	Number of Samples Exceeding
Yakima R. at Cle Elum (river mile 183)	cadmium	6
	copper	4
	mercury	2
Yakima R. at Umtanum (river mile 140)	cadmium	4
	mercury	3
	copper	2
	silver	2

The source of the data used for the listings was monitoring done by the U.S. Geological Survey (USGS) between 1987 and 1990 for the National Water Quality Assessment Program (NAWQA), as reported in Fuhrer et al. (1994, 1996).

The Ecology Environmental Assessment Program (EAP) reviewed the candidate l998 list and questioned the accuracy of the USGS metals data for the Yakima (Johnson, 1998). Metals data generated by the USGS National Stream Quality Accounting Network (NASQAN) during this period were known to be subject to contamination (Pendergast, J.F., 1991; Rickert, 1991; Windom et al., 1991). Although collected under different protocols, results from the USGS NAWQA pilot study in the upper Yakima were inconsistent with metals concentrations Ecology had measured near the mouth of the river (Johnson, 1994). Extensive quality assurance data were provided in Fuhrer et al. (1994), but did not establish accuracy at the low concentrations typical of ambient rivers and streams in Washington.

The Ecology Central Regional Office (CRO) therefore requested that EAP do additional monitoring to verify the 303(d) metals listings for the upper Yakima. The six stations listed below were selected for sampling, in consultation with CRO (see Figures 1 and 2).

1. Yakima River at Cle Elum
2. Crystal Creek at mouth
3. Swauk Creek at mouth
4. Yakima River at Irene Rinehart Park
5. Wilson Creek at Canyon Road Bridge
6. Yakima River at Umtanum

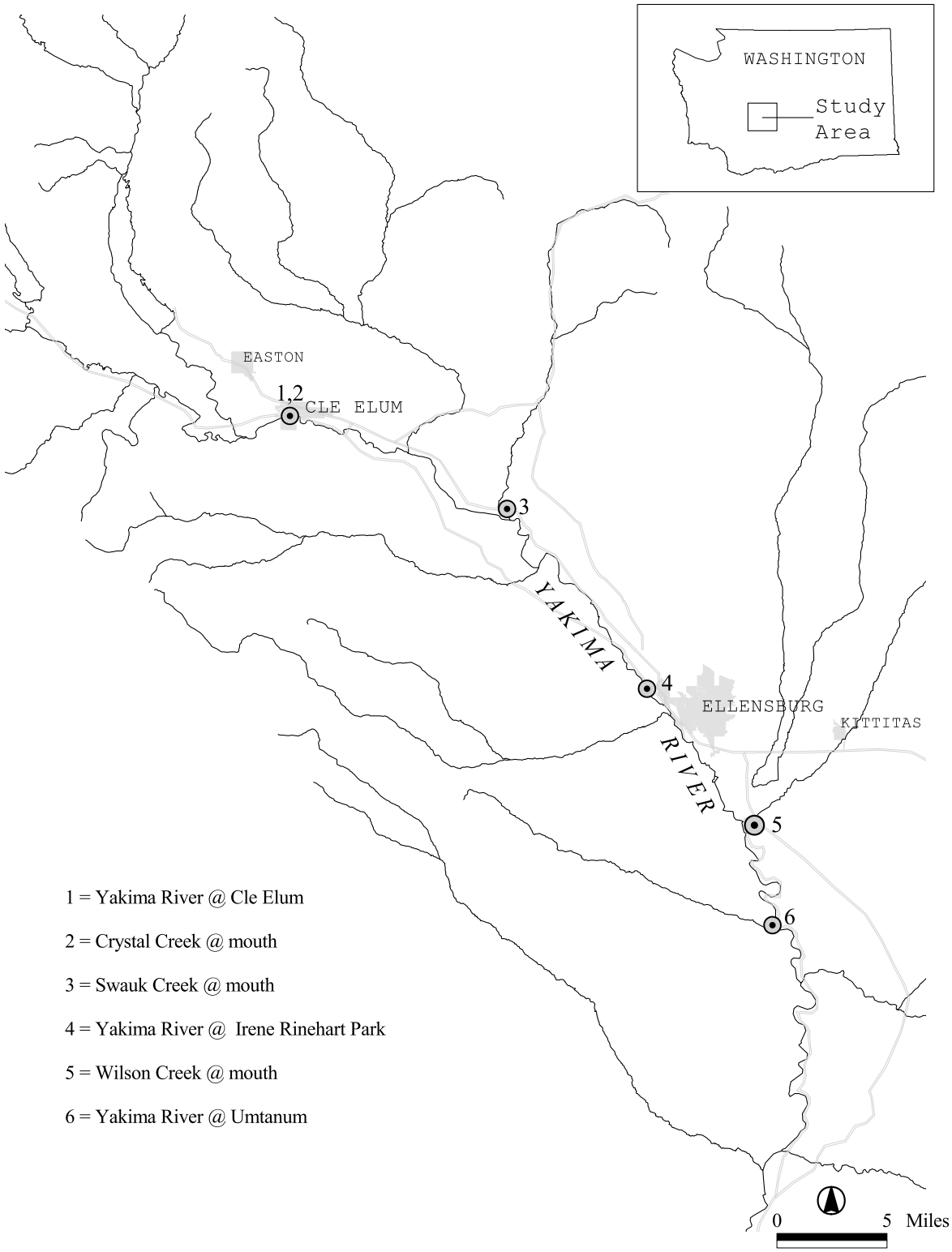
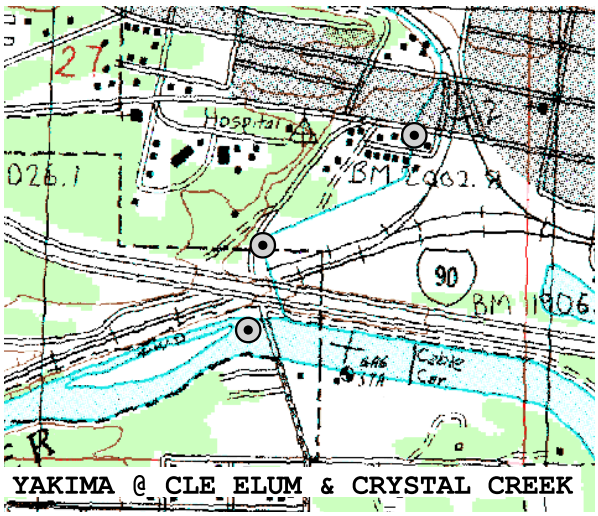
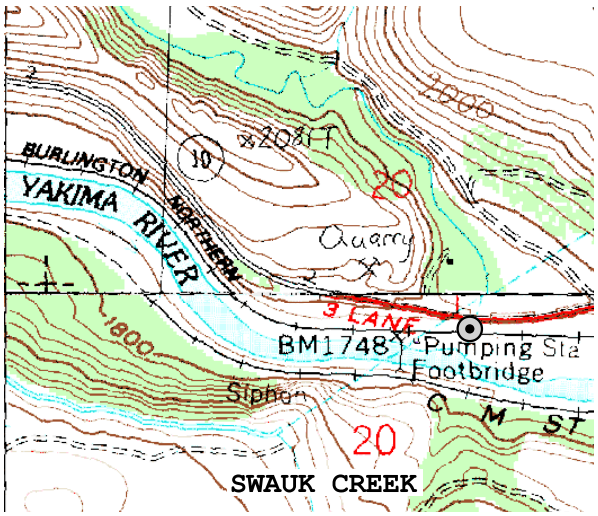
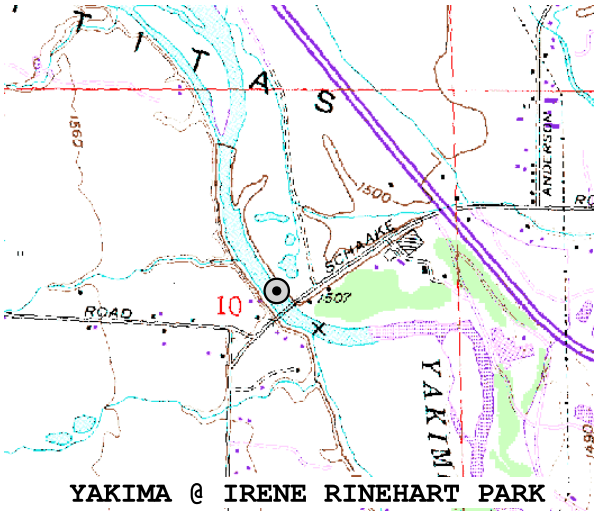
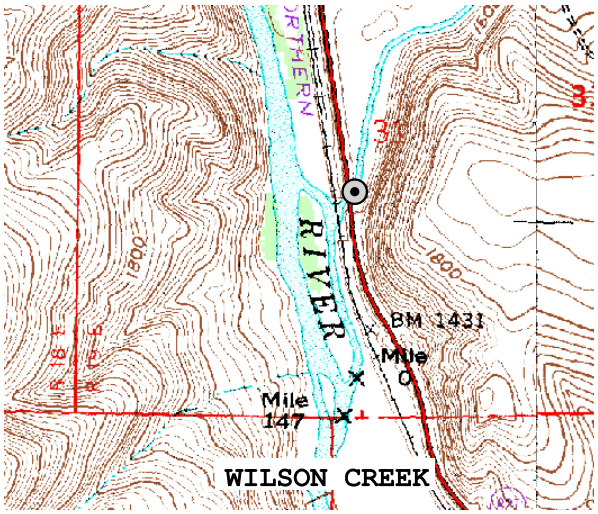


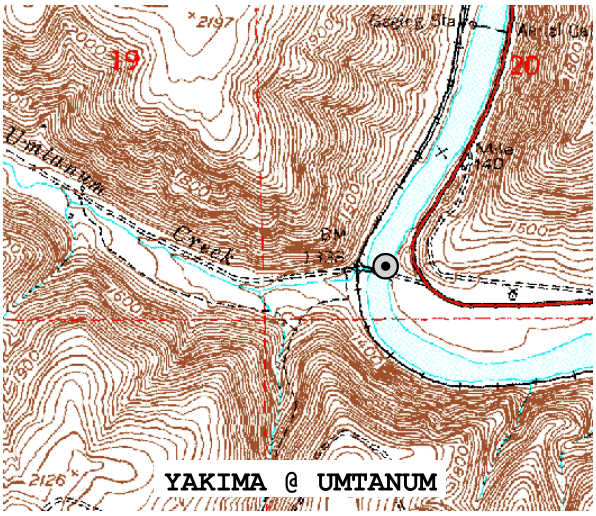
Figure 1. Upper Yakima River Sampling Sites for 303(d) Metals, March 1999 - January 2000











Latitude x Longitude	
Yakima @ Cle Elum	47 11.3 2 x 120 56.54
Crystal Creek (upper)	47 11.45 x 120 56.39
Crystal Creek (lower)	47 11.37 x 120 56.53
Swauk Creek	47 07.26 x 120 44.12
Yakima @ Rinehart Park	46 58.43 x 120 34.00
Wilson Creek	46 55.02 x 120 30.24
Yakima @ Umtanum	46 51.21 x 120 28.58

Figure 2. Location Detail for Sampling Sites

Crystal, Swauk, and Wilson creeks were viewed as potential metals sources to the river.

The Crystal Creek drainage includes the Roslyn coal mining area, active from the 1880s to the 1930s. Water leaching through tailings piles and draining from mine shafts enters Crystal Creek. The Roslyn waste water treatment plant (WWTP) also discharges to the creek. Because of sluggish flow at the mouth of Crystal Creek during July and August, some samples were taken upstream of the mouth (see Figure 2). The Yakima River at Cle Elum samples were taken above Crystal Creek.

Placer mining for gold occurs along Swauk Creek and its tributaries. Elevated lead and zinc concentrations have been observed in water samples from the upper drainage (Raforth et al., 2000).

Wilson Creek is the largest tributary to this reach of the Yakima. It has had historic water quality problems due to receiving irrigation return flows and operational spills from delivery canals. Copper sulfate is used to kill algae in the irrigation canals from April through October. The Yakima River at Irene Rinehart Park station (river mile 153) was included in the monitoring program to provide metals data above Wilson Creek.

Water samples were collected at each of the above sites once every other month from March 1999 to January 2000. Sampling procedures followed the guidance on clean sampling techniques in EPA (1995) *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*. The samples were analyzed at the Ecology Manchester Environmental Laboratory using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) and, for mercury, Cold Vapor Atomic Absorption (CVAA).

Metals analyzed included zinc, copper, lead, cadmium, mercury, and silver. Although zinc and lead were not among the 303(d) listings, accurate data on these metals were needed for NPDES permits. In keeping with state water quality standards, zinc, copper, silver, cadmium, and lead were analyzed as dissolved (0.45 micron filtered samples). Total mercury (whole water samples) was analyzed for comparison to the chronic standard. Ancillary parameters included flow, temperature, conductivity, total suspended solids, and hardness. The flow data were obtained from the EAP Stream Hydrology Unit or U.S. Bureau of Reclamation.

Methods

Field

All water samples were simple grabs, either taken by hand after wading out into the stream or with the sample container on the end of a plastic pole. The three stations on the Yakima main stem were sampled from the left bank (viewed facing downstream).

Metals samples were taken directly in pre-cleaned 500 mL teflon bottles. Samples for dissolved metals were vacuum-filtered in the field through a disposable 0.45 micron cellulose-nitrate filter (#450-0045, type S). Filtering was done in a polyethylene glove box. Non-talc, disposable gloves were worn during the filtering procedure. The filtrate was transferred to a clean teflon bottle. Samples were acidified to pH<2 with sub-boiled 1:1 nitric acid at Manchester Laboratory within one day of collection. Sample containers and preservation for other water quality parameters are described in MEL (1999). All samples were double-bagged in polyethylene and placed on ice for transport to Manchester Laboratory. Chain-of-custody was maintained.

The teflon bottles, acid vials, and filter units were pre-cleaned for low-level metals analysis using procedures described in Kammin et al. (1995). Briefly, the bottles and vials were soaked in 1:1 nitric acid for 72 hours and rinsed with de-ionized (DI) water. The cleaned bottles were filled with DI water and placed in zip-lock bags. Filters were cleaned by allowing 1:1 nitric acid to gravity filter, then vacuum filtering 500 mL of DI water. The unit was taken apart, air-dried, reassembled, filter lids secured with tape, and placed in zip-lock bags. Cleaning was done by Manchester Laboratory in a Class 100 clean room.

Laboratory

Analytical methods for this project are listed in Table 1.

Table 1. Analytical Methods

Analysis	Method	Number
Zn, Cu, Pb, Cd, Ag	ICP/MS	EPA 200.8
Hg	CVAA	EPA 245.7
Conductivity	Wheatstone bridge	EPA 120.1
Hardness	EDTA titrimetric	SM2340B
Total Suspended Solids	Filter, Grav. 103-105°C	EPA 160.2

Zinc, copper, lead, cadmium, and silver were analyzed by U.S. Environmental Protection Agency (EPA) method 200.8, using state-of-the-art ICP-MS instrumentation (PE Sciex 6000 or TJA POEMS 3). For dissolved metals analysis, 10 mL of sample is placed into a pre-cleaned plastic sample tube, 20 uL of internal standard solution is mixed with the sample, and the solution is placed in a covered autosample tray to await injection into the ICP-MS. Once the instrument has passed its daily performance check, it is standardized using a blank and four standards ranging from 2 - 50 ug/L in concentration. Three replicate analyses are performed on the field and QA samples.

Internal standards are used throughout the analysis to correct for instrument drift. If the response varies by more than 25%, samples are either diluted or re-analyzed, or a different internal standard is used. Check standards are analyzed at a frequency of 10% and the analysis results rejected if different from the standards by more than 10%. Samples are spiked to check for matrix interferences. A natural reference sample (NRCC SLRS) is used to verify instrument performance at ambient levels. When possible, at least two isotopes are monitored for each analyte.

Blank contamination and random sample contamination is monitored by analyzing random samples in duplicate. If the duplicate analysis shows indications of blank contamination, all the samples in that set are re-analyzed.

Mercury samples were prepared by digesting with a purified bromide/bromate solution. Analysis was by CVAA using EPA method 245.7.

Data Quality

Holding Time

All metals were analyzed within holding times specified by EPA (28 days for mercury, 180 days for other metals).

Matrix Spikes

Water samples from the Yakima River at Umtanum and Crystal Creek were spiked with known concentrations of the metals of interest to assess bias from interferences in the sample matrix (Table 2). Recoveries of zinc, copper, lead, cadmium, and silver spikes were 84 - 100%. Mercury recoveries were 95 - 119%. Method acceptance criteria are 75 - 125%. The spiking levels were 10 ug/L for zinc, copper, and silver; 1 ug/L for lead and cadmium; and 0.02 ug/L for mercury.

Table 2. Matrix Spike Recoveries (%)

Sample Type	Date	Sample No.	Zinc	Copper	Cadmium	Lead	Mercury	Silver
Matrix Spike	03/31/99	138110	99	94	94	94	119	91
	07/13/99	288024	87	90	89	96	98	85
Matrix Spike Duplicate	03/31/99	138110	100	95	94	94	117	91
	07/13/99	288024	87	90	89	94	95	84

Precision

Precision estimates based on duplicate matrix spike recoveries were all within the acceptance criteria of +/-20%.

Laboratory Control Samples

A laboratory control sample (High Purity Standards, TMDW) was analyzed with each sample set (Table 3). Recoveries were 85 - 129%. Certified values were 70 ug/L zinc, 40 ug/L lead, 20 ug/L copper, 10 ug/L cadmium, and 2 ug/L silver. The LCS used for mercury was a 0.025 ug/L dilution of a second source stock standard.

Table 3. Recoveries on Laboratory Control Samples[a] (%)

Date	Zinc	Copper	Lead	Cadmium	Mercury	Silver
03/31/99	102	99	93	94	85	94
05/11/99	103	97	95	95	106	93
07/13/99	111	95	129	100	100	94
09/15/99	86	96	97	101	97	99
11/09/99	86	96	97	101	98	99
01/25/00	99	104	104	107	93	106

[a]High Purity Standards TMDW

Standard Reference Material

A standard reference material (SLRS-3, River Water Reference Material for Trace Metals, National Research Council Canada) was analyzed with each set of samples, except those collected in January. This material has low certified values for zinc, copper, lead, and cadmium in the range normally encountered in uncontaminated rivers and streams.

The results (Table 4) showed close agreement with certified values, except for zinc and cadmium in the March analyses and zinc in the May analyses. As noted below, there was some zinc contamination in the method blank for March and May which may explain the standard reference material (SRM) results for those dates. The high cadmium result in March is most likely from contamination in the autosampler vial (Ross, 2000).

Table 4. Results on Standard Reference Material[a] (ug/L)

Date	Zinc	Copper	Lead	Cadmium	Mercury
03/31/99	3.56	1.44	0.070	0.095	na
05/11/99	1.67	1.41	0.065	0.020	na
07/13/99	1.30	1.38	0.065	0.026	na
09/15/99	1.20	1.41	0.066	0.017	na
11/09/99	1.20	1.41	0.066	0.017	na
01/25/00	na	na	na	na	na
certified value =	1.04	1.35	0.068	0.013	nc

[a]SLRS-3 (River Water Reference Material for Trace Metals, Nat. Res. Council Canada)
na = not analyzed nc = not certified

Method Blanks

A method blank was analyzed with each sample set (Table 5). Copper, lead, cadmium, mercury, and silver were below detection limits in all cases. Zinc was detected at 0.5 ug/L in the method blanks for the March and May samples. The dissolved zinc data for these dates should be therefore considered estimates.

Table 5. Metals Concentrations in Method Blanks (ug/L)

Date	Zinc	Copper	Lead	Cadmium	Mercury	Silver
03/31/99	0.52	<0.05	<0.02	<0.02	<0.002	<0.02
05/11/99	0.52	<0.05	<0.02	<0.02	<0.002	<0.02
07/13/99	<0.4	<0.1	<0.02	<0.02	<0.002	<0.02
09/15/99	<0.4	<0.05	<0.02	<0.02	<0.002	<0.05
11/09/99	<0.5	<0.05	<0.02	<0.02	<0.002	<0.05
01/25/00	<0.4	<0.05	<0.02	<0.02	<0.002	<0.02

Field Blanks

Field blanks were used to detect metals contamination arising from sample containers or the filtration procedure (Table 6). Bottle blanks consisted of 500 mL teflon bottles cleaned and filled with DI water at Manchester Laboratory, as previously described. Filter blanks were prepared by filtering half the contents of a bottle blank, the remainder being analyzed as the bottle blank for that sample set.

Table 6. Metals Concentrations in Field Blanks (ug/L)

Sample Type	Date	Sample No.	Zinc	Copper	Lead	Cadmium	Mercury	Silver
Filter Blank	03/31/99	138113	1.2	<0.05	<0.02	<0.02	na	<0.02
	07/13/99	288019	3.0	<0.1	<0.02	<0.02	<0.002	<0.02
	11/09/99	458038	<0.5	<0.05	<0.02	<0.02	na	<0.05
Bottle Blank	03/31/99	138114	0.48	<0.05	<0.02	<0.02	<0.002	<0.02
	07/13/99	288020	2.4	<0.1	<0.02	<0.02	<0.002	<0.02
	11/09/99	458037	<3	<0.1	<0.1	<0.1	0.002	na

na = not analyzed

Field blanks were analyzed on three occasions during the project. The only metal detected was zinc in the March and July blanks. Zinc concentrations in the filter blank for these dates were only slightly greater than in the corresponding bottle blank, indicating the filtration procedure was not contributing significant amounts of zinc to the samples. As noted above, the zinc results for March are considered to be estimates. The zinc level in the bottle blanks was in the same range as the concentrations in field samples, showing the sample containers were not sources of zinc contamination.

Field Replicates

The variability of the data reported here (field + laboratory) can be gauged from results on replicate samples collected approximately five minutes apart on three occasions each at the Yakima River at Umtanum and at Crystal Creek (Table 7). Agreement between replicates was generally within 10% for copper, silver, and cadmium, and within 20% for zinc (Crystal Creek), lead, and mercury. Greater variability was encountered for zinc in the Umtanum replicates, 33 - 126%.

Table 7. Variability Between Replicate Samples (relative percent difference, RPD[a])

Sampling Date	Sample Number	Cond. (umhos/cm)	TSS (mg/L)	Hardness (mg/L)	Zinc (ug/L)	Copper (ug/L)	Lead (ug/L)	Cadmium (ug/L)	Mercury (ug/L)	Silver (ug/L)
				Crystal Creek @ mouth						
07/13/99	288016	700	2	106	0.79	1.1	0.042	<0.02	0.0028	<0.02
07/13/99	288024	701	<1	110	0.84	1.0	0.035	<0.02	0.0030	<0.02
	RPD =	0.1%	>66%	4%	6%	10%	18%	0%	7%	0%
09/15/99	378020	274	2	126	0.67	0.23	<0.02	<0.02	<0.002	<0.02
09/15/99	378021	274	3	124	0.69	0.23	<0.02	<0.02	<0.002	<0.02
	RPD =	0%	40%	2%	3%	0%	0%	0%	0%	0%
11/09/99	458030	486	<1	124	1.5	2.2	0.067	<0.02	<0.002	<0.05
11/09/99	458036	488	<1	123	1.8	2.3	0.081	<0.02	<0.002	<0.05
	RPD =	0.4%	0%	1%	18%	1%	19%	0%	0%	0%
				Yakima River @ Umtanum						
03/31/99	138110	107	7	46	2.1	0.38	<0.02	<0.02	<0.002	<0.02
03/31/99	138111	107	6	45	1.5	0.40	<0.02	<0.02	<0.002	<0.02
	RPD =	0%	15%	0.2%	33%	5%	0%	0%	0%	0%
05/11/99	198025	157	5	60	0.81	0.59	<0.02	<0.02	<0.002	<0.02
05/11/99	198026	160	5	62	1.6	0.60	<0.02	<0.02	0.0023	<0.02
	RPD =	2%	0%	3%	64%	1%	0%	0%	>14%	0%
01/25/00	048135	101	2	42	1.8	0.49	<0.02	<0.02	<0.002	<0.02
01/25/00	048136	101	2	43	0.41	0.35	<0.02	<0.02	<0.002	<0.02
	RPD =	0%	0%	2%	126%	33%	0%	0%	0%	0%

[a]RPD = range as percent of replicate mean

Results and Discussion

Metals Concentrations

Table 8 shows the flow and general water quality conditions in the upper Yakima River main stem and the three tributary stations during periods when metals samples were collected.

Figure 3 plots the average daily flow for the Yakima River at Cle Elum and Wilson Creek for March 1999 through January 2000, with sampling dates indicated. As can be seen from the figure, the water samples encompassed a variety of flow regimes, although the extreme flows that occurred in the Yakima during late June and late December were missed.

The metals data are in Table 9. Summary statistics (median, maximum, and detection frequency) are calculated in Table 10.

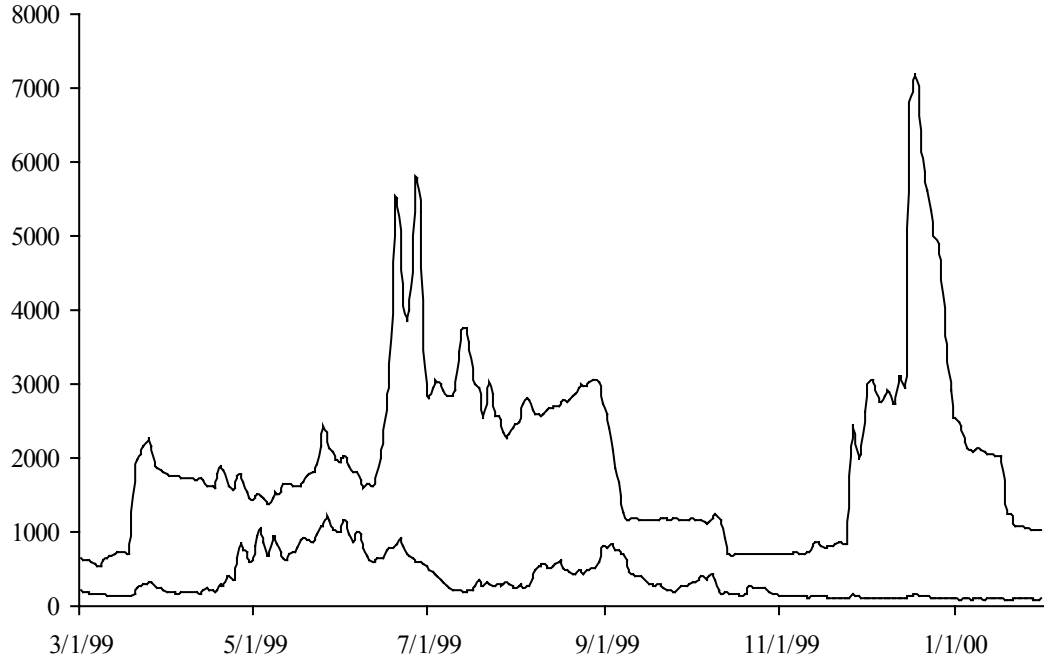


Figure 3. Sampling Dates Compared to Flows in the Yakima River and Wilson Creek (cfs)

Table 8. Flow and General Water Quality Conditions, Upper Yakima River, 03/99 - 01/00

Location	Sampling Date	Flow (cfs)	Temp. (°C)	Cond. (umhos/cm)	TSS (mg/L)	Hardness (mg/L)
Yakima R. @ Cle Elum	03/31/99	1790	2.9	64	2	27
	05/11/99	1610	6.0	65	2	29
	07/13/99	3770	4.0	50	2	23
	09/15/99	1170	11.9	69	<1	30
	11/09/99	710	7.6	67	1	30
	01/25/00	1060	2.4	55	<1	24
Crystal Creek @ mouth	03/31/99	21	4.4	409	57	69
	05/11/99	2.6	6.0	487	3	82
	07/13/99	0.5	5.0	700	1	108
	09/15/99	0.5	12.5	274	2	125
	11/09/99	0.9	6.7	487	<1	124
	01/25/00	1.0	1.8	490	3	99
Swauk Creek @ mouth	03/31/99	127	3.1	170	10	81
	05/11/99	117	4.8	148	8	67
	07/13/99	14	4.8	147	2	66
	09/15/99	1.4	16.0	184	<1	80
	11/09/99	10	6.5	190	<1	89
	01/25/00	27	0.4	193	<1	89
Yakima R. @ Rinehart Park	03/31/99	3000	3.7	93	7	40
	05/11/99	2550	7.3	89	4	41
	07/13/99	4130	4.7	58	7	27
	09/15/99	650	16.2	82	1	35
	11/09/99	880	7.9	78	1	35
	01/25/00	1221	2.5	71	<1	31
Wilson Creek @ mouth	03/31/99	200	6.2	242	20	102
	05/11/99	638	9.1	223	41	95
	07/13/99	198	6.1	246	27	104
	09/15/99	313	15.3	232	19	101
	11/09/99	124	10.4	380	7	166
	01/25/00	110	4.6	358	10	146
Yakima River @ Umtanum	03/31/99	2915	4.8	107	6	46
	05/11/99	3300	9.4	158	5	61
	07/13/99	4510	5.8	75	7	34
	09/15/99	1430	16.8	132	5	58
	11/09/99	1070	8.4	128	2	57
	01/25/00	1479	2.6	101	2	42

Table 9. Metals Concentrations, Upper Yakima River, 03/99 - 01/00 (ug/L)
[Metals analyzed as dissolved (0.45 micron filtered), except for total mercury.]

Location	Sampling Date	Zinc	Copper	Lead	Cadmium	Mercury	Silver
Yakima R. @ Cle Elum	03/31/99	**2.1**	**0.21**	<0.02	<0.02	<0.002	<0.02
	05/11/99	**1.1**	**0.16**	<0.02	<0.02	<0.002	<0.02
	07/13/99	**0.41**	**0.12**	<0.02	<0.02	<0.002	<0.02
	09/15/99	<0.4	**0.19**	<0.02	<0.02	<0.002	<0.02
	11/09/99	<0.5	**0.22**	<0.02	<0.02	<0.002	<0.05
	01/25/00	<0.4	**0.26**	<0.02	<0.02	<0.002	<0.02
Crystal Creek @ mouth	03/31/99	**1.8**	**2.3**	**0.099**	**0.025**	<0.002	<0.02
	05/11/99	**1.1**	**1.8**	**0.054**	<0.02	**0.0027**	<0.02
	07/13/99	**0.83**	**1.0**	**0.037**	<0.02	**0.0030**	<0.02
	09/15/99	**0.68**	**0.23**	<0.02	<0.02	<0.002	<0.02
	11/09/99	**1.6**	**2.2**	**0.074**	<0.02	<0.002	<0.05
	01/25/00	**1.9**	**2.3**	<0.02	<0.02	**0.0053**	<0.02
Swauk Creek @ mouth	03/31/99	**1.8**	**0.61**	**0.021**	<0.02	<0.002	<0.02
	05/11/99	**0.83**	**0.48**	<0.02	<0.02	**0.0035**	<0.02
	07/13/99	**1.4**	**0.97**	**0.056**	<0.02	**0.0045**	<0.02
	09/15/99	<0.4	**0.39**	<0.02	<0.02	<0.002	<0.02
	11/09/99	<0.5	**0.29**	<0.02	<0.02	**0.0023**	<0.05
	01/25/00	<0.4	**0.41**	<0.02	<0.02	<0.002	<0.02
Yakima R. @ Rinehart Park	03/31/99	**1.3**	**0.36**	<0.02	<0.02	<0.002	<0.02
	05/11/99	<0.4	**0.27**	<0.02	<0.02	<0.002	<0.02
	07/13/99	**0.69**	**0.16**	<0.02	<0.02	<0.002	<0.02
	09/15/99	<0.4	**0.35**	<0.02	<0.02	<0.002	<0.02
	11/09/99	<0.5	**0.21**	<0.02	<0.02	<0.002	<0.05
	01/25/00	<0.4	**0.25**	<0.02	<0.02	<0.002	<0.02
Wilson Creek @ mouth	03/31/99	**0.76**	**0.71**	<0.02	<0.02	<0.002	<0.02
	05/11/99	**1.5**	**1.1**	<0.02	<0.02	**0.0033**	<0.02
	07/13/99	**0.92**	**1.4**	<0.02	<0.02	**0.0031**	<0.02
	09/15/99	<0.4	**0.78**	<0.02	<0.02	<0.002	<0.02
	11/09/99	**1.5**	**0.60**	**0.092**	<0.02	<0.002	<0.05
	01/25/00	**0.52**	**0.88**	<0.02	<0.02	**0.0025**	<0.02
Yakima River @ Umtanum	03/31/99	**1.8**	**0.39**	<0.02	<0.02	<0.002	<0.02
	05/11/99	**1.2**	**0.60**	<0.02	<0.02	**0.0022**	<0.02
	07/13/99	**0.64**	**0.32**	<0.02	<0.02	**0.0019**	<0.02
	09/15/99	<0.4	**0.54**	<0.02	<0.02	<0.002	<0.02
	11/09/99	**0.76**	**0.33**	<0.02	<0.02	<0.002	<0.05
	01/25/00	**1.8**	**0.49**	<0.02	<0.02	<0.002	<0.02

Metals detections highlighted in **BOLD**

Table 10. Summary Statistics on Metals Concentrations, Upper Yakima River, 03/99 - 01/00 (ug/L)

Location	Zinc			Copper			Lead		
	median	max.	det. freq.	median	max.	det. freq.	median	max.	det. freq.
Yakima @ Cle Elum	**0.46**	**2.1**	3/6	**0.20**	**0.26**	6/6	<0.02	<0.02	0/6
Crystal Creek	**1.3**	**1.9**	6/6	**2.0**	**2.3**	6/6	<0.02	**0.099**	4/6
Swauk Creek	**0.67**	**1.8**	6/6	**0.45**	**0.97**	6/6	<0.02	**0.056**	2/6
Yakima @ Rinehart Park	**0.50**	**1.3**	2/6	**0.26**	**0.36**	6/6	<0.02	<0.02	0/6
Wilson Creek	**0.84**	**1.5**	5/6	**0.83**	**1.4**	6/6	<0.02	**0.092**	1/6
Yakima @ Umtanum	**1.0**	**1.8**	5/6	**0.44**	**0.60**	6/6	<0.02	<0.02	0/6

Location	Cadmium			Mercury			Silver		
	median	max.	det. freq.	median	max.	det. freq.	median	max.	det. freq.
Yakima @ Cle Elum	<0.02	<0.02	0/6	<0.002	<0.002	0/6	<0.02	<0.05	0/6
Crystal Creek	<0.02	**0.025**	1/6	**0.0024**	**0.0053**	3/6	<0.02	<0.05	0/6
Swauk Creek	<0.02	<0.02	0/6	**0.0022**	**0.0045**	3/6	<0.02	<0.05	0/6
Yakima @ Rinehart Park	<0.02	<0.02	0/6	<0.002	<0.002	0/6	<0.02	<0.05	0/6
Wilson Creek	<0.02	<0.02	0/6	**0.0022**	**0.0033**	3/6	<0.02	<0.05	0/6
Yakima @ Umtanum	<0.02	<0.02	0/6	<0.002	**0.0022**	2/6	<0.02	<0.05	0/6

Detections highlighted in **BOLD.**

Zinc and copper were routinely detectable in both the main stem and tributaries. The lowest concentrations tended to occur in the late summer and fall. March and January were the months with the highest zinc and copper concentrations in the main stem, except for copper levels at Umtanum which were slightly higher during the spring and summer.

Copper concentrations showed a significant increase ($p<0.05$, Kruskal-Wallis) going downstream from Cle Elum (r.m. 183) to Rinehart Park (r.m. 153) to Umtanum (r.m. 140), where median concentrations were 0.20, 0.26, and 0.44 ug/L, respectively. The highest copper concentrations occurred in Crystal and Wilson creeks, with median values of 2.0 and 0.83 ug/L, respectively. The copper loading from Wilson Creek was sufficient to account for about half of the increase in copper concentrations between the Yakima at Rinehart Park and at Umtanum. The copper loads in Crystal Creek were too low to influence copper levels in the river. Several other tributaries and the Ellensburg and Cle Elum WWTPs are possible copper contributors between Cle Elum and Umtanum.

Zinc concentrations were generally comparable in the main stem and tributaries. Zinc was not quantified consistently enough to identify any downstream trend. Detection was more frequent in the tributaries than in the main stem, with overall median concentrations ranging from 0.50 to 1.3 ug/L.

Lead, cadmium, and mercury were only detected in the tributaries, except for a trace of mercury in the Yakima at Umtanum in May and July, 0.0019 - 0.0022 ug/L. The detections primarily occurred in the spring to mid-summer. Most of the cadmium and mercury concentrations reported were near the detection limit.

The highest lead concentrations, 0.037 - 0.099 ug/L, were observed in Crystal Creek. Lead was detected more frequently in Crystal Creek, 4 of 6 samples, than in Swauk Creek, 2 of 6 samples, or Wilson Creek, 1 of 6 samples. Crystal Creek also had the only detection of cadmium, 0.025 ug/L in March.

Half of the samples from Crystal, Swauk, and Wilson creeks had detectable amounts of mercury. The levels appeared comparable, with the concentrations detected ranging from 0.0023 to 0.0053 ug/L.

Silver was not detected in the Yakima main stem or in tributaries at or above 0.02 - 0.05 ug/L.

Water Quality Standards

Table 11 shows how the metals concentrations Ecology measured in the upper Yakima drainage compare to Washington State water quality standards (173-201A WAC). The standards for zinc, copper, lead, cadmium, and silver vary with hardness, metals toxicity generally decreasing with increasing hardness. Equations for calculating hardness dependent standards are in Appendix A.

As shown in Table 11, no exceedances of state standards were encountered in the present study, either in the main stem or in the tributaries. In most instances, metals concentrations were an order of magnitude or more below the standards for chronic exposure.

Figure 4 shows in more detail how concentrations of the most frequently detected metals – zinc, copper, lead, and mercury – compare to the chronic standards. The hardness recorded for each sample was used to calculate the zinc, copper, and lead standards. In this figure, metals concentration:standard ratios greater than 1.0 would exceed the chronic standard. The detection limit was used to calculate the ratio for non-detected values. The metals that came closest to standards were copper and mercury in Crystal and Swauk creeks, where maximum concentrations were about 1/3 to 1/2 the standard.

USGS Data

Tables 12 and 13 show the USGS historical data behind the 303(d) metals listings for dissolved copper, cadmium, mercury, and silver in the upper Yakima River (Fuhrer et al., 1994). Concentrations exceeding current state water quality standards are highlighted. The number of exceedances shown for cadmium and silver are fewer than indicated on the 1998 303(d) list,

Table 11. Ranges in Metals Concentrations and Associated State Water Quality Standards, Upper Yakima River, 03/99 - 01/00 (ug/L)

Metal	Main Stem (n = 18)	Tributaries (n = 18)
Zinc concentrations	<0.4 - 2.1	<0.4 - 1.9
Chronic standards	30 - 68	74 - 161
Acute standards	33 - 75	80 - 176
Copper concentrations	0.12 - 0.60	0.23 - 2.3
Chronic standards	3.2 - 7.4	8.0 - 18
Acute standards	4.3 - 11	12 - 27
Lead concentrations	<0.02	<0.02 - 0.099
Chronic standards	0.5 - 1.5	1.6 - 4.3
Acute standards	13 - 38	41 - 112
Cadmium concentrations	<0.02	<0.02 - 0.025
Chronic standards	0.35 - 0.72	0.77 - 1.5
Acute standards	0.75 - 2.2	2.4 - 6.4
Mercury concentrations	<0.002 - 0.0022	<0.002 - 0.0053
Chronic standard	0.012	0.012
Acute standard	2.1	2.1
Silver concentrations	<0.02	<0.02
Chronic standards	- -	- -
Acute standards	0.28 - 1.5	1.7 - 8.2

There is no chronic state standard for silver. Standards ranges shown are for minimum and maximum hardness values.

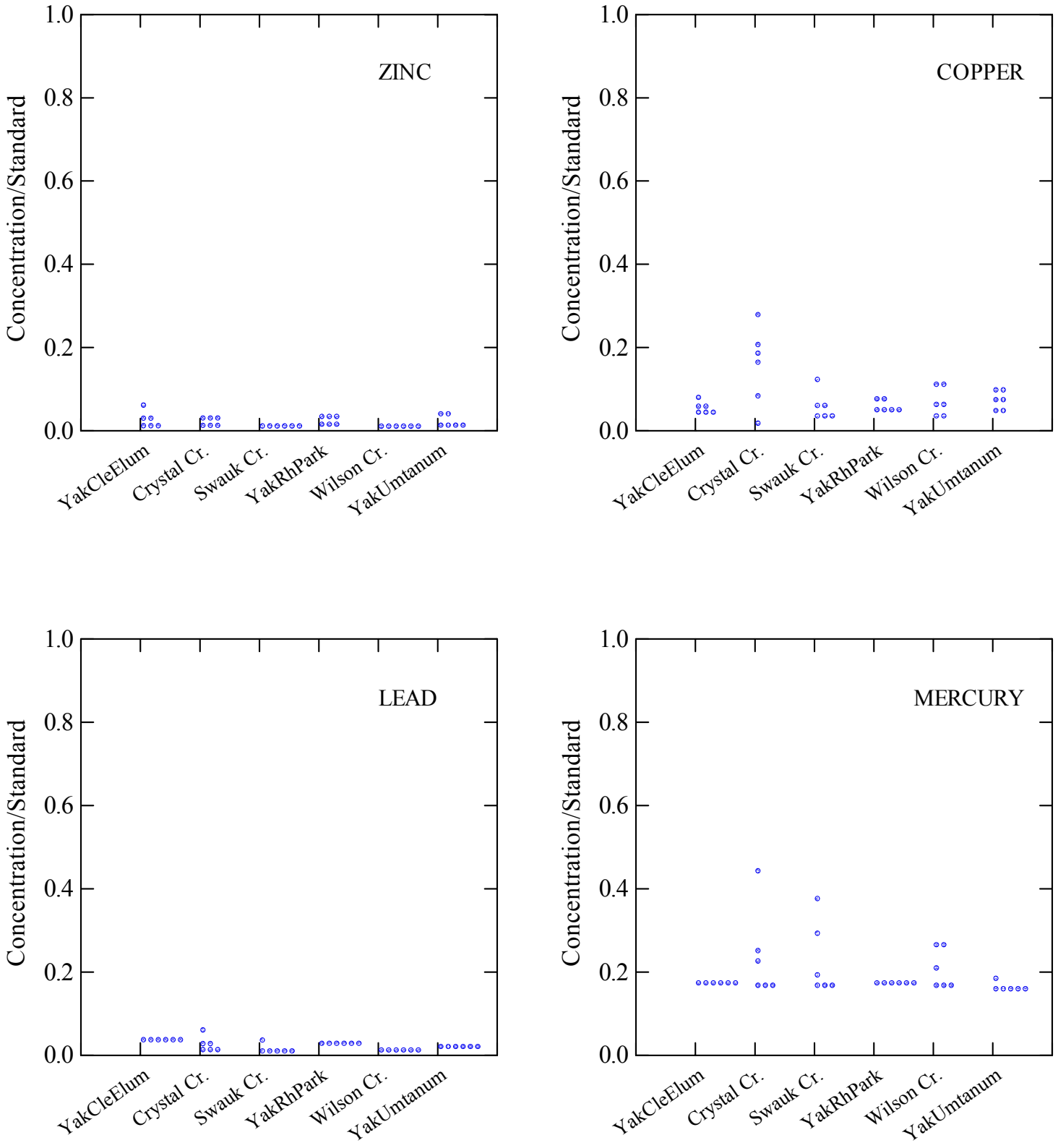


Figure 4. Metals Concentrations Compared to State Chronic Water Quality Standards (Ratios >1 would exceed standards; detection limit used for non-detected values.)

Table 12. USGS Historical Data on Dissolved Metals Exceeding State Standards in the Yakima River @ Cle Elum (station 12479500; from Fuhrer et al., 1994) (ug/L)

Date	Hardness	Copper	Cadmium	Mercury	Silver
04/14/87	26	<0.5	**0.4**	<0.1	- -
04/30/87	24	<0.5	<0.1	<0.1	<1
05/12/87	24	<0.5	<0.1	<0.1	- -
06/11/87	22	**0.7**	**0.4**	<0.1	- -
07/14/87	21	<0.5	**0.3**	**0.6**	- -
08/10/87	21	<0.5	**0.2**	<0.1	<1
09/08/87	22	**1.5**	<0.1	<0.1	- -
11/10/87	35	<0.5	<0.1	<0.1	<1
12/07/87	32	<0.5	<0.1	<0.1	- -
01/12/88	30	<0.5	**1.5**	<0.1	- -
02/09/88	28	**0.5**	<0.1	<0.1	- -
03/08/88	30	<0.5	**0.1**	<0.1	- -
04/12/88	28	<0.5	**0.1**	<0.1	- -
04/16/88	23	<0.5	**0.2**	<0.1	- -
05/10/88	25	**0.8**	**0.2**	<0.1	- -
06/14/88	24	**1.4**	**0.4**	<0.1	- -
07/12/88	21	**0.8**	**0.1**	<0.1	- -
08/09/88	22	<0.5	**0.1**	<0.1	- -
09/13/88	25	**0.6**	**0.2**	<0.1	- -
09/20/88	27	<0.8	**0.2**	<0.1	- -
09/20/88	27	<10	<0.1	<0.1	<1
09/21/88	- -	**0.6**	**0.2**	<0.1	**1**
10/11/88	27	**0.8**	**0.2**	<0.1	- -
11/08/88	26	**1.2**	**0.2**	<0.1	- -
12/13/88	24	**0.9**	**0.2**	**0.2**	- -
01/12/89	28	<0.5	**0.2**	<0.1	- -
01/31/89	36	**1.5**	**0.1**	<0.1	- -
02/14/89	32	**0.6**	<0.1	<0.1	- -
03/14/89	34	**1.6**	**0.4**	<0.1	- -
04/06/89	24	**0.9**	<0.2	<0.1	- -
04/11/89	26	**1.0**	<0.2	<0.1	- -
05/09/89	20	**2.0**	**0.3**	<0.1	- -
06/13/89	24	**1.2**	<0.1	<0.1	- -
07/11/89	22	**1.1**	<0.1	<0.1	- -
08/09/89	22	**0.5**	<0.1	<0.1	- -
09/12/89	26	<0.5	<0.1	<0.1	- -
10/11/89	27	**0.6**	<0.1	<0.1	- -
11/14/89	24	**14**	**0.7**	<0.1	- -
12/12/89	27	**7.4**	<0.1	<0.1	- -
01/09/90	26	**5.3**	**0.1**	<0.1	- -
01/10/90	21	**3.0**	**0.1**	<0.1	<1
02/13/90	27	**6.3**	<0.1	<0.1	- -
03/13/90	32	**2.8**	<0.1	<0.1	- -

Detections highlighted in **BOLD.** Concentrations exceeding current standards are in boxes.

Table 13. USGS Historical Data on Dissolved Metals Exceeding State Standards in the Yakima River @ Umtanum (station 12484500; from Fuhrer et al., 1994) (ug/L)

Date	Hardness	Copper	Cadmium	Mercury	Silver
04/15/87	43	**1.0**	**0.5**	<0.1	- -
05/01/87	46	**2.1**	**1.2**	<0.1	<1
06/10/87	41	**1.7**	**0.2**	<0.1	- -
07/15/87	33	**1.8**	<0.1	**0.2**	- -
08/18/87	35	**1.0**	<0.1	<0.1	**1**
09/09/87	44	**2.7**	**1.2**	<0.1	- -
12/09/87	68	**1.0**	<0.1	<0.1	- -
01/13/88	70	**0.6**	<0.1	<0.1	- -
02/10/88	54	**1.1**	<0.1	<0.1	- -
03/08/88	58	<10	**1.0**	<0.1	**1**
03/09/88	54	**0.8**	**0.2**	<0.1	- -
04/13/88	49	**0.6**	**0.2**	<0.1	- -
04/15/88	39	**0.7**	**0.1**	<0.1	- -
05/11/88	54	**1.0**	<0.1	<0.1	- -
06/15/88	45	**1.2**	**0.2**	<0.1	- -
07/13/88	- -	**1.2**	**0.1**	<0.1	- -
08/10/88	34	<0.5	**0.3**	<0.1	- -
09/14/88	61	**1.4**	**0.3**	<0.1	- -
09/21/88	61	**1.4**	<0.1	<0.1	<1
09/22/88	66	**0.7**	<0.1	<0.1	<1
09/22/88	66	**0.9**	<0.1	<0.1	<1
10/12/88	68	**1.3**	**0.2**	<0.1	- -
11/09/88	51	**0.5**	**0.3**	<0.1	- -
12/14/88	41	**1.0**	**0.3**	<0.1	- -
01/11/89	50	**1.4**	**0.1**	**0.2**	- -
01/31/89	42	**1.6**	**2.1**	<0.1	- -
02/15/89	56	<0.5	<0.1	<0.1	- -
03/15/89	60	**1.9**	**0.5**	<0.1	- -
04/06/89	42	**1.3**	<0.2	**0.6**	- -
04/12/89	45	**1.6**	<0.2	<0.1	- -
05/10/89	35	**1.4**	**0.1**	<0.1	- -
06/14/89	42	**0.7**	<0.1	<0.1	- -
07/12/89	34	<0.5	<0.1	<0.1	- -
08/10/89	37	**2.2**	**0.1**	<0.1	- -
09/13/89	59	**0.8**	<0.1	<0.1	- -
10/12/89	59	**20**	**0.2**	<0.1	- -
11/15/89	46	**7.0**	**0.2**	<0.1	- -
12/05/89	41	**4.6**	**0.2**	<0.1	<1
12/13/89	50	**4.1**	<0.1	<0.1	- -
01/10/90	42	**2.5**	<0.1	<0.1	- -
02/14/90	43	**3.7**	**0.1**	<0.1	- -
03/13/90	54	**0.7**	<0.1	<0.1	- -

Detections highlighted in **BOLD.** Concentrations exceeding current standards are in boxes.

because those exceedances were based on older EPA criteria for unfiltered water samples, which USGS used as screening values for their dissolved metals data.

The validity and usefulness of the USGS data set is questionable for a number of reasons:

- The limits of detection for cadmium, mercury, and silver are not low enough to measure typical concentrations in river water (see following discussion). With regard to mercury, USGS has reviewed these data and cautions against "concluding the presence of mercury in dissolved form" due to "the infrequent occurrence of filtered mercury in this basin and the affinity of mercury to contaminate samples between the time of collection and processing in the laboratory" (Fuhrer, 2000).

- The cadmium levels reported as routinely being present in the upper river are an order of magnitude above concentrations found in other Columbia River tributaries, including the lower Yakima River (see following discussion.) USGS cautions against concluding that the data are unreasonable based in part on cadmium enrichment in suspended sediment and aquatic biota in the upper basin (Fuhrer, 2000).

- No filter blanks were analyzed for mercury or silver.

- No filter blanks were analyzed for copper or cadmium for sampling done prior to March 1989. All but one of the cadmium violations occurred prior to this date. According to USGS, there were no substantive changes in sample collection or cleaning procedures prior to March 1989, and they consider the March 1989 field blank data to apply to the samples collected prior to that date (Fuhrer, 2000).

- Analysis of standard reference material (SRM) included only one measurement for silver (Table 14). The certified concentration, 7 ug/L, was far above the near detection limit levels reported to have exceeded standards in Fuhrer et al. (1994).

- SRM accuracy was poor for cadmium and mercury. Because of the much lower levels of detection, the August 1989 SRM data for mercury do not apply to the upper Yakima data. USGS suspects, but could not verify, that the August 1989 SRM result reported for mercury is a typographical error and should read <0.1 ug/L (Fuhrer, 2000).

Although the USGS data for copper are biased high, no reason could be found to discount their finding elevated copper concentrations during the winter of 1989-90. The high copper levels measured one day apart at Cle Elum (14 ug/L) and Umtanum (7.0 ug/L) during November 1989 were attributed to an early winter storm that affected the Kittitas Valley (Fuhrer et al., 1996). Storms later that year were also suggested as the cause of several other elevated copper measurements at Cle Elum in the range of 3.0 to 7.4 ug/L. USGS had no explanation for the high copper value of 20 µg/L reported for Umtanum in October 1989 (copper was not elevated at Cle Elum the day before) other than to suggest a local anthropogenic source. Storm events were not sampled in the present study by Ecology.

Table 14. Results Reported by USGS (Fuhrer et al., 1994) on Standard Reference Materials Analyzed in Connection with 1987-1990 Metals Samples from the Yakima River (ug/L)

	Copper	Cadmium	Silver	Mercury	
certified value =	16.8	16.3	7	0.9	
11/87 result	20	17	6	na	
10/88 result	15	32	na	0.7	
03/89 result	14	17	na	1.79	
certified value =	1.0	0.24	nr	0.67	0.49
03/88 result	1.6	0.3	nr	0.6	- -
05/88 result	1.3	<0.1	nr	- -	0.9
certified value =	2.2	nr	nr	0.14	
05/89 result	2.7	nr	nr	<.1	
certified value =	0.168	0.163	nr	0.01	
08/89 result	<.5	<.1	nr	0.01	

na = not analyzed
nr = not reported

USGS recently began a new round of sampling in the Yakima basin as part of the NAWQA program. As of this writing, the available metals data consist of a single set of samples collected in August 1999 at the Yakima River at Cle Elum, Wilson Creek, Cherry Creek (tributary to lower Wilson Creek), and the Yakima River at Umtanum. The results (Table 15) show dissolved lead, cadmium, and silver were not detectable (<1.0 ug/L). Low concentrations of dissolved zinc and copper, 1.3 - 2.0 ug/L, were detected in Wilson and/or Cherry creeks. These findings are consistent with results from the present study. Mercury was not analyzed.

Metals Concentrations in the Columbia River Drainage

Table 16 summarizes the data Ecology has obtained since 1994 on concentrations of dissolved zinc, copper, lead, cadmium, and total mercury in the Columbia River main stem and tributaries, including the lower Yakima River. Sampling and analytical methods were similar to the present study. Most of these samples were analyzed by Manchester Laboratory. The lower Yakima and Columbia River at Warrendale data were from samples collected by Ecology but analyzed by the Battelle Marine Sciences Laboratory in Sequim, Washington. No silver data were available for comparison to the present study.

Table 15. USGS Data on Dissolved Metals in Water Samples Collected August 2, 1999 (ug/L) [provided by Curt Hughes, USGS, Portland, OR]

Location	Zinc	Copper	Lead	Cadmium	Mercury	Silver
Yakima River @ Cle Elum	<1	<1	<1	<1	na	<1
Wilson Cr. above Cherry Cr.	<1	**1.3**	<1	<1	na	<1
Cherry Creek	**1.5**	**2.0**	<1	<1	na	<1
Yakima River @ Umtanum	<1	<1	<1	<1	na	<1

Detections highlighted in **BOLD**
na = not analyzed

These data show that dissolved metals concentrations in the Columbia River drainage are typically low and broadly comparable between sampling sites. Except for a mercury outlier in the Walla Walla River data, the only location where state standards have been violated is the Spokane River, which is subject to contamination from the Coeur d'Alene Mining District in Idaho. Historically, there were also standards violations in the Columbia River at Northport, due to discharges from the Cominco lead-zinc smelter in Trail, British Columbia.

A number of natural factors act to limit the concentrations of dissolved metals in rivers, such as binding to organic or inorganic compounds and adsorption to sediment particles and other surfaces (Renner, 1997). A pH above neutral, characteristic of the Yakima River and other Columbia River tributaries, also favors adsorption. In the absence of large sources of contamination, exceedances of the dissolved metals standards are not commonly encountered in major rivers like the upper Yakima.

Table 16. Summary of Ecology Data on Metals Concentrations in the Columbia River Drainage (ug/L) [medians (90th percentile); dissolved metals except total mercury]

Location	Zinc	Copper	Lead	Cadmium	Mercury
Columbia R. @ Northport[a]	3.0	0.84	0.069	0.040	<0.001
(n=29; 43 for mercury)	(4.1)	(1.6)	(0.23)	(0.078)	(0.003)
Spokane R. @ Stateline[a]	78	0.52	0.23	0.28	<0.002
(n=38; 34 for mercury)	(103)	(0.75)	(1.5)	(0.37)	(0.003)
Similkameen R. @ Nighthawk[a]	1.2	0.97	0.03	<0.02	<0.002
(n=13)	(4.0)	(2.3)	(0.31)	(0.040)	(0.003)
Wenatchee R. @ Wenatchee[a]	2.9	0.45	0.03	<0.02	<0.002
(n=8)	(14)	(1.0)	(0.14)	(0.025)	(0.003)
Columbia R. near Vernita[a]	2.9	0.92	0.075	<0.04	<0.002
(n=12)	(5.4)	(1.2)	(0.20)	(0.063)	(0.002)
Yakima @ Cle Elum[b]	0.46	0.20	<0.02	<0.02	<0.002
(n=6)	(1.6)	(0.24)	(<0.02)	(<0.02)	(<0.002)
Yakima @ Umtanum[b]	1.0	0.44	<0.02	<0.02	<0.002
(n=6)	(1.8)	(0.57)	(<0.02)	(<0.02)	(0.0021)
Yakima R. @ Kiona[c]	1.3	0.82	0.072	0.005	na
(n=4)	(1.8)	(1.1)	(0.10)	(0.007)	na
Walla Walla R. near Touchet[a]	0.98	1.1	0.13	0.020	<0.002
(n=6)	(1.2)	(1.4)	(0.79)	(0.029)	(0.022)
Columbia R. @ Umatilla[a]	1.4	1.0	0.046	<0.04	<0.001
(n=6)	(4.4)	(1.1)	(0.14)	(0.060)	(<0.002)
Cowlitz R. @ Kelso[a]	1.2	0.74	<0.03	<0.03	<0.001
(n=11)	(5.0)	(0.98)	(0.051)	(<0.04)	(0.010)
Columbia R. @ Warrendale[d]	0.26*	0.81*	0.040*	0.012*	<0.001
(n=6)	- -	- -	- -	- -	- -

[a]1994 - 1999 routine monitoring data, Ecology Environmental Assessment Program
[b]Present study
[c]Johnson (1994) na = not analyzed
[d]Johnson and Hopkins (1991) *blank corrected data

Recommendation

Remove the upper Yakima River from the 303(d) list for historically reported violations of the state water quality standards for copper, cadmium, mercury, and silver.

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Appendix A. Formulas for Washington State Standards Metals Criteria (WAC 173-201A)

Cadmium - acute = $(1.136672-[(\ln \text{hardness})(0.041838)])(e^{(1.128[\ln(\text{hardness})]-3.828)})$

Cadmium - chronic = $(1.101672-[(\ln \text{hardness})(0.041838)])(e^{(0.7852[\ln(\text{hardness})]-3.490)})$

Copper - acute = $(0.960)(e^{(0.9422[\ln(\text{hardness})]-1.464)})$

Copper - chronic = $(0.960)(e^{(0.8545[\ln(\text{hardness})]-1.465)})$

Lead - acute = $(1.46203-[(\ln \text{hardness})(0.145712)])(e^{(1.273[\ln(\text{hardness})]-1.460)})$

Lead - chronic = $(1.46203-[(\ln \text{hardness})(0.145712)])(e^{(1.273[\ln(\text{hardness})]-4.705)})$

Silver - acute = $(0.85)(e^{(1.72[\ln(\text{hardness})]-6.52)})$

Zinc - acute = $(0.978)(e^{(0.8473[\ln(\text{hardness})]+0.8604)})$

Zinc - chronic = $(0.986)(e^{(0.8473[\ln(\text{hardness})]+0.7614)})$

Appendix B. Dept. of Ecology Yakima River Data from Verification Sampling for 303(d) Metals Listings
[Metals analyzed as dissolved (0.45 micron filtered), except for total mercury.]

Location/Sample Type	Sampling Date	Sample Number	Flow (cfs)	Temp. (°C)	Cond. (umhos/cm)	TSS (mg/L)	Hardness (mg/L)	Zinc (ug/L)	Copper (ug/L)	Silver (ug/L)	Cadmium (ug/L)	Lead (ug/L)	Mercury (ug/L)
Yakima R. @ Cle Elum	03/31/99	138105	1790	2.9	64	2	27	**2.1**	**0.21**	<0.02	<0.02	<0.02	<0.002
	05/11/99	198020	1610	6.0	65	2	29	**1.1**	**0.16**	<0.02	<0.02	<0.02	<0.002
	07/13/99	288015	3770	4.0	50	2	23	**0.41**	**0.12**	<0.02	<0.02	<0.02	<0.002
	09/15/99	378022	1170	11.9	69	<1	30	<0.4	**0.19**	<0.02	<0.02	<0.02	<0.002
	11/09/99	458031	710	7.6	67	1	30	<0.5	**0.22**	<0.05	<0.02	<0.02	<0.002
	01/25/00	048131	1060	2.4	55	<1	24	<0.4	**0.26**	<0.02	<0.02	<0.02	<0.002
Crystal Creek @ mouth	03/31/99	138106	21	4.4	409	57	69	**1.8**	**2.3**	<0.02	**0.025**	**0.099**	<0.002
	05/11/99	198021	2.6	6.0	487	3	82	**1.1**	**1.8**	<0.02	<0.02	**0.054**	**0.0027**
	07/13/99	288016	0.5	5.0	700	2	106	**0.79**	**1.1**	<0.02	<0.02	**0.042**	**0.0028**
	09/15/99	378020	0.5	12.5	274	2	126	**0.67**	**0.23**	<0.02	<0.02	<0.02	<0.002
	11/09/99	458030	0.9	6.7	486	<1	124	**1.5**	**2.2**	<0.05	<0.02	**0.067**	<0.002
	01/25/00	048130	1.0	1.8	490	3	99	**1.9**	**2.3**	<0.02	<0.02	<0.02	**0.0053**
Crystal Creek @ mouth - rep.	07/13/99	288024	0.5	na	701	<1	110	**0.84**	**1.0**	<0.02	<0.02	**0.035**	**0.0030**
	09/15/99	378021	0.5	na	274	3	124	**0.69**	**0.23**	<0.02	<0.02	<0.02	<0.002
	11/09/99	458036	0.9	na	488	<1	123	**1.8**	**2.3**	<0.05	<0.02	**0.081**	<0.002
Swauk Creek @ mouth	03/31/99	138107	127	3.1	170	10	81	**1.8**	**0.61**	<0.02	<0.02	**0.021**	<0.002
	05/11/99	198022	117	4.8	148	8	67	**0.83**	**0.48**	<0.02	<0.02	<0.02	**0.0035**
	07/13/99	288017	14	4.8	147	2	66	**1.4**	**0.97**	<0.02	<0.02	**0.056**	**0.0045**
	09/15/99	378023	1.4	16.0	184	<1	80	<0.4	**0.39**	<0.02	<0.02	<0.02	<0.002
	11/09/99	458032	10	6.5	190	<1	89	<0.5	**0.29**	<0.05	<0.02	<0.02	**0.0023**
	01/25/00	048132	27	0.4	193	<1	89	<0.4	**0.41**	<0.02	<0.02	<0.02	<0.002
Yakima R. @ Rinehart Park	03/31/99	138108	3000	3.7	93	7	40	**1.3**	**0.36**	<0.02	<0.02	<0.02	<0.002
	05/11/99	198023	2550	7.3	89	4	41	<0.4	**0.27**	<0.02	<0.02	<0.02	<0.002
	07/13/99	288018	4130	4.7	58	7	27	**0.69**	**0.16**	<0.02	<0.02	<0.02	<0.002
	09/15/99	378024	650	16.2	82	1	35	<0.4	**0.35**	<0.02	<0.02	<0.02	<0.002
	11/09/99	458033	880	7.9	78	1	35	<0.5	**0.21**	<0.05	<0.02	<0.02	<0.002
	01/25/00	048133	1221	2.5	71	<1	31	<0.4	**0.25**	<0.02	<0.02	<0.02	<0.002

Appendix B. Yakima River Data (continued)

Location/Sample Type	Sampling Date	Sample Number	Flow (cfs)	Temp. (°C)	Cond. (umhos/cm)	TSS (mg/L)	Hardness (mg/L)	Zinc (ug/L)	Copper (ug/L)	Silver (ug/L)	Cadmium (ug/L)	Lead (ug/L)	Mercury (ug/L)
Wilson Creek @ mouth	03/31/99	138109	200	6.2	242	20	102	**0.76**	**0.71**	<0.02	<0.02	<0.02	<0.002
	05/11/99	198024	638	9.1	223	41	95	**1.5**	**1.1**	<0.02	<0.02	<0.02	**0.0033**
	07/13/99	288022	198	6.1	246	27	104	**0.92**	**1.4**	<0.02	<0.02	<0.02	**0.0031**
	09/15/99	378025	313	15.3	232	19	101	<0.4	**0.78**	<0.02	<0.02	<0.02	<0.002
	11/09/99	458034	124	10.4	380	7	166	**1.5**	**0.60**	<0.05	<0.02	**0.092**	<0.002
	01/25/00	048134	110	4.6	358	10	146	**0.52**	**0.88**	<0.02	<0.02	<0.02	**0.0025**
Yakima River @ Umtanum	03/31/99	138110	2915	4.8	107	7	46	**2.1**	**0.38**	<0.02	<0.02	<0.02	<0.002
	05/11/99	198025	3300	9.4	157	5	60	**0.81**	**0.59**	<0.02	<0.02	<0.02	<0.002
	07/13/99	288023	4510	5.8	75	7	34	**0.64**	**0.32**	<0.02	<0.02	<0.02	**0.0019**
	09/15/99	378026	1430	16.8	132	5	58	<0.4	**0.54**	<0.02	<0.02	<0.02	<0.002
	11/09/99	458035	1070	8.4	128	2	57	**1.1**	**0.31**	<0.05	<0.02	<0.02	<0.002
	01/25/00	048135	1479	2.6	101	2	42	**1.8**	**0.49**	<0.02	<0.02	<0.02	<0.002
Yakima River @ Umtanum - rep.	03/31/99	138111	2915	na	107	6	45	**1.5**	**0.40**	<0.02	<0.02	<0.02	<0.002
	05/11/99	198026	3300	na	160	5	62	**1.6**	**0.60**	<0.02	<0.02	<0.02	**0.0023**
	01/25/00	048136	1479	na	101	2	43	**0.41**	**0.35**	<0.02	<0.02	<0.02	<0.002
Filter Blank	03/31/99	138113	na	na	na	na	na	**1.2**	<0.05	<0.02	<0.02	<0.02	na
	07/13/99	288019	na	na	na	na	na	**3.0**	<0.1	<0.02	<0.02	<0.02	<0.002
	11/09/99	458038	na	na	na	na	na	<0.5	<0.05	<0.05	<0.02	<0.02	na
Bottle Blank	03/31/99	138114	na	na	na	na	na	**0.48**	<0.05	<0.02	<0.02	<0.02	<0.002
	07/13/99	288020	na	na	na	na	na	**2.4**	<0.1	<0.02	<0.02	<0.02	<0.002
	11/09/99	458037	na	na	na	na	na	<3	<0.1	na	<0.1	<0.1	**0.0023**
Laboratory Method Blank	03/31/99	- -	na	na	na	na	<0.2	**0.52**	<0.05	<0.02	<0.02	<0.02	<0.002
	05/11/99	- -	na	na	na	na	<0.4	**0.52**	<0.05	<0.02	<0.02	<0.02	<0.002
	07/13/99	- -	na	na	na	na	<0.2	<0.4	<0.1	<0.02	<0.02	<0.02	<0.002
	09/15/99	- -	na	na	na	na	<0.3	<0.4	<0.05	<0.05	<0.02	<0.02	<0.002
	11/09/99	- -	na	na	na	na	<0.2	<0.5	<0.05	<0.05	<0.02	<0.02	<0.002
	01/25/00	- -	na	na	na	na	<0.2	<0.4	<0.05	<0.02	<0.02	<0.02	<0.002

Appendix B. Yakima River Data (continued)

Location/Sample Type	Sampling Date	Sample Number	Flow (cfs)	Temp. (^{o}C)	Cond. (umhos/cm)	TSS (mg/L)	Hardness (mg/L)	Zinc (ug/L)	Copper (ug/L)	Silver (ug/L)	Cadmium (ug/L)	Lead (ug/L)	Mercury (ug/L)
Standard Reference Material	03/31/99	- -	na	na	na	na	na	**3.56**	**1.44**	<0.02	**0.095**	**0.070**	na
	05/11/99	- -	na	na	na	na	na	**1.67**	**1.41**	<0.02	**0.020**	**0.065**	na
	07/13/99	- -	na	na	na	na	na	**1.30**	**1.38**	<0.02	**0.026**	**0.065**	na
	09/15/99	- -	na	na	na	na	na	**1.20**	**1.41**	<0.05	**0.017**	**0.066**	na
	11/09/99	- -	na	na	na	na	na	**1.20**	**1.41**	<0.05	**0.017**	**0.066**	na
	01/25/00	- -	na	na	na	na	na	na	na	na	na	na	na
						Certified value =		1.04	1.35	nc	0.013	0.068	nc
Laboratory Control Sample (%)	03/31/99	- -	na	na	na	na	103	102	99	94	94	93	85
	05/11/99	- -	na	na	na	na	102	103	97	93	95	95	106
	07/13/99	- -	na	na	na	na	98	111	95	94	100	129	100
	09/15/99	- -	na	na	na	na	108	86	96	99	101	97	97
	11/09/99	- -	na	na	na	na	99	86	96	99	101	97	98
	01/25/00	- -	na	na	na	na	101	99	104	106	107	104	93
Matrix Spike Recovery (%)	03/31/99	138110	na	na	na	na	na	99	94	91	94	94	119
	07/13/99	288024	na	na	na	na	na	87	90	85	89	96	98
Matrix Spike Dup. Rec. (%)	03/31/99	138110	na	na	na	na	na	100	95	91	94	94	117
	07/13/99	288024	na	na	na	na	na	87	90	84	89	94	95

Note: Metals detections highlighted in **BOLD**
na = not analyzed or not applicable
nc = not certified