WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

ZINC, COPPER, LEAD, AND CADMIUM CONCENTRATIONS IN FOUR WASHINGTON RIVERS

October 1994

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WA-10-1020 and WA-37-1010
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Zinc, Copper, Lead, and Cadmium Concentrations in Four Washington Rivers

by
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Acknowledgements

A number of Ecology personnel contributed valuable and much appreciated assistance during the course of this survey. Mark Hicks developed the initial study proposal. Greg Pelletier and Brad Hopkins assisted in sample collection. Bill Kammin provided technical guidance on metals analysis and data quality. Manchester Laboratory staff took extra pains to ensure the accuracy and completeness of the data. Scott Breidenbach made Figure 1. Jim Cubbage advised on preparation of graphs. Review comments by Bill Yake, Larry Goldstein, Greg Pelletier, Dale Davis, and Bill Kammin helped improve the final report.

Abstract

Total and dissolved zinc, copper, lead, and cadmium concentrations were measured in the Green, Duwamish, Puyallup, and Yakima Rivers during July 1992 - May 1993. Clean sampling techniques and a preconcentration step (APDC coprecipitation) allowed metals concentrations to be consistently quantified in all samples. The data are evaluated in terms of water quality criteria, seasonal patterns, correlations with other water quality variables, and distribution between dissolved and particulate metal.

Introduction

There is a lack of reliable information on the concentrations of metals in Washington's rivers. Most of the historical data come from the U.S. Geological Survey's (USGS) National Stream Quality Accounting Network. These data are now known to contain inaccuracies, particularly with regard to low-level concentrations of zinc, copper, lead, and cadmium (Windom *et al.*, 1991). USGS attributes this problem to sample contamination during collection (Pendergast, 1991). Additionally, the detection limits achieved by USGS and in most other investigations have often not been low enough to consistently quantify the metals of interest.

The Washington State Department of Ecology's (Ecology) Basin Planning and Standards section required better metals data to develop and determine compliance with state water quality criteria. They requested that the Environmental Investigations and Laboratory Services program conduct a survey of selected rivers using sampling and analytical methods appropriate for measuring background concentrations. The results of this effort are reported here.

The river metals survey was conducted between July 1992 and May 1993. Study objectives were as follows:

- obtain accurate data on zinc, copper, lead, and cadmium concentrations in rivers with substantially different water quality characteristics;
- assess compliance with state water quality criteria;
- identify seasonal patterns and correlations with other water quality variables;
- evaluate distribution between dissolved and particulate metals; and
- make recommendations on metals sampling and analysis for future agency investigations (Appendix A).

Four stations from Ecology's Ambient Monitoring network were selected for study (Figure 1). These were the Green River @ Kanaskat, Duwamish River @ Tukwila, Puyallup River @ Meridian Street, and Yakima River @ Kiona.

The Green River above Kanaskat drains a relatively undeveloped watershed and was considered representative of background conditions in western Washington. The Duwamish River, a continuation of the Green, receives urban runoff from the Auburn-Kent-Renton area. Glaciers at the headwaters of the Puyallup cause this river to have an unusually high load of suspended solids. During summer, the lower Yakima River at Kiona consists almost entirely of irrigation return flows. This river has high pH and hardness relative to the other three.

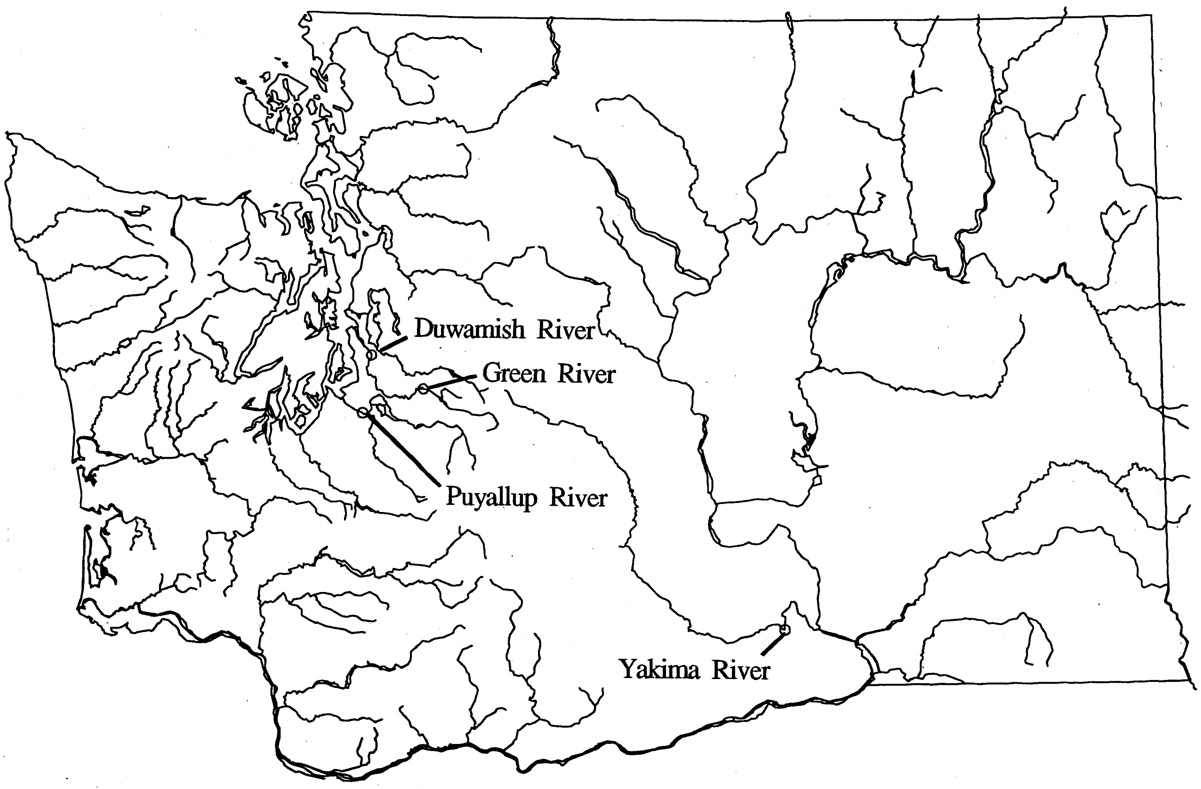

Figure 1. Sampling Sites for EILS 1992-93 Metals Survey.

Water samples were collected from each river once every other month for one year beginning in July. Zinc, copper, lead, and cadmium were analyzed as total and dissolved metals. Data were also obtained on temperature, pH, specific conductivity, total hardness, total alkalinity, total suspended solids (TSS), total dissolved solids (TDS), and total organic carbon (TOC). Samples were collected for dissolved organic carbon, but the field blanks proved too high to use the data.

Total and dissolved copper, lead, and cadmium were analyzed by coprecipitation. This refers to a preconcentration technique that allows lower detection limits than sample digestions routinely employed in most investigations.

Total metals were also analyzed using the total recoverable method. This analysis has been the method used in the majority of past studies. Although it was unlikely to detect some of the lower metal concentrations anticipated in the survey, the analysis was included because state water quality criteria were written in terms of total recoverable metals. Effective December 26, 1992, the criteria for zinc, copper, lead, cadmium, and several other metals were revised to apply to the dissolved fraction (WAC 172-201A).

Methods and Materials

Sample Collection

All samples were simple grabs collected by hand approximately one foot below the water surface. These were obtained either by wading in a few feet from the river bank or dipping with a sample bottle attached to a polyethylene pole.

Metals samples were taken in 500 mL teflon bottles. Samples for total metals were preserved with 2 mL concentrated HCl immediately on collection (0.5 mL Baker Instra-Analyzed for Trace Metals + 2 mL deionized water). Samples for dissolved metals were vacuum-filtered in the field through a 0.45 um cellulose nitrate filter unit (Nalgene #450-0045, type S) before being acidified (Figure 2). The acid was carried in small teflon vials, one per sample.

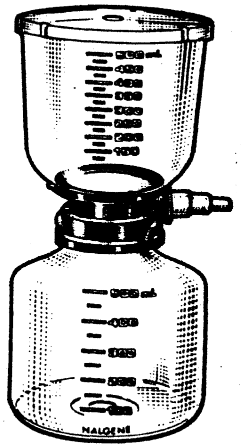

Figure 2. Filter Apparatus for Dissolved Metals.

Temperature was measured with a precision thermometer. pH values were determined with an Orion model 250A meter. Sample containers and preservation for other water quality variables are described in Huntamer and Hyre (1991). Each sample was placed in a polyethylene bag and held on ice for transport to the Ecology/EPA Manchester Environmental Laboratory.

Cleaning Procedures

Cleaning of teflon sample bottles and vials and the Nalgene filter units was done as follows: New teflon bottles and vials were soaked in hot concentrated HNO_3 for two days, cooled, then rinsed five times with deionized water and dried in a laminar flow hood. Tops were replaced and the bottles and vials stored in polyethylene bags.

Used teflon was rinsed three times in deionized water, then soaked in a 1:1 HNO_3 bath for several days. After soaking, the teflon was rinsed five times with deionized water, dried, and stored as above.

The top half of the filter unit was soaked with 5% HNO_3 for 15 minutes and the acid filtered through to the lower half of the unit. The lower half was topped up if necessary, capped, and soaked for approximately 20 minutes (inverting unit after 10 minutes). Both sections were rinsed three times with deionized water and the top half then rinsed by vacuum filtering to clean the filter. Filter units were dried in a laminar flow hood, assembled, and stored in polyethylene bags. Cleaning was done by the Battelle Marine Sciences Laboratory in Sequim, Washington.

Chemical Analysis

Battelle Laboratory

Total and dissolved copper, lead, and cadmium were analyzed at Battelle by coprecipitation with cobalt (II) ions and ammoniumpyrrolidinedithiocarbamate (APDC), and analyzed by graphite furnace atomic absorption spectroscopy (GFAA) (Bloom and Crecelius, 1984). Zinc was analyzed directly by GFAA after the sample was adjusted to pH 2. Samples for total and dissolved metals were analyzed identically by Battelle.

In brief, the coprecipitation procedure involves bringing the sample pH to 2.0 and adding 1.0 mL each of cobalt (200 mg/L) and APDC (2% w/v) solutions to 250 mL of sample. The samples are then filtered through 0.4 μm polycarbonate membrane filters, the filters digested with concentrated HNO_3, and evaporated to dryness. Next, 2.0 mL of phosphate diluting solution is added and the samples gently heated (70-80°C) to dissolve the metals on the filters. Samples are then stored until analyzed.

Manchester Laboratory

Total recoverable metals were analyzed at the Manchester Laboratory. Samples were prepared according to EPA Method 200.2, modified for GFAA analysis. Zinc was determined by inductively-coupled plasma emission spectroscopy (ICP) techniques; copper, lead, and cadmium were analyzed by GFAA.

Extra precautions were taken to reduce contamination during sample digestion. This included use of teflon beakers and watch glasses cleaned by soaking in distilled 1:1 HNO_3 and rinsed with type II deionized water. The laboratory room and hoods were cleaned prior to use specifically for this study's samples.

Samples for other water quality determinations were also analyzed at Manchester. Methods are described in Huntamer and Hyre (1991). Flow data were obtained from Morey Miles, USGS, Tacoma.

In this report, the Battelle total metals data are referred to as total/coprecipitated metals to differentiate from the total recoverable data from Manchester Laboratory.

Field Procedures to Assess Data Quality

Field Blanks

Bottle and filter blanks were analyzed every other field collection to detect contamination arising from sample containers, preservation, or handling. Bottle blanks consisted of teflon sample bottles filled with deionized water at the Battelle Laboratory and acidified in the field. Filter blanks were prepared in the field by filtering deionized water through the Nalgene units and acidifying. Because of the higher detection limits of the total recoverable method, analysis of field blanks was limited to Battelle Laboratory.

Standard Reference Materials

Each laboratory received two standard reference materials (SRM) with every set of samples. The SRMs were submitted blind to independently assess the accuracy of the analyses. The first SRM was SLRS-2, "Riverine Water Reference Material for Trace Metals," prepared by the National Research Council Canada. This material is certified for the low dissolved metals concentrations typical of uncontaminated rivers. The second SRM, National Institute of Standards and Technology's "Trace Elements in Water" (1643c), has metals concentrations one-to-two orders of magnitude above those in SLRS-2. Battelle also analyzed non-blind samples of these SRMs at their own initiative.

Replicate & Split Samples

Additional samples were analyzed to provide estimates of field and analytical variability. On alternating months at the Duwamish or Yakima River, two separate sets of samples (field replicates) were taken approximately 15 minutes apart to assess short-term changes in water quality. One set of these samples was split in the field or laboratory (duplicates) as a means of separating analytical from total (laboratory + field) variability. Metals analysis of these samples was also limited to Battelle.

Quality Assurance Review of Metals Data

Bill Kammin, director of Ecology's Manchester Laboratory, prepared written quality assurance reviews that evaluated the validity and usefulness of all metals data. The review included sample holding times, instrument calibration, procedural (method) blanks, matrix spikes and SRM analyses (Battelle data only), precision data, and laboratory control sample (LCS) analyses. A summary of Kammin's findings follows:

Total Recoverable Metals

All analyses were performed within the EPA Contract Laboratory Program (CLP) required holding time of 180 days. Initial and continuing calibration verification standards were consistently within relevant CLP control limits. AA calibration gave a correlation of .995 or greater, as required by CLP. Except for one cadmium spike with 70% recovery, recoveries and precision of spikes and spike duplicates were within the CLP acceptance limits of +/-25% and +/-20%, respectively. Laboratory control sample analyses were within the windows established for each parameter.

With one exception, procedural blanks showed no analytes at or above the instrument detection limits of 4.0 ppb zinc, 1.0 ppb copper, 1.0 ppb lead, and 0.1 ppb cadmium. The procedural blank for samples collected during November had 40 ppb zinc. November samples with zinc concentrations below this level were qualified as estimates (J flag). Samples with greater than 40 ppb zinc were qualified to indicate the blank may have contributed to the result (B flag).

Total/Coprecipitated Metals

CLP holding times were met for all analyses. Because the dissolved samples from September were accidently disposed of at Battelle before they could be analyzed, no dissolved data are available for this time period.

Continuing calibration and blanks for samples collected through January 1993 were run at a frequency of 5%, rather than the 10% called for in CLP. Spikes and LCS analyses were not requested to be run. SRM analyses showed a consistent positive bias for each metal (these data are presented under Results and Discussion).

Metal concentrations in some procedural blanks (Appendix B.5) were equivalent to or exceeded method detection limits for zinc (0.6 ppb), copper (0.025 ppb), lead (0.035 ppb), and cadmium (0.01 ppb). This trace level contamination increases the uncertainty of near detection limit measurements. All sample results less than ten times the highest blank were qualified (B). Sample results less than the highest blank value were qualified as estimates (J).

Results and Discussion

Data Set

The complete data obtained during the survey are in Appendix B. Following EPA recommendations, the metals data have not been corrected for procedural blanks. For clarity of presentation, data qualifiers shown in the Appendix B are not carried into the tables or figures. The reader should remain aware of data quality concerns described above, particularly the uncertainty of concentrations reported in the region of the detection limit.

Field Blanks

The field blank data are in Table 1. Metal concentrations in the bottle blanks prepared by Battelle were at or near detection limits for zinc, copper, lead, and cadmium. Results on filter blanks compared closely to the bottle blanks, demonstrating that the field filtering procedure did not introduce significant contamination to the samples.

Table 1. Results on field blanks (µg/L, total/coprecipitated metals).

Sample Set	Blank Type	Zinc	Copper	Lead	Cadmium
July	Bottle	0.98	0.058	0.035	0.005
	Filter	0.78	0.095	0.035	0.006
November	Bottle	0.90	0.076	0.031	0.001
	Filter	1.2	1.8	0.031	0.001
March	Bottle	1.3	0.016	0.040	0.001
	Filter	1.8	0.016	0.030	0.001

Standard Reference Materials

Table 2 summarizes the laboratories' performance on SRMs. As already noted, the total/coprecipitated analysis showed a positive bias relative to certified values. Results were typically high by approximately 1.0 μg/L zinc, 0.5 μg/L copper, 0.05 μg/L lead, and 0.01 μg/L cadmium, the bias for zinc and copper being roughly equal to the method blank.

The total recoverable analysis was the more accurate of the two methods. However, with the exception of copper, this method was unable to detect the low metals concentrations in SLRS-2.

Table 2. Summary of results on standard reference materials (μg/L, mean +/- s.d.).

Metal	Analysis	SLRS-2	NIST 1643c
Zinc	Total/coprecipitated	4.82+/-2.26*	110+/-24
	Total recoverable	not detected	81.6+/-20.2
	Certified value =	3.33+/-0.15	73.9+/-0.9
Copper	Total/coprecipitated	3.22+/-0.62	25.7+/-3.1
	Total recoverable	2.8+/-0.9	20.0+/-2.4
	Certified value =	2.76+/-0.17	22.3+/-2.8
Lead	Total/coprecipitated	0.180+/-0.035	36.2+/-3.2
	Total recoverable	not detected	38.1+/-1.2
	Certified value =	0.129+/-0.011	35.3+/-0.9
Cadmium	Total/coprecipitated	0.042+/-0.012	13.1+/-1.9
	Total recoverable	not detected	12.6+/-0.5
	Certified value =	0.028+/-0.004	12.2+/-1.0

Laboratory vs. Field Variability

Table 3 compares results on laboratory duplicates and field replicates (pooled data for Duwamish and Yakima Rivers). Except for zinc, differences observed between field replicates appeared to be due more to imprecision of the chemical analysis than to concentration variation within the rivers. Filtering the samples did not introduce substantial additional variability to the results.

Compared to differences observed between the bimonthly samples (Appendix B.1), the combined effects of sampling, analytical, and short-term field variability appeared to be small. A similar conclusion extends to the other water quality variables measured during the survey (Appendix B.7).

Table 3. Estimates of analytical and total variability (µg/L, total/coprecipitated metal, +/- s.d.).

	Unfiltered (n=6)		Filtered (n=5)	
Metal	Analytical	Total	Analytical	Total
Zinc	+/- 0.22	+/- 0.56	+/- 0.19	+/- 0.34
Copper	+/- 0.18	+/- 0.16	+/- 0.05	+/- 0.09
Lead	+/- 0.03	+/- 0.04	+/- 0.01	+/- 0.04
Cadmium	+/-0.009	+/- 0.004	+/- 0.001	+/- 0.002

Metal Concentrations in River Water

Total/Coprecipitated Metals

The concentrations of total/coprecipitated metals measured in the four rivers are summarized in Table 4.

Table 4. Summary of results for total/coprecipitated metals (µg/L, median (range), n=6)

River	Zinc	Copper	Lead	Cadmium
Green	1.3	0.41	0.099	0.006
	(0.38-7.5)	(0.26-17.0)	(0.035-2.0)	(0.002-0.051)
Duwamish	2.2	0.96	0.26	0.012
	(0.88-9.5)	(0.69-3.8)	(0.13-2.0)	(0.005-0.041)
Yakima	3.0	2.2	0.64	0.015
	(1.3-5.7)	(1.0-2.9)	(0.21-1.0)	(0.010-0.045)
Puyallup	16.9	17.0	1.5	0.026
	(1.4-43.5)	(1.1-41.4)	(0.19-4.5)	(0.005-0.091)

For all metals there was a consistent trend toward increasing concentrations of total metal in the following order: Green < Duwamish < Yakima < Puyallup Rivers. Except for the Puyallup, concentration differences between rivers were generally not large. Excluding the considerably higher zinc and copper concentrations in the Puyallup River, median values were in the relatively narrow range of 1.3-3.0 μg/L zinc, 0.41-2.2 μg/L copper, 0.99-1.5 μg/L lead, and 0.006-0.026 μg/L cadmium. Median concentrations of total zinc and copper were 16.9 and 17.0 μg/L, respectively, in the Puyallup River.

The results are compared graphically in Figure 3. Some of the concentration differences observed were statistically significant (Wilcoxon rank-sum test, $p \leq .05$). Zinc and copper levels in the Puyallup were significantly higher than in the other rivers. Lead concentrations were also significantly elevated in the Puyallup compared to those in the Duwamish and Green Rivers, but were not different from those in the Yakima. Both the Puyallup and Yakima Rivers had significantly higher cadmium levels than the Green River. For the Duwamish and Green Rivers, a significant difference only occurred for lead.

Total Recoverable Metals

The total recoverable data are summarized in Table 5. Detection limits achieved in this analysis were not low enough to consistently quantify zinc, copper, or lead. Cadmium concentrations in all but one of the water samples were too low to detect.

Table 5. Summary of results for total recoverable metals (μg/L, median (range), n=6).

River	Zinc	Copper	Lead	Cadmium
Green	8.0	1.0 U*	1.0 U	0.10 U
	(4U-14)	(1.0U-8.3)	(1.0U-1.9)	(no detects)
Duwamish	6.3	1.4	1.0 U	0.10 U
	(4U-8.8)	(1.0U-2.2)	(1.0U-2.2)	(no detects)
Yakima	3.8	2.0	1.0 U	0.10 U
	(4U-12)	(1.0U-3.4)	(1.0U-1.0)	(no detects)
Puyallup	24	11.6	1.7	0.10 U
	(4U-33)	(1.0U-32.4)	(1.0U-6.3)	(0.10U-0.12)

*U = not detected

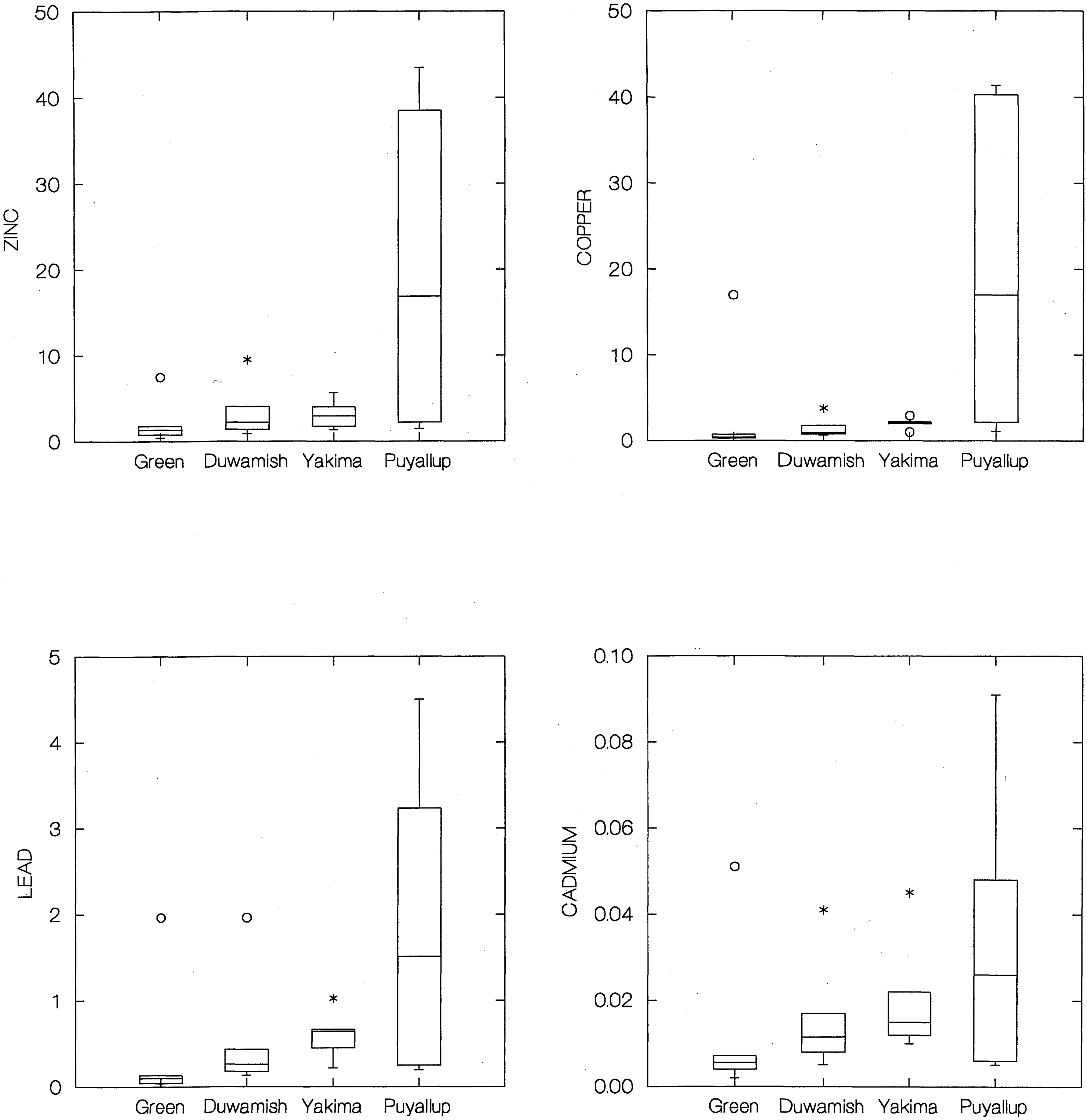

Figure 3. Total/Coprecipitated Metal Concentrations (ug/L)

Figure 4 compares the total recoverable and total/coprecipitated data. In those instances where metals were detected in both analyses, similar data were obtained for copper and lead. Results for zinc were inconsistent between the two methods. Because of the number of non-detects in the total recoverable analysis, the remainder of this discussion draws on the total/coprecipitated data only.

Dissolved Metals

Concentrations of dissolved metals are summarized in Table 6 and Figure 5. Dissolved concentrations compared more closely between rivers than total metals. Median concentrations were within a factor of 2-to-3 for each metal, ranging from 1.0-1.8 μg/L zinc, 0.33-1.0 μg/L copper, 0.040-0.13 μg/L lead, and 0.005-0.10 μg/L cadmium.

Table 6. Summary of results for dissolved metals (μg/L, median (range), n=5).

River	Zinc	Copper	Lead	Cadmium
Green	1.0	0.33	0.040	0.005
	(0.88-1.2)	(0.21-0.43)	(0.031-0.012)	(0.002-0.008)
Duwamish	1.8	0.65	0.11	0.007
	(0.50-5.8)	(0.54-2.0)	(0.035-0.30)	(0.004-0.021)
Yakima*	1.3	0.82	0.072	0.005
	(0.34-2.0)	(0.64-1.2)	(0.035-0.10)	(0.003-0.007)
Puyallup	1.4	1.0	0.13	0.010
	(0.63-1.6)	(0.81-1.8)	(0.082-0.36)	(0.003-0.039)

*n=4

Statistically significant differences were confined to the Green River, which had significantly lower dissolved copper and lead than the Puyallup River and low dissolved lead and cadmium compared to the Duwamish River. Differences in dissolved zinc concentrations between rivers were not significant.

Seasonal Patterns

The total/coprecipitated data are plotted by month of sample collection in Figure 6. Because only six samples were analyzed for the year, seasonal patterns implied by this figure may be misleading.

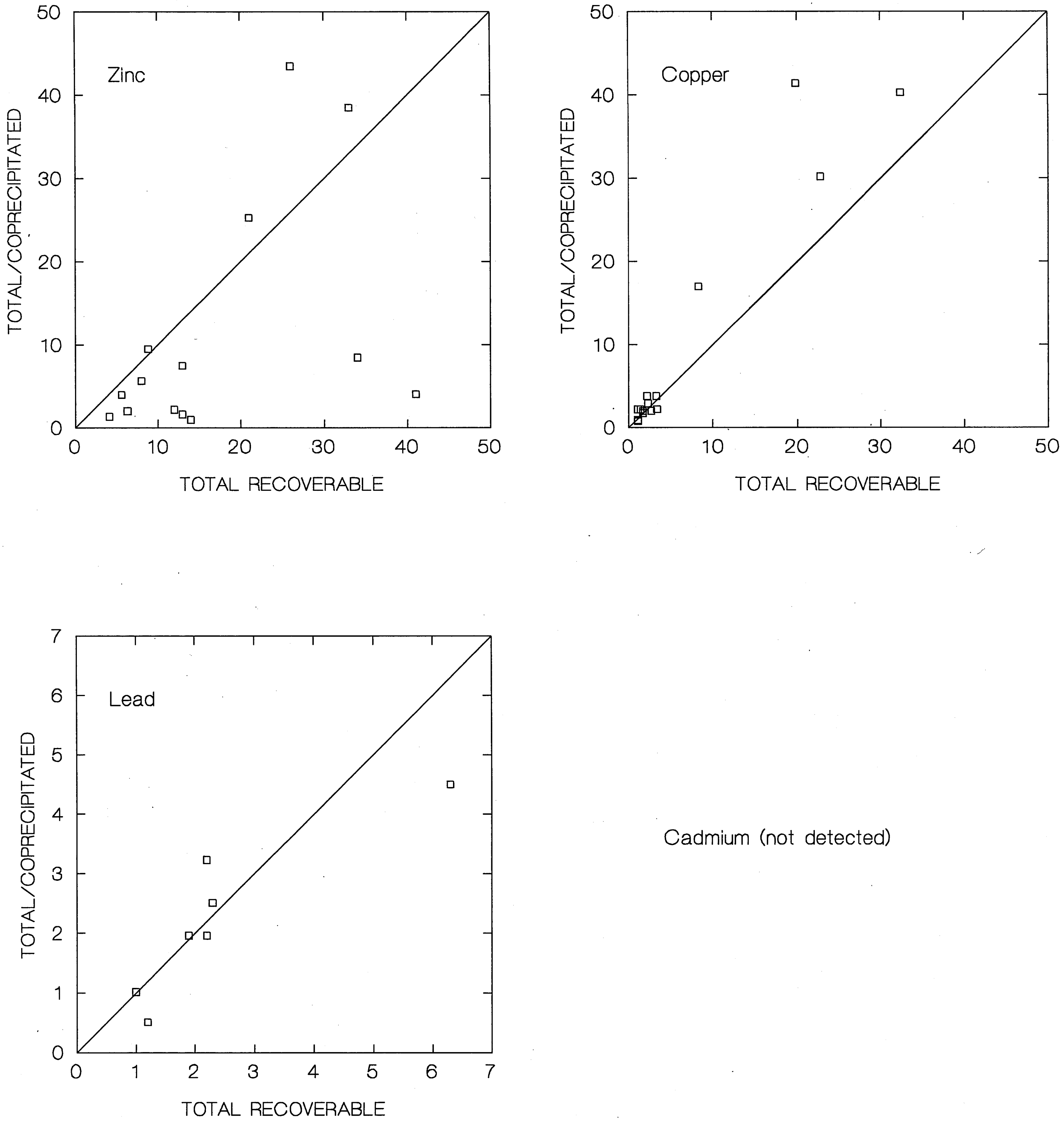

Figure 4. Total/Coprecipitated vs. Total Recoverable Metal (ug/L)

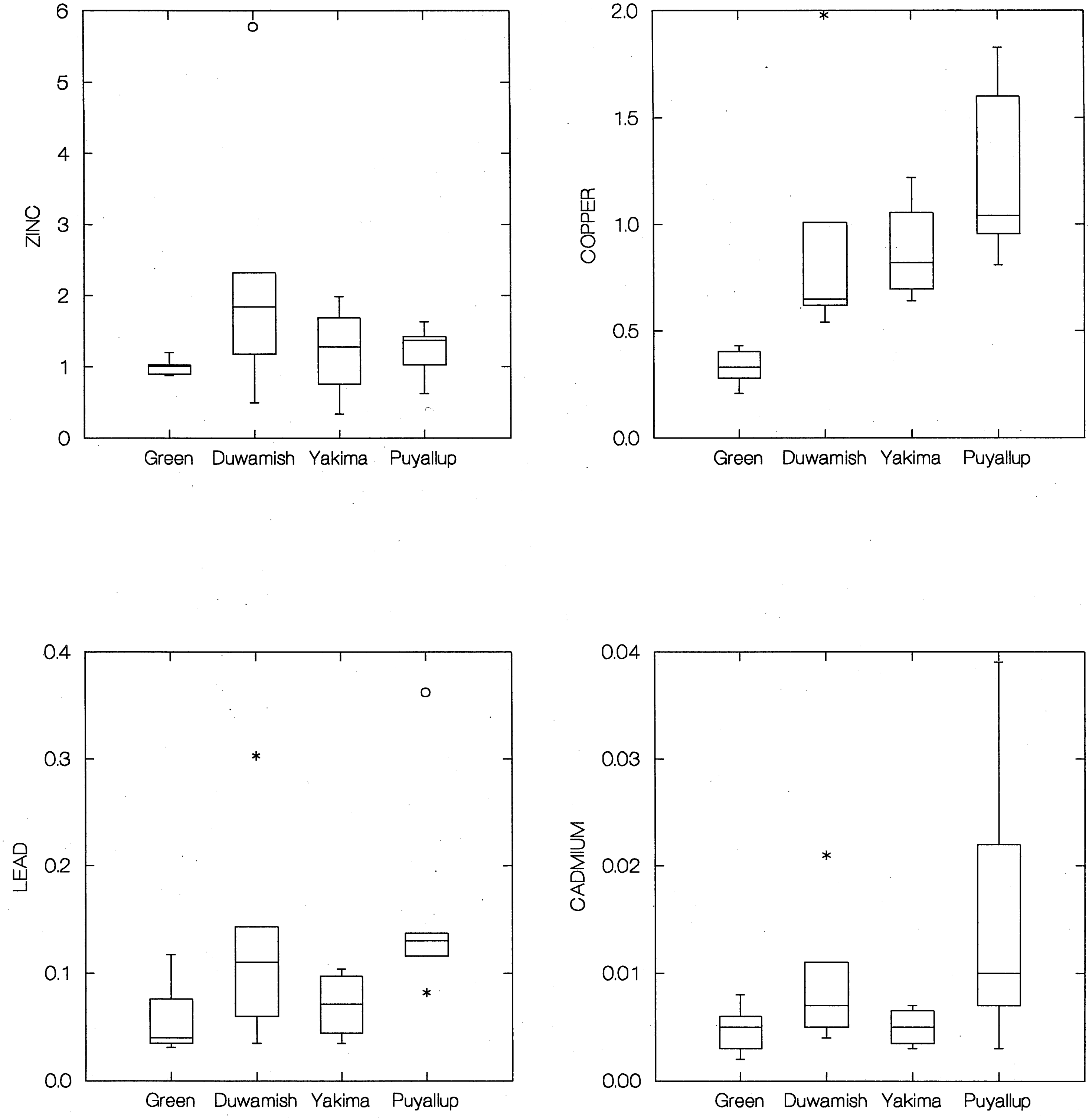

Figure 5. Dissolved Metal Concentrations (ug/L)

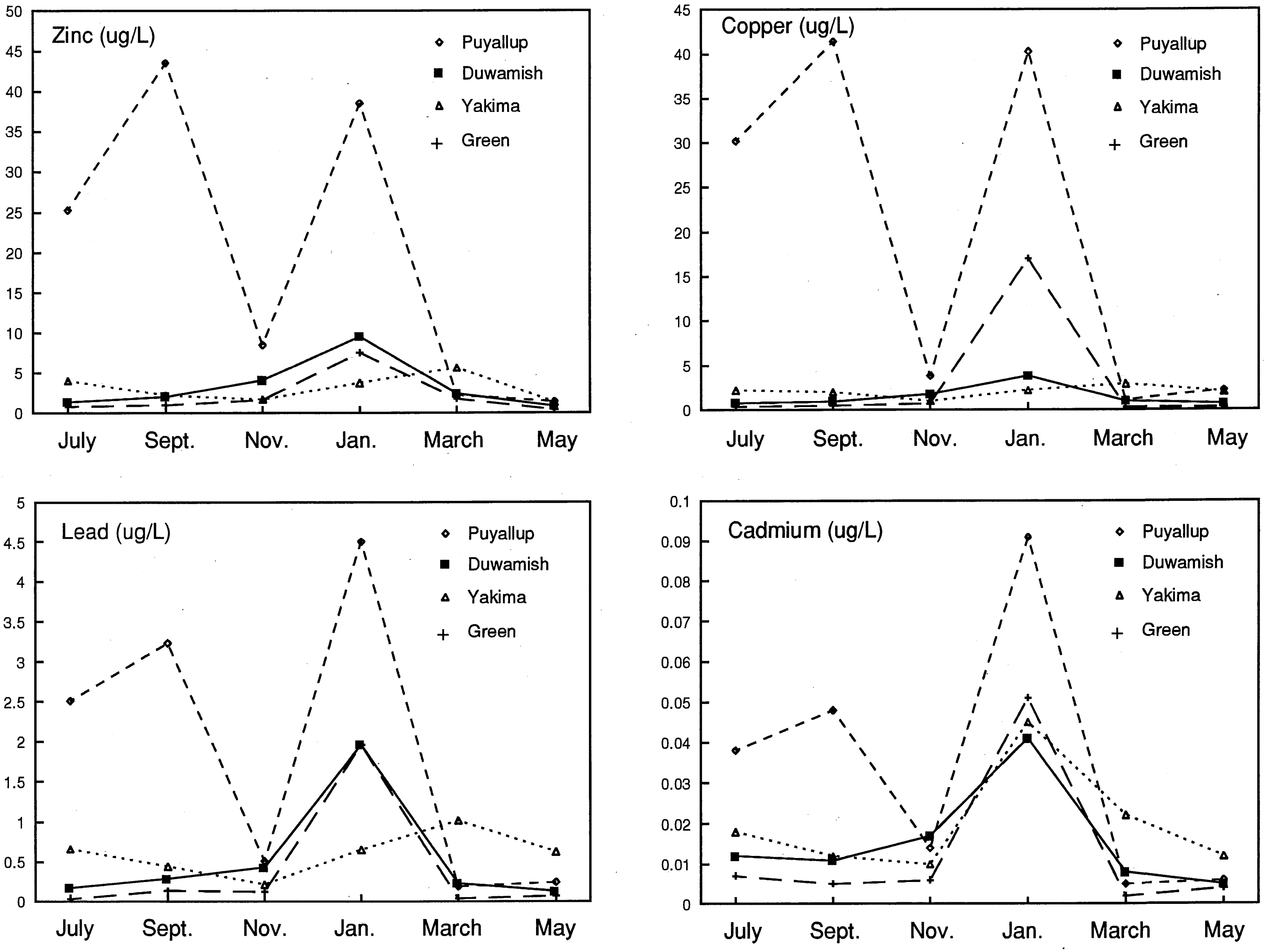

Figure 6. Seasonal Patterns in Total/Coprecipitated Metals

The Puyallup River exhibited the widest range in metal concentrations, while concentrations were least variable in the Yakima. Concentration changes in the Green River were consistently reflected in downstream samples from the Duwamish. For all rivers the highest metal concentrations tended to occur during the winter months of November, January, and March.

The corresponding dissolved data (not plotted) showed little evidence of marked seasonality in concentration levels (Appendix B.1).

Compliance With Water Quality Criteria

State metals criteria for protecting aquatic life apply to the dissolved fraction and are calculated with the following equations (WAC 172-201A):

	Chronic Criteria	Acute Criteria
Zinc	$\leq (0.891)(e^{(0.8473[\ln(\text{hardness})]+0.7614)})$	$\leq (0.891)(e^{(0.8473[\ln(\text{hardness})]+0.8604)})$
Copper	$\leq (0.862)(e^{(0.8545[\ln(\text{hardness})]-1.465)})$	$\leq (0.862)(e^{(0.9422[\ln(\text{hardness})]-1.464)})$
Lead	$\leq (0.687)(e^{(1.273[\ln(\text{hardness})]-4.705)})$	$\leq (0.687)(e^{(1.273[\ln(\text{hardness})]-1.460)})$
Cadmium	$\leq (0.865)(e^{(0.7852[\ln(\text{hardness})]-3.490)})$	$\leq (0.865)(e^{(1.128[\ln(\text{hardness})]-3.828)})$

For example, at a hardness of 25 mg/L, the chronic criteria are 29.2 μg/L zinc, 3.1 μg/L copper, 0.37 μg/L lead, and 0.33 μg/L cadmium. The acute criteria at the same hardness are 32.2 μg/L zinc, 4.1 μg/L copper, 9.6 μg/L lead, and 0.71 μg/L cadmium. A four-day average concentration is not to exceed the chronic criteria more than once every three years. The acute criteria are not to be exceeded by a one-hour average concentration more than once every three years.

None of the dissolved metal concentrations measured in the Green, Duwamish, Yakima, or Puyallup Rivers approached criteria for acute exposure. Figure 7 illustrates how the dissolved concentrations compare to the chronic criteria. The hardness determined at the time of sample collection was used to calculate the appropriate criterion.

Violation of chronic criteria was observed only once in the survey. The lead concentration in the Puyallup River during May, 0.36 μg/L, was slightly above the chronic criterion of 0.31 μg/L (@ hardness = 21.5 mg/L). In all other instances, metal concentrations were rarely much above half the chronic criteria values.

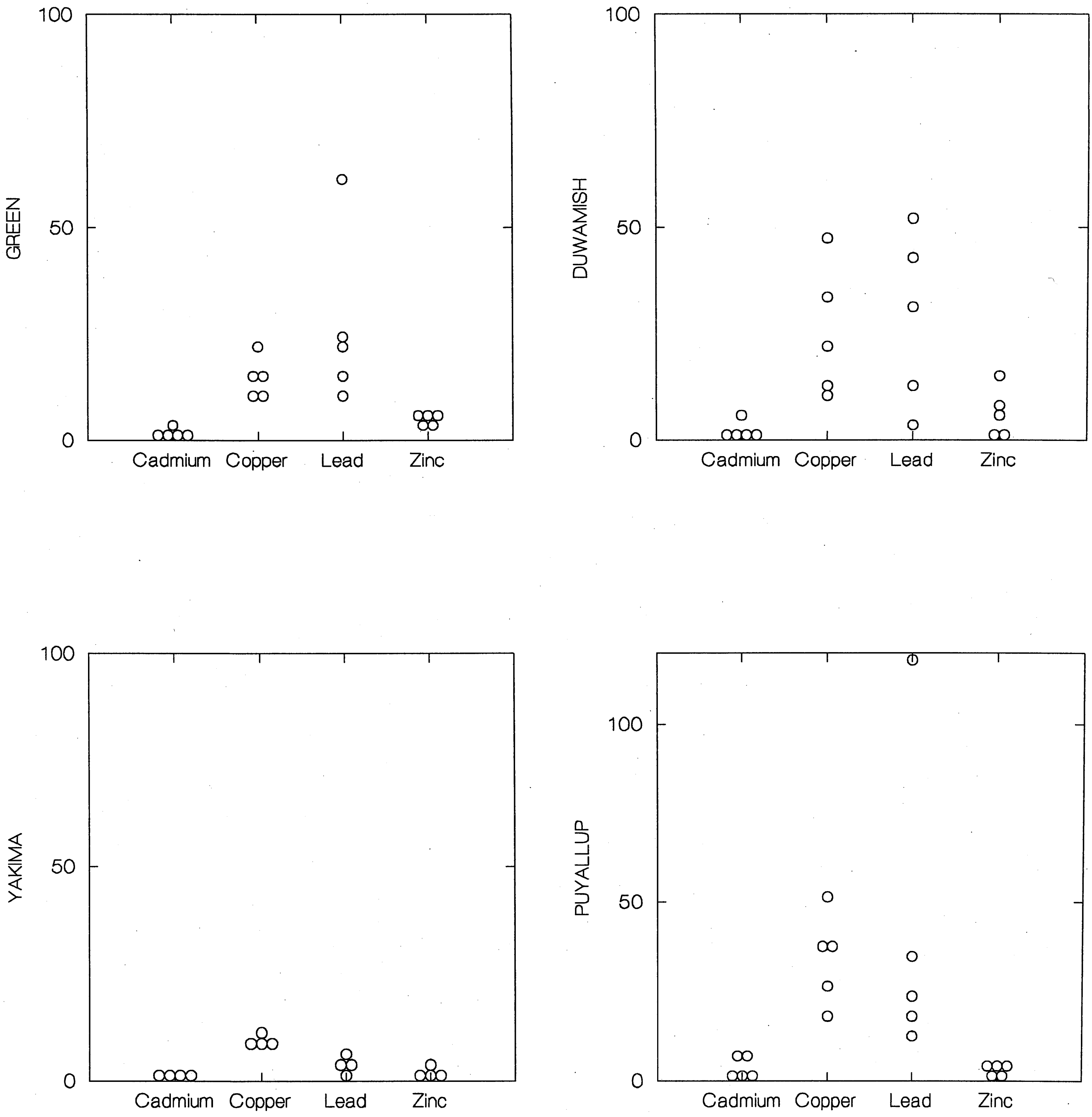

Figure 7. Dissolved Metals as Percent of Chronic WQ Criteria

In terms of water quality criteria, lead and copper were at the highest levels in all four rivers. Zinc concentrations were always less than 15% of criteria and cadmium concentrations never exceeded 7% of criteria.

Based on these results, the Yakima River had the largest margin of safety for potential toxicity due to zinc, copper, lead, or cadmium. The Duwamish and Puyallup Rivers had the least room to accommodate increases in copper or lead concentrations.

Correlations With Other Water Quality Variables

The data were examined for relationships between metal concentrations and other water quality properties (Kendall's tau).

There were relatively few data on which to base strong conclusions. The only consistent relationship was with TSS and, to a lesser degree, flow (Table 7). Hardness, pH, and TOC showed the least evidence of correlation with metal concentrations.

Except for zinc in the Puyallup River, there was a moderate to strong correlation between total metals and TSS in all rivers and for the data set as a whole. Dissolved metals correlated less frequently with TSS than total. The strongest evidence for a relationship between metal concentrations, TSS, and flow was in the Duwamish River.

A correlation with flow implies that metals loads are not significantly associated with ongoing point sources, where one would expect a negative correlation with flow. These results seem to indicate the major processes affecting metals concentrations in some of the rivers (e.g., zinc, copper, and lead in the Duwamish River) were non-point and background runoff.

Dissolved Metals as Percent of Total

Table 8 shows the percentage of total metal that was in the dissolved phase. The fraction of dissolved metals varied widely, both within and between rivers. This appeared to be related to TSS concentrations, in keeping with the correlations identified above.

The Green and Puyallup Rivers had the largest excursions in TSS and widest range in percentage of dissolved metal. Lead was primarily associated with particulates in all rivers. Zinc, copper, and cadmium were either mostly in the dissolved or particulate phase depending on the river and TSS concentration in question.

Figure 8 illustrates the inverse relationship between dissolved metals and TSS more clearly. There was a moderate to strong negative correlation with TSS for all metals: zinc (-.759), copper (-.856), lead (-.633), and cadmium (-.508). These data are further analyzed in terms of partition coefficients in Appendix C.

Table 7. Correlation of metal concentrations with TSS and flow (Kendall's tau).

Variable	River	Zinc	Copper	Lead	Cadmium
Total/Coprecipitated Metal (n=6):					
TSS	All Rivers	.533	.689	.647	.566
	Green	.467	1.000	.600	.733
	Duwamish	.467	.467	.600	.333
	Puyallup	.276	.414	.552	.552
	Yakima	.467	.733	.733	.690
Flow	Green	.600	.333	.467	.067
	Duwamish	.600	.600	.467	.200
	Puyallup	-.200	-.067	.067	.067
	Yakima	.067	.333	.333	.276
Dissolved Metal (n=5):					
TSS	All Rivers	.224	.504	.243	.277
	Green	-.200	.800	-.200	.600
	Duwamish	.800	.800	1.000	.400
	Puyallup	.600	.600	.000	.400
	Yakima*	.667	-.333	.667	-.333
Flow	Green	.400	.200	.000	.000
	Duwamish	.600	.600	.800	.200
	Puyallup	.200	.600	.400	-.400
	Yakima*	.667	-.333	.667	-.333

*n=4

Comparison to Other Metals Data

Several other studies have produced comparable metals data on Washington rivers. Ecology conducted two additional surveys during 1992-1993 that shared the sampling techniques, analytical methods, and quality assurance described in the present report. The first was an

Table 8. Dissolved metals as percent of total (%, median (range)).

River	Zinc	Copper	Lead	Cadmium
Green	73	81	25	83
(n=5)	(12-100)	(2-97)	(4-100)	(12-100)
Duwamish	61	66	33	63
(n=5)	(57-86)	(52-80)	(15-50)	(41-92)
Yakima	32	36	8	22
(n=4)	(29-37)	(26-55)	(5-16)	(13-39)
Puyallup	17	42	16	100
(n=5)	(4-47)	(3-72)	(3-100)	(11-100)

evaluation of zinc, copper, lead, cadmium, and mercury for the Spokane River conducted by the Watershed Assessments Section (Pelletier, 1994-in prep.). The second was development of a water sampling device for the Ambient Monitoring Section (Hopkins, unpublished)[1]. Two earlier Ecology surveys obtained metals data on the Columbia River (Johnson and Hopkins, 1991; Johnson, 1991). NOAA has also reported data on dissolved metals in the Duwamish and Puyallup Rivers (Paulson, 1988).

Results from these studies are summarized in Table 9. NOAA's measurements of dissolved zinc, copper, and lead in the Puyallup and Duwamish Rivers compare closely to findings of the present survey. High concentrations zinc, lead, and cadmium occur in the upper Columbia and/or Spokane River due to a large smelter in British Columbia (Johnson *et al.*, 1990) and historical mining in the Coeur d'Alene drainage (Mink *et al.*, 1971; Yake 1979). The data presently available suggest that, in the absence of such significant sources, concentrations of zinc, copper, lead, and cadmium - particularly the dissolved phase - may be broadly comparable among Washington's larger rivers.

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[1] Hopkins also analyzed mercury concentrations in the Green, Duwamish, and Puyallup Rivers; the data are in Appendix D.

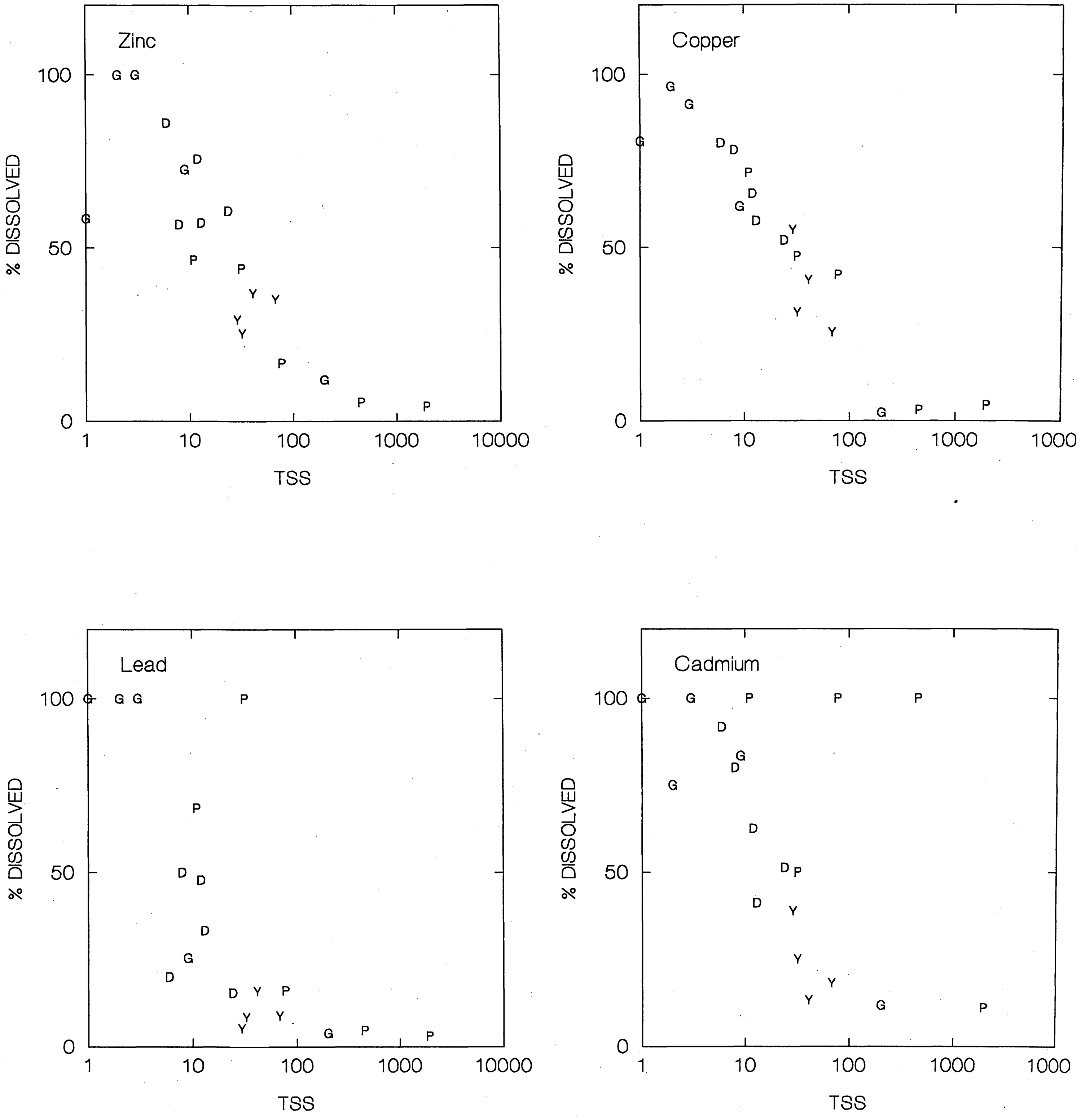

Figure 8. Percent Dissolved Metals vs. TSS
(G=Green, D=Duwamish, P=Puyallup, Y=Yakima)

Table 9. Selected metals data from other recent surveys (µg/L).

River	Zinc	Copper	Lead	Cadmium	Reference
TOTAL/COPRECIPITATED:					
Snohomish (n=2-4)	3.1	1.3	0.17	0.014	Hopkins (unpublished)
Lower Columbia (n=9)	1.4	1.7	0.35	0.029	Johnson & Hopkins (1991)
Upper Columbia (n=1)	2.1	1.7	3.2	0.17	Johnson (1991)
Spokane (n=5-6)	109	0.74	1.1	0.28	Pelletier (in prep.)
DISSOLVED:					
Puyallup (n=1-5)	2.2	0.65	0.040	na	Paulson *et al.* (1988)
Duwamish (n=4-6)	1.1	0.62	0.020	na	"
Snohomish (n=2-4)	1.6	0.72	0.11	0.012	Hopkins (unpublished)
Lower Columbia (n=9)	0.26	0.84	0.034	0.013	Johnson & Hopkins (1991)
Spokane (n=5-6)	107	0.86	0.23	0.24	Pelletier (in prep.)

median values, except NOAA data are means

na = not analyzed

Summary

Use of clean sampling techniques and a preconcentration step (APDC coprecipitation) allowed consistent quantification of zinc, copper, lead, and cadmium concentrations in water from the Green, Duwamish, Puyallup, and Yakima Rivers. Analysis of total recoverable metals gave better accuracy than the total/coprecipitated method, but was frequently unable to detect zinc, lead, and cadmium. Metal concentrations in procedural blanks for the total/coprecipitated analysis sometimes exceeded method detection limits, lending uncertainty to measurements near the detection limit.

Analysis of standard reference materials showed the total/coprecipitated data had a slight but consistent positive bias. Results on split samples and field replicates suggested the combined effects of sampling, analytical, and short-term field variability were insignificant relative to concentrations differences observed between bimonthly samples.

There was a consistent trend toward increasing concentrations of total metals in the following order: Green < Duwamish < Yakima < Puyallup. Except for zinc and copper in the Puyallup River, differences in total metal concentrations between the four rivers were generally not large.

Dissolved metal concentrations compared more closely between rivers. Median concentrations were in the narrow range of 1.0-1.8 μg/L zinc, 0.33-1.0 μg/L copper, 0.040-0.13 μg/L lead, and 0.005-0.10 μg/L cadmium. The Green River showed significantly lower concentrations of dissolved lead and cadmium than the Duwamish River and low dissolved copper and lead compared to the Puyallup River. Between-river differences in dissolved zinc concentrations were not significant.

Except for one instance of elevated lead in the Puyallup River, all metal concentrations were within state water quality criteria for protecting aquatic life against effects of chronic exposure. Acute water quality criteria were never approached. From the standpoint of compliance with criteria, the Duwamish and Puyallup River appeared least able to accommodate increases in copper or lead concentrations. Dissolved zinc and cadmium concentrations were consistently only a small fraction of chronic criteria values in all four rivers.

The highest metal concentrations tended to occur during the winter. The only water quality variables that showed consistent correlation with concentrations of total and dissolved metals were TSS and, secondarily, flow.

Lead was primarily in particulate form in all rivers. The other metals were variously associated with the dissolved or particulate phases depending on the river and TSS concentration in question. The percentage of metals that was dissolved showed a clear inverse correlation to TSS concentrations: zinc (-.759), copper (-.856), lead (-.633), and cadmium (-.508).

Metal concentrations measured during this survey were in good agreement with other recent Ecology and NOAA data on Washington rivers. In the absence of significant sources of contamination, concentrations of dissolved zinc, copper, lead, and cadmium appear to be generally similar among the state's larger rivers.

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APPENDIX A.

RECOMMENDATIONS FOR FUTURE METALS SAMPLING

RECOMMENDATIONS FOR FUTURE METALS SAMPLING

A variety of sampling and analysis methods have been used or recommended for obtaining accurate data on metal concentrations in freshwater. The cleaning, sampling collection, filtering, and preservation procedures employed in the present survey (developed at Battelle Laboratory) are simple to follow and permit collection of uncontaminated samples.

The construction of the Nalgene filter apparatus minimizes chances of contaminating the filtrate and requires only an inexpensive hand pump to operate. No clean-air bench or glove box was used. This would further reduce the risk of contamination but slow the pace of sample collection. One of the survey's dissolved samples was obviously contaminated (Appendix B.1), most likely during field filtering.

Because the filter is fixed within the unit, there is the drawback that it can only be used once. Water samples with high solids - such as those from the Puyallup River - may load the filter up quickly, requiring two units to obtain minimum sample size (250 mL in this case).

The quality assurance samples analyzed in the survey are recommended by EPA (bottle blanks, filter blanks, split samples) or left to the discretion of the investigator (SRMs, field replicates). All were useful. One of the SRMs selected, NRCC SLRS-2, is particularly appropriate for evaluating the accuracy of dissolved metal determinations. Through use of SRMs, a bias was detected in the total/coprecipitated data that may have otherwise been missed.

Both of the analytical methods employed in the survey had shortcomings. The Battelle Laboratory now prefers use of ICP-mass spectroscopy for analyzing APDC concentrates and reports results within 10% of certified values for copper, lead, and cadmium in SLRS-2 (Crecelius, 1993). This method also yielded good results on seawater.

Manchester Laboratory has substantially improved their capability to analyze low concentrations of metals in freshwater. Advances have been made in several areas including: 1) installing a class 100 clean hood, 2) development and documentation of a cleaning process for sample bottles, filters, and acid preservative, and 3) implementation of a new microwave digestion method. Details of the improvements and validation of the new procedures at Manchester have been documented by the laboratory (Kammin, 1993).

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APPENDIX B.

DATA SET

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Appendix B.1 Metal Concentrations in Field Samples (ug/L)

River	Date	Zn(tc)	Zn(tr)	Zn(d)	Cu(tc)	Cu(tr)	Cu(d)	Pb(tc)	Pb(tr)	Pb(d)	Cd(tc)	Cd(tr)	Cd(d)
Green	27 July 92	0.784 J	4.0 U	0.882 J	0.362	1.0 U	0.331	0.035	1.0 U	0.035 U	0.007 J	0.10 U	0.008 J
	22 Sept. 92	0.98 B	14 P	la	0.464 B	1.0 U	la	0.133 B	1.0 U	la	0.005 B	0.10 U	la
	23 Nov. 92	1.65 B	13 J	1.20 B	0.696	1.0 U	0.431	0.122 B	1.0 U	0.031 B	0.006 B	0.10 U	0.005 B
	25 Jan. 93	7.49 B	13 P	0.90 B	17.0	8.3 P	0.405	1.96	1.9 P	0.076 B	0.051	0.10 U	0.006 B
	29 March 93	1.76 B	4 U	1.03 B	0.26	1.0 U	0.21	0.04 B	1.0 U	0.04 B	0.002 B	0.10 U	0.002 B
	24 May 93	0.38 J	4 U	1.01 J	0.29	1.0 U	0.28	0.075 J	1.0 U	0.117 J	0.004 J	0.10 U	0.003 J
Duwamish	27 July 92	1.37 J	4.1 P	1.18 J	0.772	1.1 J	0.620	0.175	1.0 U	0.035 U	0.012 J	0.10 U	0.011 J
	22 Sept. 92	2.03 B	6.3 P	la	0.928	1.1 P	la	0.284	1.0 U	la	0.011 B	0.10 U	la
	23 Nov. 92	4.05	41 B	2.32	1.75	1.7 P	1.01	0.429	1.0 U	0.143 B	0.017 B	0.10 U	0.007 B
	25 Jan. 93	9.52 B	8.8 P	5.78 B	3.80	2.2 P	1.98	1.96	2.2 P	0.303	0.041	0.10 U	0.021
	29 March 93	2.43 B	4 U	1.84 B	0.99	1.0 U	0.65	0.23 B	1.0 U	0.11 B	0.008 B	0.10 U	0.005 B
	24 May 93	0.88 J	4 U	0.50 J	0.69	1.0 U	0.54	0.128 J	1.0 U	0.064 J	0.005 J	0.10 U	0.004 J
Puyallup	27 July 92	25.3	21	1.37 J	30.2	22.7 J	0.956	2.51	2.3 P	0.116	0.038	0.10 U	0.039
	22 Sept. 92	43.5	26	la	41.4	19.8	la	3.23	2.2 P	la	0.048	0.10 U	la
	23 Nov. 92	8.47	34 J	1.42 B	3.80	3.3 P	1.60	0.510	1.2 P	0.082 B	0.014 B	0.10 U	0.022 B
	25 Jan. 93	38.5	33 P	1.63 B	40.3	32.4	1.83	4.50	6.3 P	0.137 B	0.091	0.12 P	0.010 B
	29 March 93	2.21 B	4 U	1.03 B	1.13	1.0 U	0.81	0.19 B	1.0 U	0.13 B	0.005 B	0.10 U	0.007 B
	24 May 93	1.43 J	4 U	0.63 J	2.19	1.4 P	1.04	0.245 J	1.0 U	0.362 B	0.006 J	0.10 U	0.003 J
Yakima	28 July 92	4.02	5.6 P	1.18 J	2.21	3.4 J	1.22	0.663	1.0 U	0.035	0.018 J	0.10 U	0.007 J
	23 Sept. 92	2.20 B	12 P	la	2.02	1.7 P	la	0.446	1.0 U	la	0.012 B	0.10 U	la
	24 Nov. 92	1.72	4 U	11.6 R	1.01	1.0 U	71.6 R	0.214	1.0 U	12.6 R	0.010 B	0.10 U	0.023 R
	26 Jan. 93	3.74 B	4 U	1.38 B	2.19	1.1 P	0.890	0.654	1.0 U	0.104 B	0.045	0.10 U	0.006 B
	30 March 93	5.66 B	8 P	1.99 B	2.92	2.3 P	0.75	1.02	1.0 P	0.09 B	0.022	0.10 U	0.004 B
	25 May 93	1.34 J	4 U	0.34 J	2.04	2.7 P	0.64	0.628 B	1.0 U	0.053 J	0.012 B	0.10 U	0.003 J

data qualifiers defined at end of appendix

Appendix B.2 Metal Concentrations in Duplicate (splits) and Replicated Samples (ug/L)

River	Date	Zn(tc)	Zn(tr)	Zn(d)	Cu(tc)	Cu(tr)	Cu(d)	Pb(tc)	Pb(tr)	Pb(d)	Cd(tc)	Cd(tr)	Cd(d)
Duwamish	27 July 92	1.37 J	4.1 P	1.18 J	0.772	1.1 J	0.620	0.175	1.0 U	0.035 U	0.012 J	0.10 U	0.011 J
duplicate		1.37 J	7.4 P	0.686 J	1.19	1.1 J	0.546	0.175	1.0 U	0.035 U	0.013 J	0.10 U	0.009 J
replicate		1.76 J	5.4 P	1.37 J	0.824	1.0 U	3.14 R	0.186	1.0 U	0.070	0.011 J	0.10 U	0.012 J
Duwamish	23 Nov. 92	4.05	41 B	2.32	1.75	1.7 P	1.01	0.429	1.0 U	0.143 B	0.017 B	0.10 U	0.007 B
duplicate		4.12	na	2.10	1.72	na	0.926	0.449	na	0.122 B	0.015 B	na	0.008 B
replicate		4.42	33 J	1.50 B	1.81	1.7 P	1.14	0.347	4.3 P	0.092 B	0.016 B	0.10 U	0.007 B
Duwamish	29 March 93	2.43 B	4 U	1.84 B	0.99	1.0 U	0.65	0.23 B	1.0 U	0.11 B	0.008 B	0.10 U	0.005 B
duplicate		2.35 B	na	1.62 B	1.03	na	0.54	0.25	na	0.13 B	0.008 B	na	0.005 B
replicate		2.72 B	4 P	14.4 R	0.91	1.0 U	0.50	0.24 B	1.0 U	0.10 B	0.008 B	0.10 U	0.001 J
Yakima	23 Sept. 92	2.20 B	12 P	la	2.02	1.7 P	la	0.446	1.0 U	la	0.012 B	0.10 U	la
duplicate		2.20 B	6.7 P	la	2.49	1.4 P	la	0.427	1.0 U	la	0.016 B	0.10 U	la
replicate		3.99 B	28	la	1.86	2.7 P	la	0.370	1.0 U	la	0.012 B	0.10 U	la
Yakima	26 Jan. 93	3.74 B	4 U	1.38 B	2.19	1.1 P	0.890	0.654	1.0 U	0.104 B	0.045	0.10 U	0.006 B
duplicate		4.48 B	na	1.46 B	2.15	na	0.915	0.569	na	0.085 B	0.015 B	na	0.008 B
replicate		3.74 B	5.1 P	13.2 R	2.40	1.2 P	77.4 R	0.541	1.0 U	2.84 R	0.016 B	0.10 U	0.032 R
Yakima	25 May 93	1.34 J	4 U	0.34 J	2.04	2.7 P	0.64	0.628 B	1.0 U	0.053 J	0.012 B	0.10 U	0.003 J
duplicate		1.43 J	na	0.38 J	1.97	na	0.67	0.607 B	na	0.064 J	0.011 B	na	0.002 J
replicate		1.26 J	4 U	0.46 J	1.78	1.4 P	0.76	0.607 B	1.0 U	0.149 J	0.010 B	0.10 U	0.004 J

data qualifiers defined at end of appendix

Appendix B.3 Analyses of Standard Reference Materials (ug/L)

SRM	Sample Set	Zn(tc)		Zn(tr)		Cu(tc)	Cu(tr)		Pb(tc)		Pb(tr)		Cd(tc)		Cd(tr)	
SLRS-2	July	8.43		13	P	4.08	3.8	P	0.186		1.0	U	0.048		0.10	U
(submitted blind)	Sept.	la		na		la	na		la		na		lost		na	
"	Nov.	4.95		na		3.42	na		0.235		na		0.060		na	
"	Jan.	4.80	B	na		3.37	na		0.18		na		0.038		na	
"	March	3.38	B	4	U	2.51	2.2	P	0.15	B	1.0	U	0.032		0.10	U
"	May	2.52	J	4	U	2.74	2.3	P	0.149	J	1.0	U	0.033	B	0.10	U
(not blind)	July	3.92		na		3.09	na		0.175		na		0.048		na	
"	July	4.51		na		2.92	na		0.175		na		0.046		na	
"	Sept.-Jan.	4.26		na		3.80	na		0.163		na		0.049		na	
"	Sept.-Jan.	4.39		na		3.96	na		0.173		na		0.051		na	
"	Sept.-Jan.	4.42		na		3.75	na		0.190		na		0.049		na	
"	Sept.-Jan.	4.23		na		3.75	na		0.190		na		0.044		na	
"	Sept.-Jan.	4.55		na		3.63	na		na		na		0.038		na	
"	March	4.26		na		3.23	na		0.180		na		0.035		na	
"	March	na		na		3.06	na		na		na		na		na	
"	May	4.24		na		3.00	na		0.192		na		0.038		na	
"	May	na		na		2.37	na		0.181		na		0.038		na	
SLRS Certified Values =		3.33+/-0.15				2.76+/-0.17			0.129+/-0.011				0.028+/-0.004			
NIST 1643c	July	81.7		89.5		26.0	24.6	J	31.7		39.3		11.6		11.9	
(submitted blind)	Sept.	122		74.8		31.0	18.8		41.3		37.9		16.2		12.1	
	Nov.	136		119	B	26.0	21.0		37.3		36.6		13.4		12.6	
	Jan.	134		64.0		25.9	19.0		36.6		38.2		12.6		13.0	
	March	86.7		72.8		23.7	18.7		34.7		37.0		11.7		13.2	
	May	100		69.7		21.8	18.1		35.7		39.6		51.6	R	12.8	
NIST Certified Values =		73.9+/-0.9				22.3+/-2.8			35.3+/-0.9				12.2+/-1.0			

data qualifiers defined at end of appendix

Appendix B.4 Metals Concentrations in Field Blanks (ug/L)

Sample Set	Type	Zn	Cu	Pb	Cd
July	Bottle	0.98 J	0.058 J	0.035 U	0.005 J
	Filter	0.78 J	0.095	0.035 U	0.006 J
November	Bottle	0.90 B	0.076 B	0.031 B	0.001 B
	Filter	1.2 B	1.8	0.031 B	0.001 B
March	Bottle	1.3 B	0.016 J	0.040 B	0.001 J
	Filter	1.8 B	0.016 J	0.030 J	0.001 J

coprecipitated metal

Appendix B.5 Battelle Laboratory Method Blanks (ug/L)

Sample Set	Zn	Cu	Pb	Cd
July	0.882	0.037	0.035 U	0.005
July	0.980	0.042	0.035 U	0.006
July	0.980	0.047	0.035 U	0.004
Sept.-Jan.	1.05	0.024	0.02 U	0.001 U
Sept.-Jan.	0.75	0.048	0.02	0.002
Sept.-Jan.	0.81	0.042	0.03 U	0.001 U
Sept.-Jan.	0.65	0.038	0.03 U	0.002 U
Sept.-Jan.	0.81	0.033 U	na	0.003
March	0.96	0.012 U	0.03	0.001
March	0.80	0.012 U	0.02 U	0.002
March	0.96	0.020	0.03	0.001
March	0.96	0.016	0.03	0.001
March	1.10	0.020	0.03	0.001
May	0.38	0.017 U	0.032 U	0.001 U
May	0.38	0.017 U	0.032	0.001 U
May	0.29	0.017 U	0.032 U	0.001 U

data qualifiers defined at end of appendix

Appendix B.6 Ancillary Water Quality Data

River	Date	Flow (cfs)	Temp. (C)	pH	Specific Cond. (umho/cm)	Total Hardness (mg/L)	Total Alkalinity (mg/L)	TSS (mg/L)	TDS (mg/L)	TOC (mg/L)	
Green	27 July 92	129	15.8	7.20	56.2	23.5	24.6	3	33	1.0	U
	22 Sept. 92	156	14.4	7.80	57.4	28.8	25.5	5	18	1.0	
	23 Nov. 92	2550	6.0	6.90	39.6	14.8	15.8	9	80	1.6	
	25 Jan. 93	2810	3.0	7.20	34.8	22.0	13.1	200	33	5.7	
	29 March 93	1330	5.9	7.70	68.1	13.8	17.0	1	31	1.2	
	24 May 93	724	11.7	7.20	41.2	14.6	18.3	2	69	2.2	
Duwamish	27 July 92	251	21.0	7.27	155	53.7	53.7	6	92	1.6	
	22 Sept. 92	263	17.0	7.45	137	44.6	48.8	123	101	1.5	
	23 Nov. 92	2540	6.1	6.90	59.5	23.3	21.2	13	66	2.5	
	25 Jan. 93	2000	7.0	7.10	99.7	35.9	31.9	24	65	3.3	
	29 March 93	1910	7.6	7.30	66.5	23.8	25.1	12	60	1.9	
	24 May 93	1090	15.5	6.80	192	33.9	34.8	8	78	2.7	
Puyallup	27 July 92	1550	16.1	6.89	131	50.2	20.7	457	117	1.0	U
	22 Sept. 92	1630	13.1	7.48	67.2	46.6	20.1	11	68	0.9	
	23 Nov. 92	3670	5.3	6.90	61.4	24.3	19.5	78	73	3.8	
	25 Jan. 93	7570	3.5	7.10	54.4	44.1	17.6	1970	56	9.1	
	29 March 93	3070	7.3	7.60	68.2	24.4	23.8	11	54	2.6	
	24 May 93	4190	11.9	7.10	53.8	21.5	20.1	32	28	2.9	
Yakima	28 July 92	1190	24.7	8.13	279	117	117	29	163	2.6	
	23 Sept. 92	1440	19.4	8.47	308	123	130	12	192	2.5	
	24 Nov. 92	1870	5.7	8.10	283	109	120	6	178	1.7	
	26 Jan. 93	3180	5.1	6.84	319	119	130	41	203	2.1	
	30 March 93	4090	10.5	7.33	187	75.3	78.2	68	274	4.4	
	25 May 93	2060	18.9	8.14	194	76.0	78.2	32	132	2.9	

data qualifiers defined at end of appendix

Appendix B.7 Ancillary Water Quality Data on Duplicate (splits) and Replicated Samples

River	Date	Temp. (C)	pH	Specific Cond. (umho/cm)	Total Hardness (mg/L)	Total Alkalinity (mg/L)	TSS (mg/L)	TDS (mg/L)	TOC (mg/L)
Duwamish	27 July 92	21.0	7.27	155	53.7	53.7	6	92	1.6
duplicate		na	na	155	52.7	53.6	12	88	1.7
replicate		na	na	157	51.7	53.3	4	92	2.4
Duwamish	23 Nov. 92	6.1	6.90	59.5	23.3	21.2	13	66	2.5
duplicate		na	na	59.5	24.3	21.1	20	62	2.6
replicate		na	na	59.5	20.8	21.3	19	63	2.5
Duwamish	29 March 93	7.6	7.30	66.5	23.8	25.1	12	60	1.9
duplicate		na	na	na	24.2	25.2	13	51	1.8
replicate		na	na	65.3	24.0	25.2	11	58	2.0
Yakima	23 Sept. 92	19.4	8.47	308	123	130	12	192	2.5
duplicate		na	na	309	114	130	11	186	2.3
replicate		na	na	302	115	130	11	189	2.3
Yakima	26 Jan. 93	5.1	6.84	319	119	130	41	203	2.1
duplicate		na	na	318	119	na	45	194	2.0
replicate		na	na	319	119	130	35	211	2.2
Yakima	25 May 93	18.9	8.14	194	76.0	78.2	32	132	2.9
duplicate		na	na	na	75.0	78.7	na	na	3.0
replicate		na	na	193	76.0	78.5	31	136	3.0

data qualifiers defined at end of appendix

APPENDIX C.

PARTITION COEFFICIENTS

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PARTITION COEFFICIENTS

Data of the type collected during this survey are useful for predicting the fate and transport of metals in rivers and streams. Accurate determination of the partition coefficient (K_p), a measure of a metal's tendency to complex with or adsorb to particulates, is critical to models used for waste load allocations and permit writing.

Theory, calculation, and use of partition coefficients are discussed in Delos *et al.* (1984) and Mills *et al.* (1985). Delos *et al.* contains results of a study analyzing over 20,000 records nationwide to determine K_p for priority pollutant metals and its relation to other water quality variables. The following are among the more important conclusions of these reports:

1) K_p has a clear and consistent relationship to TSS.
2) K_p appears to be independent of other variables like pH, alkalinity, and temperature.
3) Variability of K_p estimates can be an order of magnitude or more.
4) This uncertainty points to the need for using site-specific K_p values whenever possible.

Based on linear partitioning theory, the only data needed to calculate K_p are concentrations of dissolved metal (C_d), particulate or total metal (C_p, C_t), and TSS:

$$C_p = C_t - C_d \quad \text{and} \quad K_p = (C_p/\text{TSS}) \,/\, C_d$$

C_p/TSS is the particulate metal-to-TSS ratio in ug/g. C_t and C_d are in μg/L; K_p is normally expressed in units of L/Kg.

K_p was calculated with data from the present survey and results plotted in Figure C.1. Dissolved concentrations equaled or exceeded total concentrations in a few instances in samples from the Green and Puyallup Rivers (separate grabs). These data were excluded from the calculations. As a result, data were available for between 14 (cadmium) to 19 (copper) individual determinations of K_p..

Results show K_p values centered in the range of 10^4-10^5. For TSS concentrations between 1-1,000 mg/L, Mills *et al.* report K_p values of $1\text{x}10^4$-$1\text{x}10^6$for zinc, $6\text{x}10^3$-$1\text{x}10^6$for copper, $9\text{x}10^4$-$3\text{x}10^5$for lead, and $2\text{x}10^3$-$4\text{x}10^6$for cadmium.

Figure C.1 shows that uncertainty needs to be considered if models are to be developed to estimate K_p for sites without partitioning data. Data from other Ecology surveys mentioned elsewhere in this report and results of future investigations should be incorporated into this type of analysis to refine estimates of K_p for local rivers.

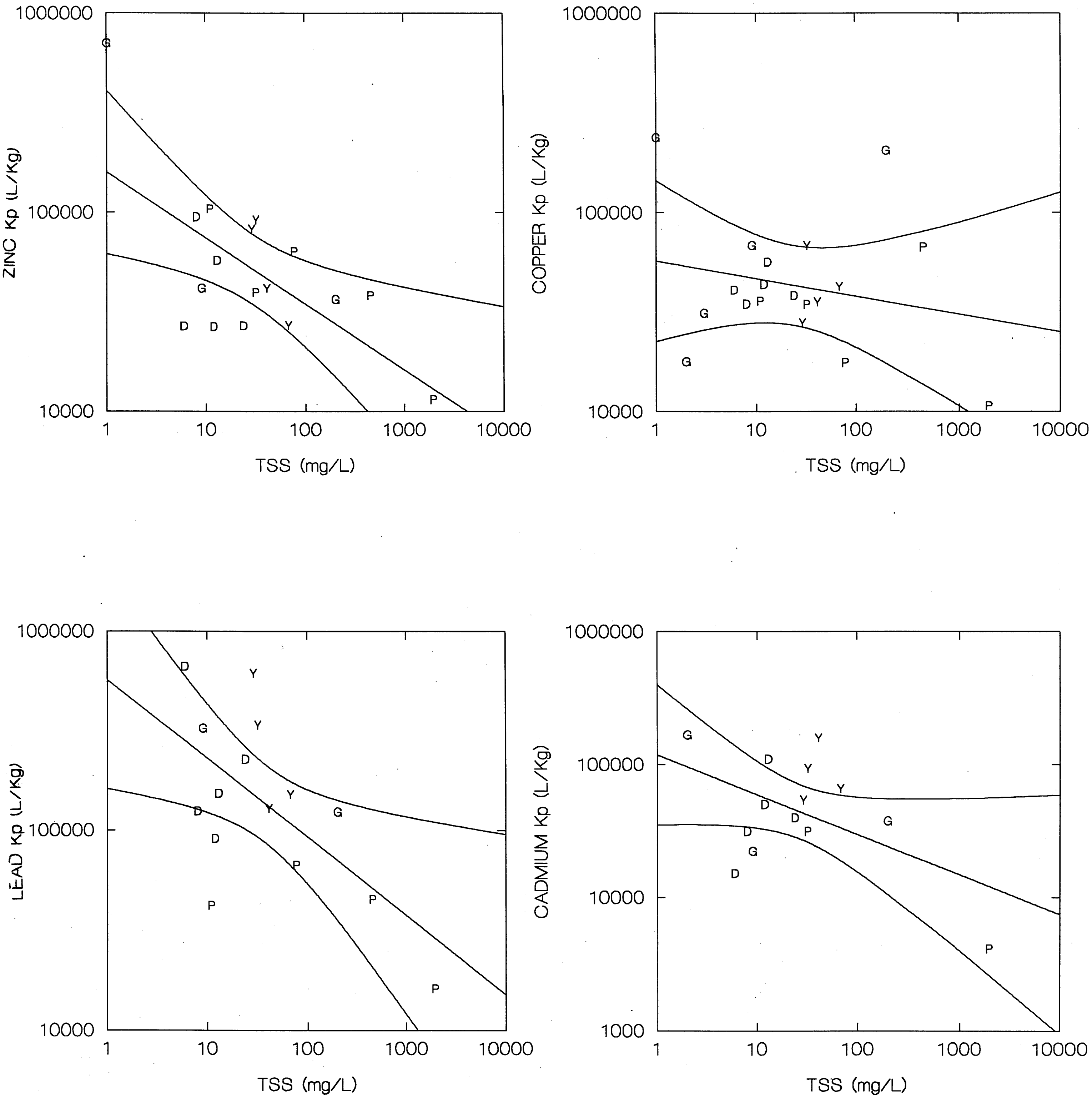

Figure C.1. Partition Coefficient vs. TSS (95% C.I.).

APPENDIX D.

MERCURY DATA

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Appendix D. Unpublished Mercury Data Provided by Brad Hopkins
Ecology Ambient Monitoring Program (ug/L)

River	Date	Total Hg
Green	27 July 92	na
	22 Sept. 92	na
	23 Nov. 92	0.0020 J
	25 Jan. 93	0.1142 J
	29 March 93	0.0018 B
	24 May 93	0.0014 J
Duwamish	27 July 92	na
	22 Sept. 92	na
	23 Nov. 92	0.0016 J
	25 Jan. 93	0.0091 J
	29 March 93	0.0046 B
	24 May 93	0.0023 B
Puyallup	27 July 92	na
	22 Sept. 92	na
	23 Nov. 92	0.0021
	25 Jan. 93	0.0283
	29 March 93	0.0031
	24 May 93	0.0030