WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

Cadmium, Copper, Mercury, Lead, and Zinc In the Spokane River:

Comparisons with Water Quality Standards and Recommendations for Total Maximum Daily Loads

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Water Body No. WA-54-1020 and WA-57-1010

Publication No. 94-99

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Abstract

A study of cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn) concentrations in the Spokane River was conducted. Samples were collected on eight occasions between July 1992 and September 1993. Three locations were sampled between river miles 63.5 and 96.0. Dissolved, total, and total recoverable metals were analyzed. Water quality criteria for dissolved Zn were not met at all three sampling locations during high and low flow seasons. Criteria for dissolved Pb were exceeded at all sampling sites during the high flow season. Criteria for Cd were exceeded in the upper river during the high flow season. Nonpoint sources of Cd, Pb, and Zn from historical mining practices in Idaho are considered to be the major reason for violation of Washington's water quality criteria and are considered likely to sustain excessive background loading for many years. Concentrations of trace metals relative to criteria in the Spokane River generally decreased proceeding downstream from the state line. The fractions of dissolved/total metals were similar throughout the study area and generally increased in the order of Pb < Cd < Zn < Cu. Most metals concentrations increased with river flow.

A seasonal strategy was proposed for total maximum daily loads (TMDLs), load allocations (LAs) from nonpoint sources, and waste load allocations (WLAs) for point sources regulated under the National Pollutant Discharge Eliminations System (NPDES). WLAs were proposed for metals with background concentrations potentially greater than the water quality criteria (Zn throughout the river all year; Pb throughout the river during the high flow season and in the upper river during the low flow season; and Cd in the upper river all year).

A phased TMDL approach is recommended which stipulates that USEPA and Idaho develop a schedule for managing and monitoring loads from Idaho to meet water quality standards for Cd, Pb, and Zn at the Washington border. The phased WLAs for point sources in Washington will ensure that Cd, Pb, and Zn concentrations are not elevated above existing concentrations that are sustained by loading from Idaho, groundwater inflows, and minor nonpoint sources in Washington. Phased WLAs will be adjusted if monitoring data show progress in reducing concentrations sustained by excessive loads from Idaho.

For metals with background concentrations less than the water quality standards (Cu and Hg throughout the river all year, Cd in the lower river all year, and Pb in the lower river during the low flow season), critical conditions of river flows, hardness, background concentrations, and fractions of dissolved/total metals were proposed for calculating water quality-based effluent limits.

Introduction

Background Information

The Spokane River has been placed on the 1992 list under Section 303(d) of the federal Clean Water Act as not meeting water quality criteria for cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn) for protection of aquatic life (Ecology, 1992). The listing was based on monitoring of total recoverable metals by Ecology. Since then the water quality criteria for Cd, Cu, Pb, and Zn were changed and now apply to the dissolved fraction (Chapter 173-201A WAC effective December 26, 1992). The Eastern Regional Office of the Department of Ecology requested an assessment of metals in the river to evaluate compliance with criteria and support a possible Total Maximum Daily Load (TMDL) as authorized in Section 303(d) of the federal Clean Water Act.

The hydrology of the Spokane River between Post Falls, Idaho, and Nine Mile Falls (Figure 1) is dominated by two processes: outlet flows from Lake Coeur d'Alene and groundwater inputs from the Spokane aquifer system (Patmont *et al.*, 1985). Other inputs are minor in comparison to these sources and include Hangman Creek and various point source discharges, which together account for less than five percent of the river flow during the low-flow season. Most of the aquifer inflow to the river occurs between river mile 88 and 78. Groundwater inflows tend to increase the hardness and decrease the trace metal concentrations in the river.

Major sources of metals in the Spokane River include leaching from mine tailings in the Coeur D'Alene River basin in Idaho. The State of Idaho has conducted a problem assessment of metals loading from abandoned tailings and plans to determine the feasibility of reducing metals loading from these sources.

Ecology has collected accurate ambient monitoring data for total recoverable Cd, Cu, Hg, Pb, and Zn at the state line (river mile 96.0), near Post Falls, Idaho (river mile 100.7), and at Riverside State Park (river mile 66.0) between 1987 and 1992. Occasional detection of total recoverable metals greater than the former criteria contributed to the 1992 Section 303(d) listing.

Dissolved metals can be measured in ambient waters and compared with the current criteria. Since effluent limits for permits issued under the National Pollutant Discharge Elimination System (NPDES) are generally expressed as total recoverable metals, it is necessary to translate between the dissolved and total recoverable concentrations in the receiving water. If no information on partitioning of dissolved metals is available, the criteria for dissolved metals are required to be interpreted as criteria for total recoverable metals under WAC 173-201A, which is equivalent to assuming all of the metals present in the receiving water are in the dissolved form.

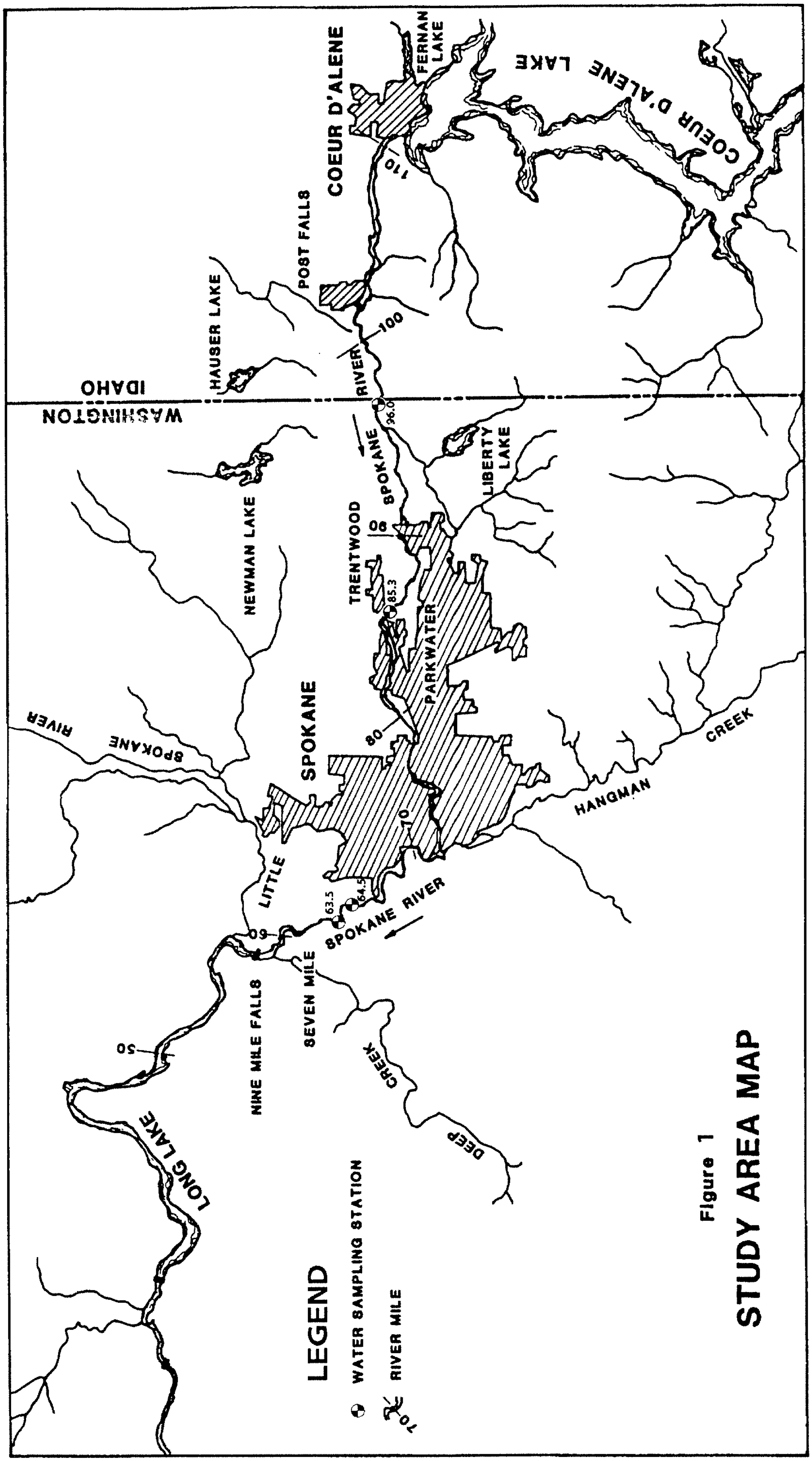

Figure 1
STUDY AREA MAP

Objectives

The survey of metals in the Spokane River was conducted between July 1992 and September 1993. Objectives of the study were as follows:

- obtain accurate data on dissolved, total, and total recoverable Cd, Cu, Hg, Pb, and Zn at various locations in the Spokane River;
- evaluate partitioning of dissolved metals to aid in translating criteria for dissolved metals to NPDES permit limits for total recoverable metals; and
- recommend approaches for implementing Ecology's TMDL process.

Sampling Design

Three stations in the Spokane River were selected to bracket locations of major point source discharges and represent spatial variability in river hardness and metals concentrations based on available Ecology ambient monitoring data. The locations of stations for this study were as follows (Figure 1):

1) Spokane River at the Stateline Bridge, which is the same location as Ecology monitoring station 57A150 at river mile 96.0;

2) Spokane River at Trent Road Bridge, which is the same location as the discontinued Ecology ambient monitoring station 57A145 at river mile 85.3; and

3) Spokane River at the Spokane Rifle Club at river mile 64.5. This station was located approximately 1 mile downstream from the rifle club (river mile 63.5) during the first sampling event (July 28, 1992) and was then moved upstream to the rifle club location for the remaining sampling events because of easier access. No significant inflows occur between river mile 63.5 and 64.5.

Samples were collected during eight events between July 1992 and September 1993 as follows:

1) July 28, 1992
2) September 24, 1992
3) November 25, 1992
4) January 27, 1993
5) March 31, 1993
6) May 25, 1993
7) August 11, 1993
8) September 8, 1993

Flows in the Spokane River at Spokane (USGS station 12422500) at the time of Ecology's sampling ranged from 1,060 cfs to 16,800 cfs (Figure 2). Four of the surveys occurred during summer low flows of less than 2,000 cfs during the months of July through September of 1992 and 1993. Two of the surveys (March and May 1993) occurred during flows greater than 15,000 cfs during spring snow melt. The remaining two surveys (November 1992 and January 1993) occurred during fall and winter conditions. Sampling events represented the range of seasonal conditions during July 1992 through September 1993.

Cd, Cu, Hg, Pb and Zn were analyzed in filtered and unfiltered samples. Data were also obtained for temperature, pH, specific conductance, total hardness, total alkalinity, total suspended solids (TSS), total dissolved solids (TDS), total organic carbon (TOC), nitrate, chloride, sulfate, calcium, magnesium, potassium, and sodium. Samples were also collected for dissolved organic carbon, but the field blanks were too high to confidently use the data.

Two methods were used to analyze unfiltered samples for metals: "total" and "total recoverable." The "total" determination for Cd, Cu, and Pb was performed on samples after a pre-concentration technique (coprecipitation) that allows lower detection limits than sample digestions normally employed in the "total recoverable" method. Dissolved Cd, Cu, and Pb were also determined after coprecipitation.

The total recoverable analysis has been the method of choice 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 originally written in terms of total recoverable metals and NPDES permit limits are generally for total recoverable metals.

Methods and Materials

Sample Collection

All samples were simple grabs collected by hand approximately one foot below the water surface. These were obtained by wading in a few feet from the river bank. Metals samples were taken in 500 mL teflon bottles. Unfiltered samples for metals were preserved with 2 mL concentrated HCl immediately after 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 μm cellulose nitrate filter unit (Nalgene #450-0045, type S) before being acidified. The acid was carried in small teflon vials, one per sample.

Temperature was measured with a mercury thermometer. pH was determined with an Orion model 250A meter. Sample containers and preservation for other water quality

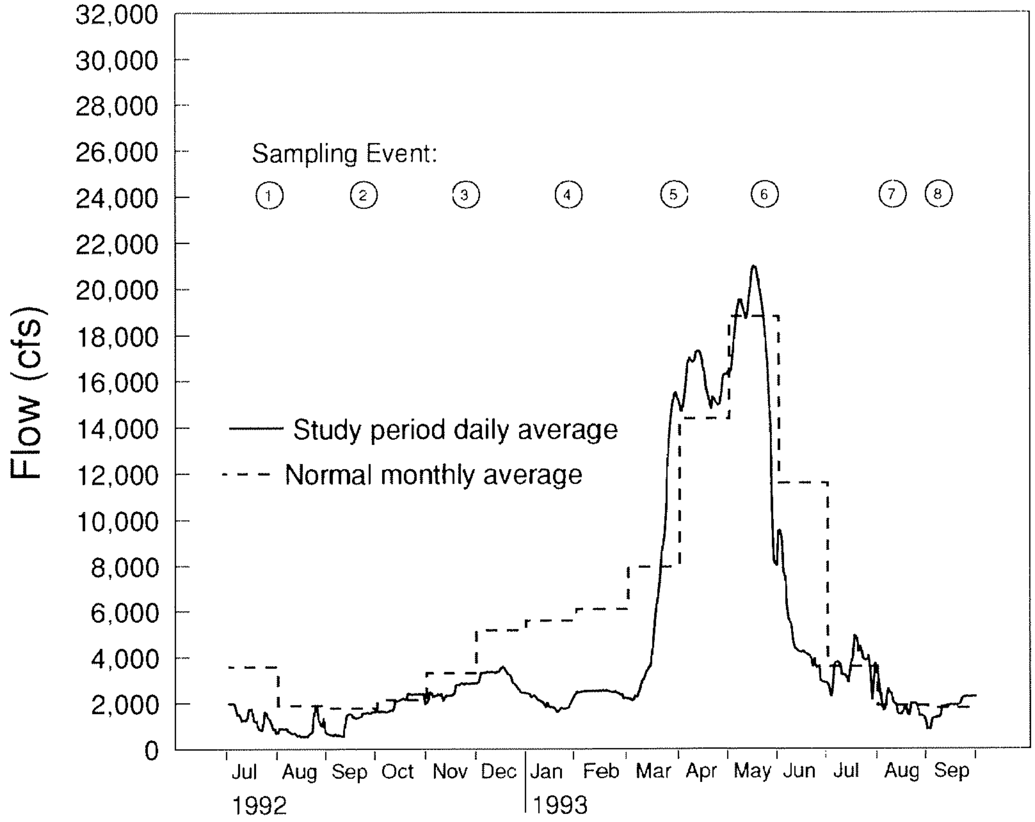

Figure 2. Flow in the Spokane River at Spokane (USGS 12422500) during sampling events for Ecology's metals survey.

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 was 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 was 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

Metals analysis by Battelle Marine Sciences Laboratory, Sequim, WA

Total and dissolved Cd, Cu, and Pb 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). Zn was analyzed directly by GFAA without coprecipitation, after the sample was adjusted to pH 2. Samples for total and dissolved metals were analyzed identically by Battelle. The only difference between samples for total and dissolved metals was the filtration step for dissolved metals, which was performed in the field as described above.

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

The method used for determination of Hg was a combination of mercury cold vapor generation coupled with detection by atomic fluorescence. This method is similar to the cold vapor atomic adsorption methods specified by USEPA (USEPA Methods 245.1, 245.2, 245.5; USEPA, 1979).

Total Recoverable Metals by Manchester Environmental Laboratory

Total recoverable Cd, Cu, Pb, and Zn were analyzed at Ecology's Manchester Environmental Laboratory. Samples were prepared according to USEPA Method 200.2, modified for GFAA analysis. Samples were digested using hot nitric acid in teflon beakers with watch-glass covers on a hot plate. Zn was determined by inductively-coupled plasma emission spectroscopy (ICP) techniques; Cd, Cu, and Pb 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 rinsing with type II deionized water. The laboratory room and hoods were cleaned prior to use specifically for this study's samples. Metals analyses for the last survey were conducted using a new class 100 clean hood for the digestion.

The method for determination of Hg was cold vapor atomic absorbance (USEPA Method 245.1 and 245.5; Huntamer and Hyre, 1991). Samples were digested with a mixture of hot nitric and sulfuric acids and with potassium persulfate and permanganate.

Ancillary Variables

Samples for other water quality determinations were also analyzed at Manchester Laboratory. Methods are described in Huntamer and Hyre (1991).

Field Procedures to Assess Data Quality

Field Blanks

Bottle and filter blanks were analyzed approximately 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 coprecipitated metals.

Reference Materials

Each laboratory received two standard reference materials (SRM) with every set of samples (except for the August 1993 sampling). 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 (NIST) "Trace Elements in Water" (1643c), has metals concentrations one-to-two orders of magnitude above those in SLRS-2. In addition to blind SRM samples, the Battelle lab reported results of internal (non-blind) analyses of SRMs including SLRS-2 and NIST's 1643b. The certified levels of trace metals in SRMs were as follows (in μg/L):

SRM	Cd	Cu	Hg	Pb	Zn
SLRS-2	0.028 ± .004	2.76 ± 0.17	NA	0.129 ± .011	3.33 ± 0.15
1643c	12.2 ± 1.0	22.3 ± 2.8	NA	35.3 ± 0.9	73.9 ± 0.9
1643b	NA	NA	1520 ± 40	NA	NA

Replicate Samples

Replicate samples were collected and submitted blind to the laboratory to provide estimates of combined field and analytical variability. On each sampling date, two replicate samples were taken approximately 15 minutes to 2 hours apart at the upstream station (Stateline Bridge at river mile 96.0) to assess short-term changes in water quality and total sampling and laboratory variability.

Quality Assurance Review of Metals Data

Bill Kammin, director of Ecology's Manchester Environmental Laboratory, prepared written quality assurance reviews that evaluated the validity and usefulness of all metals data from Manchester and Battelle. 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 concurrent study of metals in the Green, Puyallup, and Yakima Rivers also shared Quality Assurance data and review (Johnson, 1994).

Total Recoverable Metals by Manchester Environmental Laboratory

All analyses of Cd, Cu, Pb and Zn 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. LCS 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 0.1 ppb Cd, 1.0 ppb Cu, 1.0 ppb Pb, and 4.0 ppb Zn. The procedural blank for samples collected during November had 40 ppb Zn. 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).

Metals Analysis by Battelle

CLP holding times were met for all analyses of Cd, Cu, Pb, and Zn. Analyses of Hg were performed within the required holding time of 28 days except for the November 1992 samples, which were held for 42 days before analysis. Results of November 1992 analyses of Hg by Battelle are reported with a "J" qualifier to indicate that these values are estimates. Because the dissolved samples from September 1992 were accidently disposed of at Battelle before they could be analyzed, no dissolved data are available for this sampling event.

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 Cd, Cu, Pb, and Zn (these data are presented under Results and Discussion).

Metal concentrations in some procedural blanks (Appendix A.4) were equivalent to or exceeded method detection limits for Cd (0.01 ppb), Cu (0.025 ppb), Pb (0.035 ppb), Hg (0.00006 ppb), Pb (0.035 ppb), and Zn (0.6 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 Qualifiers and Treatment of Censored Values

The complete data obtained during the survey are in Appendix A. Following protocols of the Manchester Environmental Laboratory, the metals data have not been corrected for lab method blanks in Appendix A. An evaluation of the effect of subtracting lab method blanks on improving data accuracy is included in the following section on SRM results. Several qualifiers were used to flag data to indicate possible inaccuracies:

- "U" indicates that the analyte was not detected at or above the reported result;
- "J" indicates that the analyte was positively identified and the reported value is an estimate;
- "P" indicates that the value was above the instrument detection limit but below a limit for reliable quantitation and the reported value is an estimate; and
- "B" indicates that the value is less than 10 times the highest analytical blank which suggests that the sample may have been contaminated during analysis.

Most of the metals analyses contain at least some values with qualifiers (U, J, P, or B). All of the total recoverable results for Cd, Cu, Hg, and Pb (but only 10% of the total recoverable Zn) were qualified with U, J, or P. Most of the total and dissolved metals by Battelle (greater than 85% of the observations), with the exception of Hg and dissolved Pb, did not require qualifiers and were found at quantifiable levels; contamination during analysis was not likely.

For clarity of presentation, data qualifiers shown in the Appendix A are not always 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.

Detection limits for total recoverable Cd, Cu, Hg, and Pb resulted in numerous values reported as less than the detection limit (censored values). Statistical parameters (e.g., means and standard deviations) for variables with censored values were calculated using Helsel's Robust method as implemented in version 3.0 of UNCENSOR© (Newman *et al.*, 1992). Censored values were included in plots, regressions, analysis of variation, and correlation analyses by using half the detection limit as an estimate of the concentration.

Blanks

A summary of the field and lab method blank data is presented in Table 1. Metal concentrations in the field blanks were at or near detection limits for Cd, Cu, Hg, Pb, and Zn. Results of filter blanks, bottle blanks, and lab method blanks were generally comparable which demonstrated that the field sampling and filtering procedure did not introduce significant contamination to the samples.

Standard Reference Materials

Table 2 summarizes the laboratories' performance on SRMs. Results for SLRS-2 by Battelle were typically high (based on comparison of median reported values to certified values) by approximately 30% to 40% for Cd, Cu, Pb, and Zn without subtraction of lab method blanks and 21% to 34% high for Cd, Cu, and Pb with subtraction of method blanks. Subtraction of lab method blanks improved typical low-level accuracy of Zn to only 7% higher than the certified value.

Results of NIST's 1643c by Battelle showed a high bias for Zn (the median reported value was 65% higher than the certified value) and Cu (median 16% higher than certified). No significant improvement in accuracy of reporting NIST's 1643c was found by subtracting the lab method blanks.

The total recoverable analyses by Manchester were generally more accurate than total metals analyses by Battelle. However, with the exception of copper, the total recoverable method was unable to detect the low metals concentrations in SLRS-2. Subtraction of lab method blanks from reported values was not considered to be appropriate based on standard USEPA calibration methodology and marginal improvement in data accuracy.

Field Variability

Table 3 presents results of field replicates. The coefficient of variation (standard deviation as a fraction of the mean) of field replicates was generally less than 10 percent for Cd, less than 20 percent for Cu, Pb, and Zn, and 30 percent or less for Hg. Filtering the samples did not introduce substantial additional variability to the results except for Hg. Variance of split samples reported by the lab was generally less than variance of the blind field replicates. Compared to total variability including seasonal differences in metals concentrations (presented in following sections), the combined effects of sampling, analytical, and short-term field variability appeared to be minor.

Table 1. Summary of field and lab blanks (1).

	Field Bottle Blank (ug/L)	Field Filter Blank (ug/L)	Lab Method Blank (ug/L)
Cd	0.004 (0.001-0.005)	0.005 (0.001-0.014)	0.001 (0.001U-0.006)
Cu	0.058 (0.016-0.59UB)	0.095 (0.016-1.8)	0.024 (0.012U-0.64)
Hg	0.00081UB (0.00069UB-0.00093UB)	0.00087UB (0.00059UB-0.00114B)	0.00120 (0.00082-0.0018)
Pb	0.034 (0.031-0.040)	0.030 (0.028UB-0.035)	0.035U (0.02U-0.032)
Zn	0.90 (0.4UB-1.3)	0.78 (0.45UB-1.8)	0.81 (0.29-1.1)

1) Median values with range in parentheses.
U = the analyte was not detected at or above the reported result.
B = the analyte was also found in the lab method blank at a level that indicates the sample may have been contaminated.

Table 2. Summary of reported values for standard reference materials as a fraction of the certified values (1).

Standard Reference Material	Manchester	Battelle (not blank-corrected)	Battelle (blank-corrected)
SLRS-2:			
Cd	--	1.39 (1.14 - 2.14)	1.34 (1.10 - 2.09)
Cu	0.98 (0.80 - 1.38)	1.32 (0.86 - 1.48)	1.21 (0.90 - 1.46)
Pb	--	1.40 (1.16 - 1.82)	1.26 (0.96 - 1.71)
Zn	--	1.30 (0.76 - 51)	1.07 (0.65 - 51)
NIST 1643c:			
Cd	1.05 (0.98 - 1.14)	1.03 (0.68 - 4.23)	1.03 (0.68 - 4.23)
Cu	0.85 (0.81 - 1.10)	1.16 (0.89 - 1.39)	1.16 (0.89 - 1.39)
Pb	1.07 (0.94 - 1.12)	1.01 (0.70 - 1.17)	1.01 (0.70 - 1.17)
Zn	0.99 (0.87 - 1.61)	1.65 (1.11 - 2.48)	1.64 (1.09 - 2.47)
NIST 1643b:			
Hg	--	0.97 (0.46 - 1.16)	--

1) Median (range in parentheses) of the ratio of reported/certified values for all analyses of standard reference materials. Battelle data were analysed with and without subtraction of analytical blank values from the reported values.

Table 3. Summary of variability of field replicates.

	Coefficient of Variation (Standard Deviation as Percent of Mean)	Standard Deviation of Field Replicates (ug/L)
Cd		
Total Recoverable	9.5%	0.015
Total (co-precipitated)	7.9%	0.022
Dissolved (co-precipitated)	6.1%	0.016
Cu		
Total Recoverable	--	--
Total (co-precipitated)	13.0%	0.13
Dissolved (co-precipitated)	18.0%	0.16
Hg		
Total Recoverable	--	--
Total	17.4%	0.000271
Dissolved	30.5%	0.000656
Pb		
Total Recoverable	--	--
Total (co-precipitated)	11.9%	0.153
Dissolved (co-precipitated)	12.1%	0.038
Zn		
Total Recoverable	6.6%	5.1
Total	13.9%	19.7
Dissolved	8.2%	10.0

Compliance with Water Quality Criteria for Cd, Cu, Hg, Pb, and Zn

Water quality criteria to protect aquatic life (established in WAC 173-201A-040) apply to the dissolved fraction for Cd, Cu, Pb, and Zn and are calculated with the following equations for chronic (4-day average not to be exceeded more than once every three years) and acute (one-hour average not to be exceeded more than once every three years):

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

Hardness during the study ranged from 19.1 to 92 mg/L as $CaCO_3$. Hardness increases significantly proceeding downstream between stations because of the inflow of groundwater. Hardness also varies seasonally and is lowest during spring when river flows are highest. The range in chronic criteria (in μg/L) for dissolved Cd, Cu, Pb, and Zn during the study was as follows for the observed range in hardness:

Parameter	Chronic Criteria (μg/L) At Minimum Hardness of 19.1 mg/L as $CaCO_3$	Chronic Criteria (μg/L) At Maximum Hardness of 92 mg/L as $CaCO_3$
Cd	0.27	0.92
Cu	2.5	9.5
Pb	0.27	2.0
Zn	23.2	88.0

Water quality criteria for Hg apply to total recoverable fraction. The criteria for total recoverable Hg are 0.012 μg/L for chronic (4-day average not to be exceeded more than once every three years on the average) and 2.4 μg/L for acute (1-hour average not to be exceeded more than once every three years on the average).

Concentrations of dissolved Cd, Cu, Pb, and Zn and total Hg are presented and compared with chronic criteria in Figures 3, 4, 5, 6, and 7, which are box plots that display the minimum, 25th percentile, median, 75th percentile, and maximum values (SYSTAT, 1990). Sample results were compared with criteria for each station and sampling time by using hardness measurements from the same station and sampling time. Dissolved Cd, Pb, and Zn were found to exceed chronic criteria in several samples.

Concentrations of dissolved Cd, Cu, Pb, and Zn typically decreased relative to criteria proceeding from upstream to downstream stations. This occurred mainly because of increases in hardness, which resulted in increases in metals criteria proceeding downstream. Concentrations relative to criteria also varied seasonally with highest values typically associated with highest river flows during winter and spring.

Table 4 presents sample measurements of dissolved Cd, Pb, and Zn which exceeded criteria. Dissolved Cd criteria were exceeded in two samples from river mile 96.0. All Cd samples from river miles 85.3 and 63.5-64.5 were below criteria. Dissolved Pb criteria were exceeded at all three stations during the May 25, 1993 survey. Dissolved Zn was greater than acute and chronic criteria at all stations on most sampling dates.

Summary of Cd, Cu, Hg, Pb, and Zn Measurements

Summary statistics for all metals measurements are presented in Table 5. The statistical summaries are presented by station. However, no significant differences between stations were found for metals concentrations using Kruskal-Wallis analysis of variance tests (SYSTAT, 1990). Significant differences (at a probability level of less than 0.05) in metals concentrations between sampling events were found for Cd, Cu, Hg, Pb, and Zn.

Comparison of Total and Total Recoverable Metals

A comparison of total Cd, Cu, Pb, and Zn measurements by Battelle with total recoverable measurements by Manchester Environmental Laboratory is shown in Figure 8. Results of the two methods were not significantly different for Pb based on regression analysis. Total Zn by Battelle was significantly higher than total recoverable measurements by Manchester. Total Cd was significantly lower than total recoverable Cd. However, results for the two Cd methods were within 10 percent on average, which was relatively good compared with Cu and Zn. Differences between methods for Cu could not be accurately estimated because the detection limits for total recoverable Cu were too high to quantify most of the data.

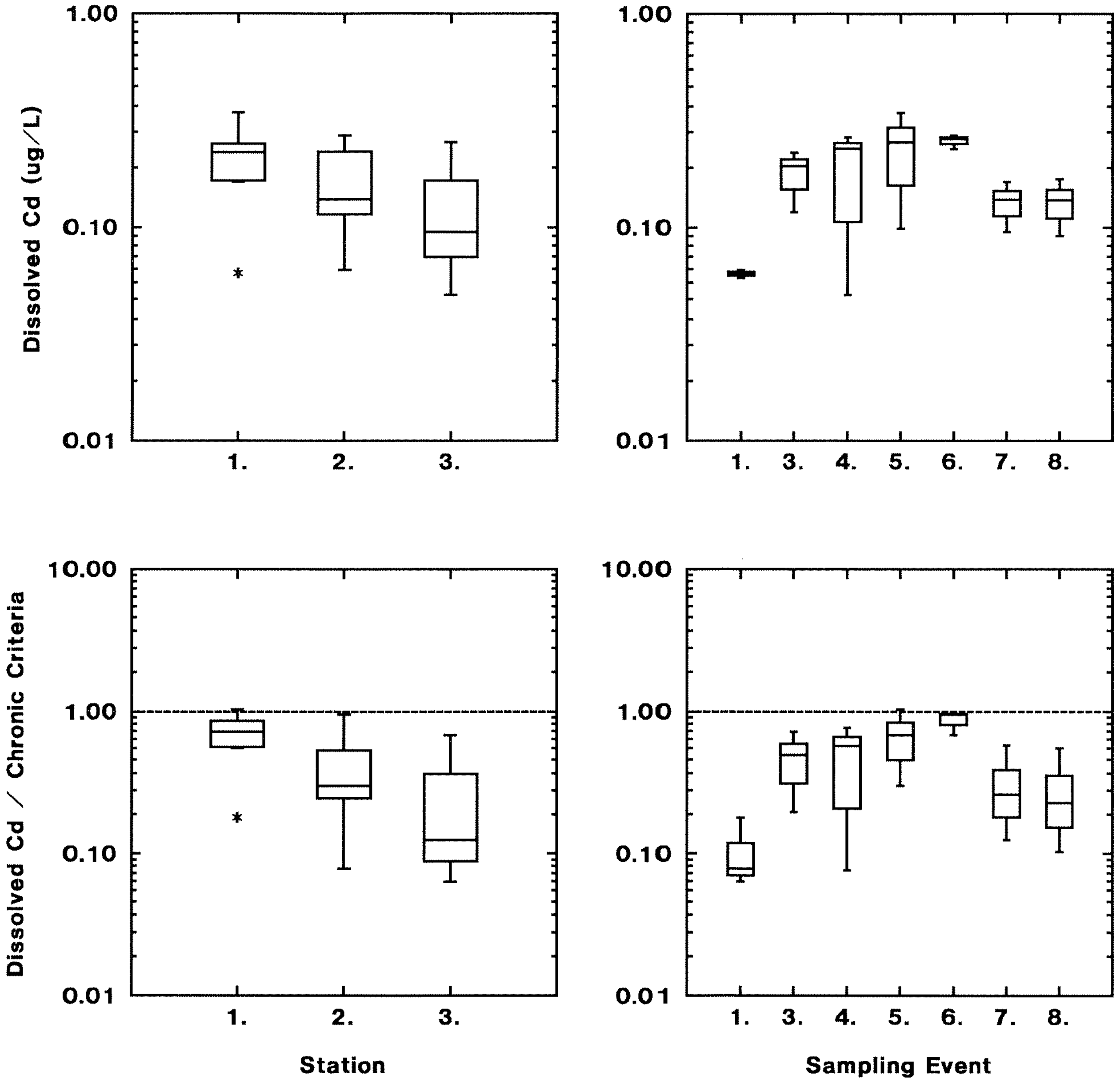

Figure 3. Box plots of dissolved Cd by station and sampling event with comparison to chronic aquatic life criteria (dissolved Cd / chronic criteria). (station 1= river mile 96.0; 2= river mile 85.3; 3= river mile 63.5-64.5) (sampling event 1= 28-Jul-92; 3= 25-Nov-92; 4= 27-Jan-93; 5= 31-Mar-93; 6= 25-May-93; 7= 11-Aug-93; 8= 8-Sep-93)

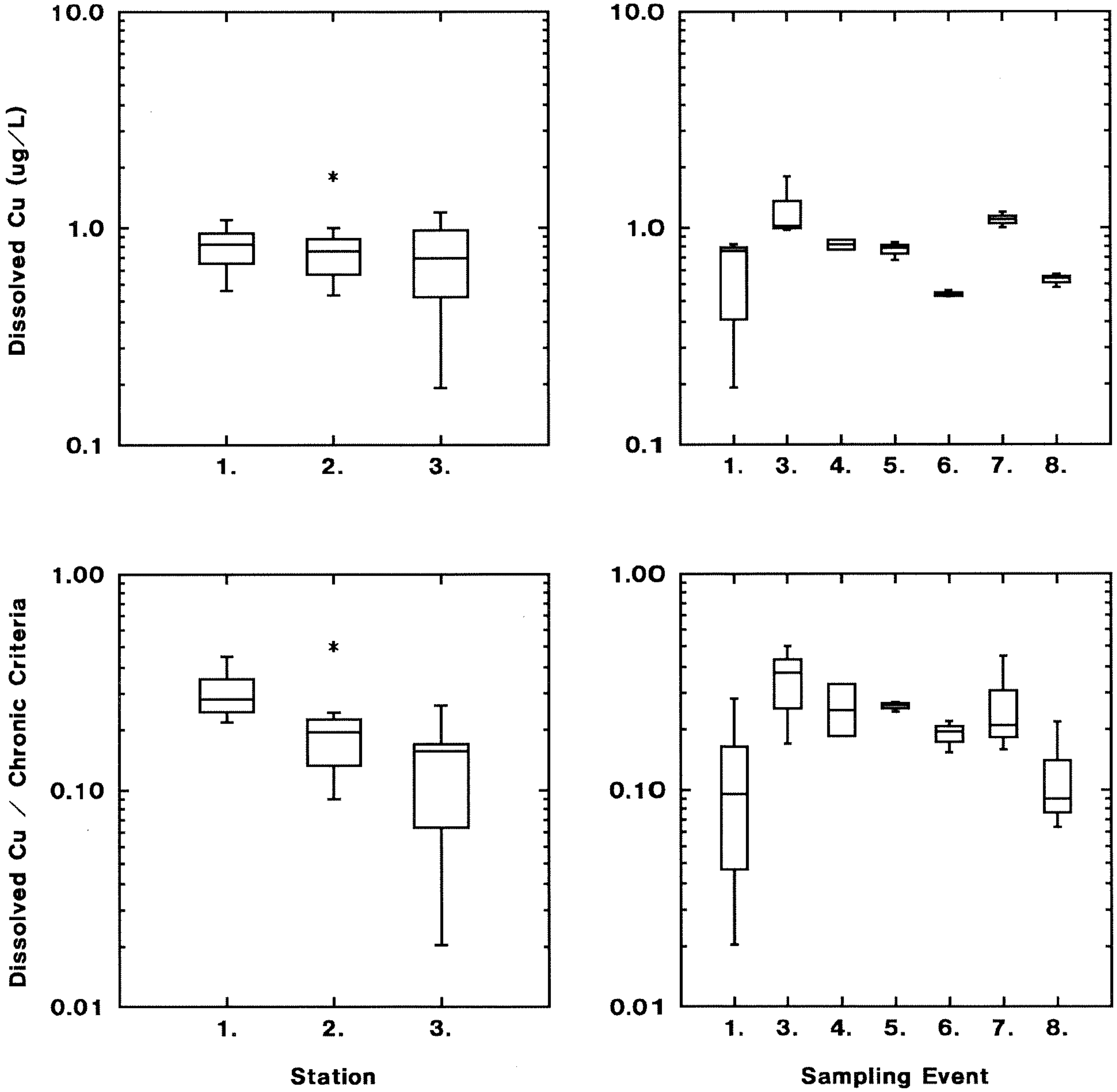

Figure 4. Box plots of dissolved Cu by station and sampling event with comparison to chronic aquatic life criteria (dissolved Cu / chronic criteria). (station 1= river mile 96.0; 2= river mile 85.3; 3= river mile 63.5-64.5) (sampling event 1= 28-Jul-92; 3= 25-Nov-92; 4= 27-Jan-93; 5= 31-Mar-93; 6= 25-May-93; 7= 11-Aug-93; 8= 8-Sep-93)

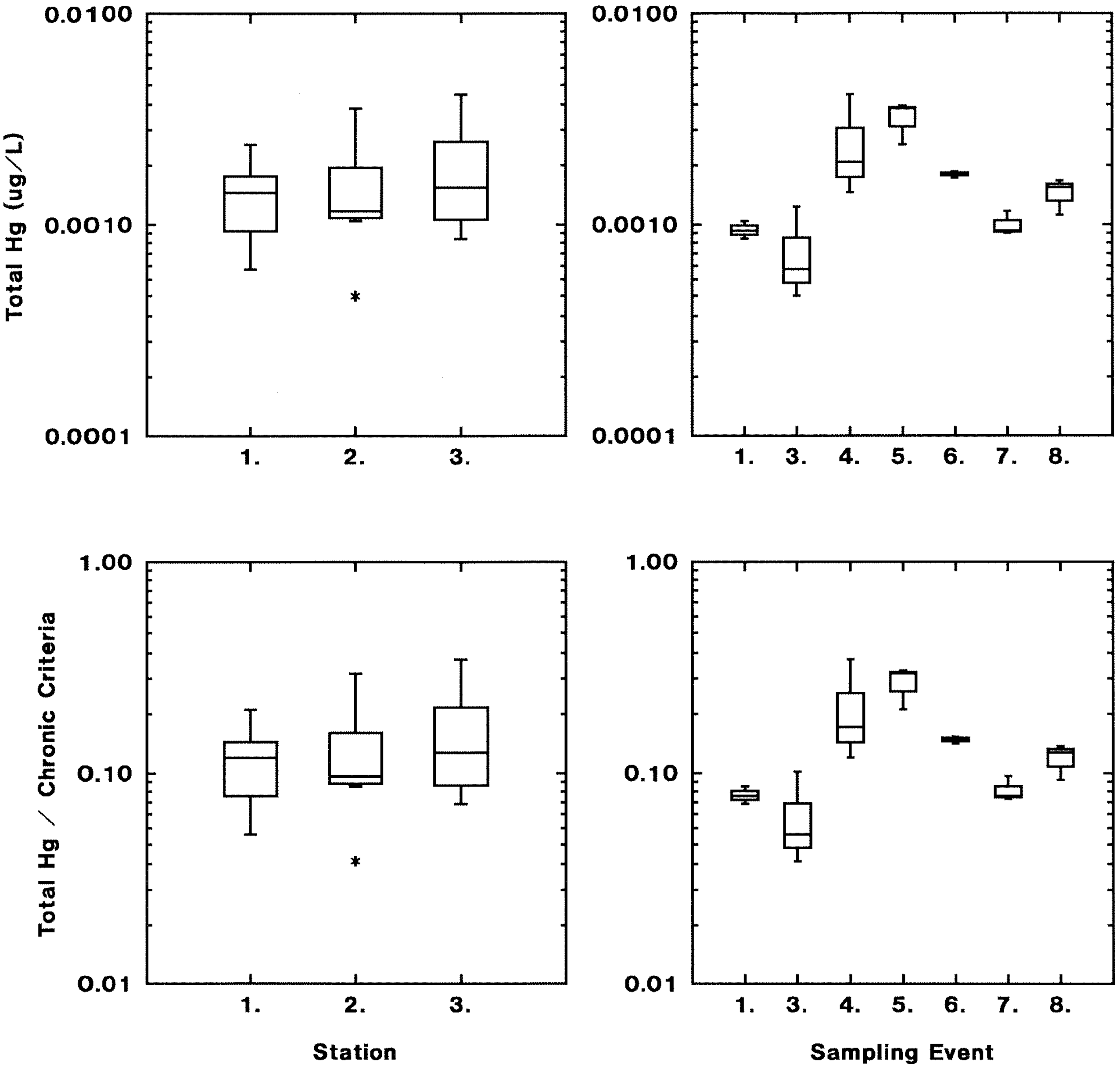

Figure 5. Box plots of total Hg by station and sampling event with comparison to chronic aquatic life criteria (total Hg / chronic criterion). (station 1= river mile 96.0; 2= river mile 85.3; 3= river mile 63.5-64.5) (sampling event 1= 28-Jul-92; 3= 25-Nov-92; 4= 27-Jan-93; 5= 31-Mar-93; 6= 25-May-93; 7= 11-Aug-93; 8= 8-Sep-93)

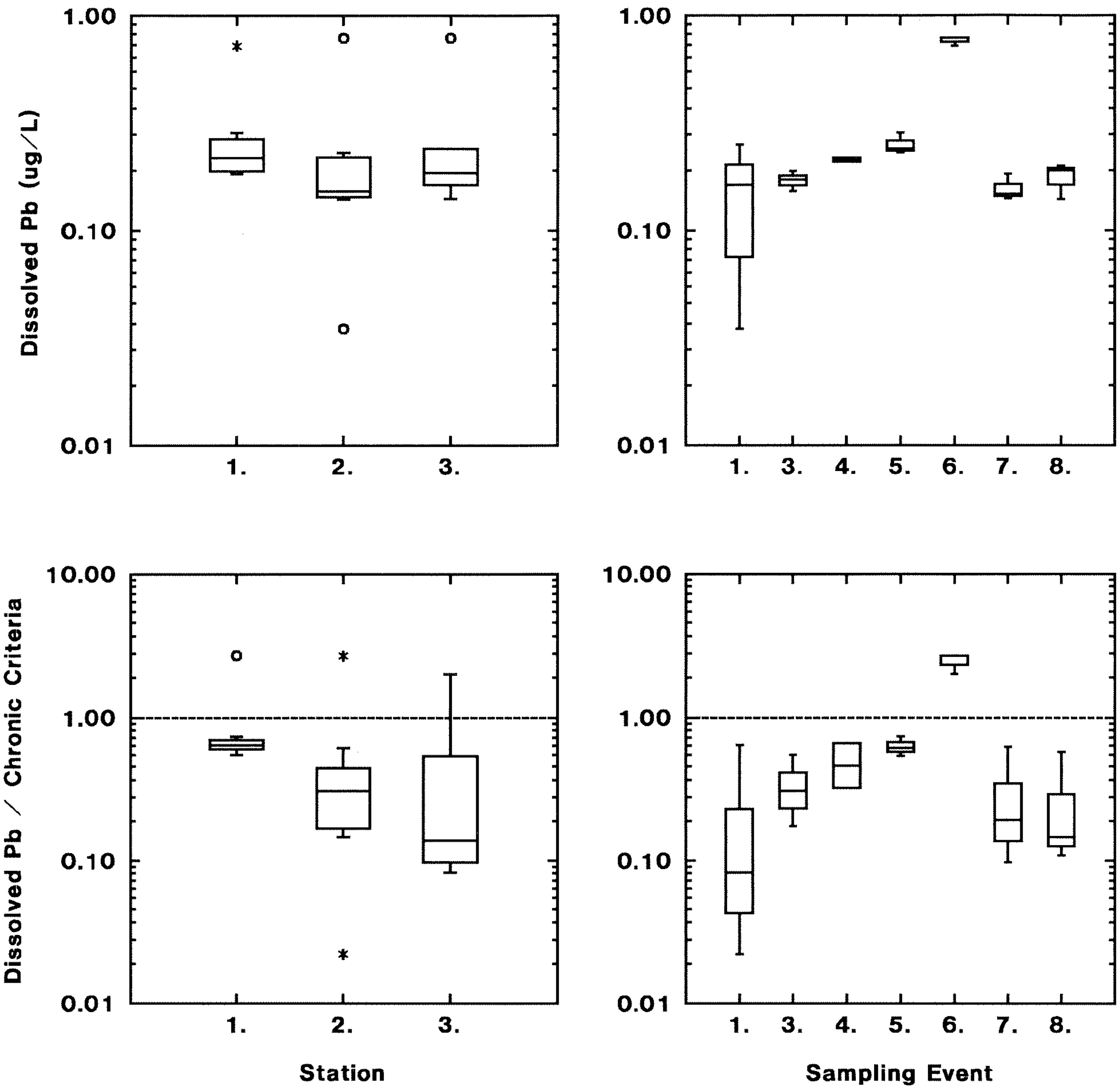

Figure 6. Box plots of dissolved Pb by station and sampling event with comparison to chronic aquatic life criteria (dissolved Pb / chronic criteria). (station 1= river mile 96.0; 2= river mile 85.3; 3= river mile 63.5-64.5) (sampling event 1= 28-Jul-92; 3= 25-Nov-92; 4= 27-Jan-93; 5= 31-Mar-93; 6= 25-May-93; 7= 11-Aug-93; 8= 8-Sep-93)

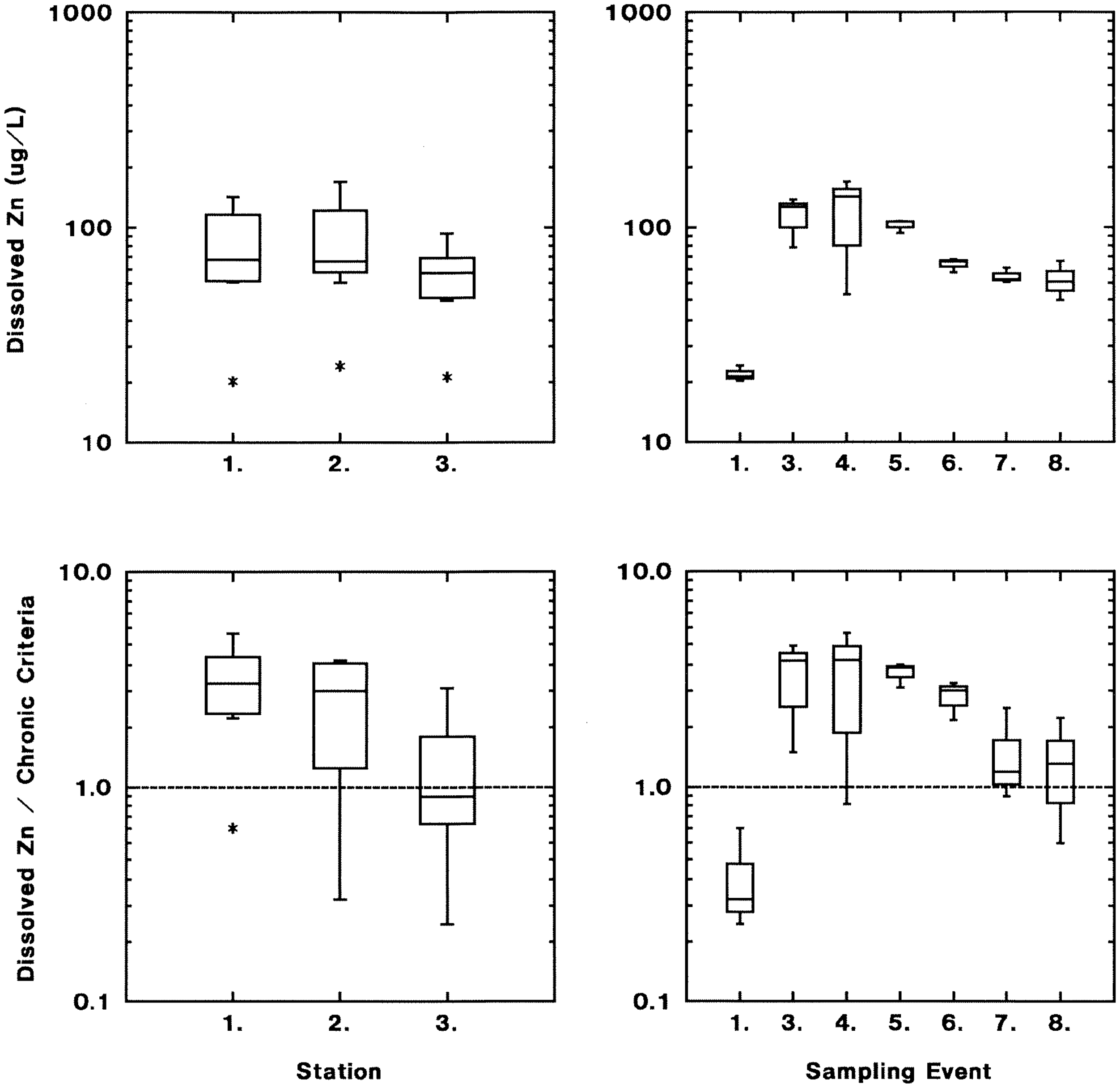

Figure 7. Box plots of dissolved Zn by station and sampling event with comparison to chronic aquatic life criteria (dissolved Zn / chronic criteria). (station 1= river mile 96.0; 2= river mile 85.3; 3= river mile 63.5-64.5) (sampling event 1= 28-Jul-92; 3= 25-Nov-92; 4= 27-Jan-93; 5= 31-Mar-93; 6= 25-May-93; 7= 11-Aug-93; 8= 8-Sep-93)

Table 4. Summary of dissolved metals samples which exceed water quality criteria.

Date	Spokane River Mile	Sampling Time	Dissolved Metal Concentration (ug/L)		Hardness (mg/L as CaCO3)	Chronic Criteria (ug/L)	Acute Criteria (ug/L)
Dissolved Cd:							
31-Mar-93	96.0	700	0.37	C	24.7	0.33	0.70
25-May-93	96.0	1630	0.27	C	19.3	0.27	0.53
Dissolved Pb:							
25-May-93	96.0	1615	0.681	C	19.1	0.27	6.8
25-May-93	85.3	1705	0.788	C	20.6	0.29	7.5
25-May-93	64.5	1515	0.788	C	26	0.39	10.1
25-May-93	96.0	1630	0.766	C	19.3	0.27	6.9
Dissolved Zn:							
25-Nov-92	96.0	848	131	CA	23.6	27.8	30.7
25-Nov-92	85.3	1000	135	CA	31.1	35.1	38.8
25-Nov-92	64.5	1112	80.6	CA	53.6	55.7	61.5
25-Nov-92	96.0	910	118	CA	23	27.2	30.0
27-Jan-93	96.0	850	156	CA	22.4	26.6	29.4
27-Jan-93	85.3	955	163	CA	38.4	42.0	46.3
27-Jan-93	96.0	910	122	CA	22.8	27.0	29.8
31-Mar-93	96.0	700	107	CA	24.7	28.9	31.9
31-Mar-93	85.3	800	107	CA	24.9	29.1	32.1
31-Mar-93	64.5	900	94.3	CA	28.5	32.6	36.0
31-Mar-93	96.0	715	105	CA	26.3	30.5	33.6
25-May-93	96.0	1615	72.4	CA	19.1	23.2	25.6
25-May-93	85.3	1705	69.3	CA	20.6	24.8	27.3
25-May-93	64.5	1515	61.6	B CA	26	30.2	33.3
25-May-93	96.0	1630	69.3	CA	19.3	23.4	25.9
11-Aug-93	96.0	1450	57.3	CA	21	25.2	27.8
11-Aug-93	85.3	1400	55.5	CA	44	47.1	52.0
11-Aug-93	96.0	1510	57.3	CA	20	24.1	26.7
08-Sep-93	96.0	1420	59.8	CA	23	27.2	30.0
08-Sep-93	85.3	1330	69.8	CA	52	54.3	59.9
08-Sep-93	96.0	1440	51.8	CA	22	26.2	28.9

Data Qualifier:

B = the analyte was also found in the analytical blank at a level which indicates the sample may have been contaminated
C = the value exceeds the chronic aquatic life criteria
CA = the value exceeds the chronic and acute aquatic life criteria

Table 5. Summary of Spokane River metals data from 28-Jul-92 through 08-Sep-93.

Parameter	Spokane River Mile	Number of Samples	Median	Mean	Standard Deviation	Coefficient of Variation	Minimum	Maximum
Total Recoverable Cd	96.0	7	0.295	0.309	0.133	0.429	0.145	0.550
(ug/L)	85.3	8	0.240	0.268	0.143	0.533	0.130	0.550
	63.5-64.5	8	0.175	0.232	0.149	0.642	0.10U	0.530
Total Cd	96.0	8	0.267	0.269	0.107	0.398	0.108	0.469
(ug/L)	85.3	8	0.222	0.251	0.112	0.447	0.091	0.464
	63.5-64.5	8	0.151	0.213	0.139	0.652	0.098	0.501
Dissolved Cd	96.0	7	0.226	0.208	0.089	0.429	0.061	0.346
(ug/L)	85.3	7	0.135	0.166	0.080	0.484	0.063	0.271
	63.5-64.5	7	0.095	0.128	0.082	0.639	0.048	0.251
Total Recoverable Cu	96.0	7	1U	--	--	--	1U	1.15
(ug/L)	85.3	8	1U	--	--	--	1U	1.40
	63.5-64.5	8	1U	--	--	--	1U	1.80
Total Cu	96.0	8	0.749	0.868	0.232	0.268	0.658	1.30
(ug/L)	85.3	8	0.865	1.040	0.475	0.456	0.610	2.04
	63.5-64.5	8	1.160	1.330	0.840	0.632	0.670	3.33
Dissolved Cu	96.0	7	0.844	0.819	0.210	0.256	0.515	1.09
(ug/L)	85.3	7	0.782	0.862	0.419	0.486	0.490	1.73
	63.5-64.5	6	0.735	0.715	0.361	0.505	0.184	1.18
Total Recoverable Hg	96.0	8	0.05U	--	--	--	0.002U	0.1U
(ug/L)	85.3	8	0.05U	--	--	--	0.002U	0.1U
	63.5-64.5	7	0.05U	--	--	--	0.002U	0.1U
Total Hg	96.0	7	0.0014	0.0014	0.0006	0.439	0.0006	0.0024
(ug/L)	85.3	7	0.0012	0.0016	0.0010	0.633	0.0005	0.0035
	63.5-64.5	7	0.0015	0.0020	0.0013	0.673	0.0009	0.0041
Dissolved Hg	96.0	6	0.0016	0.0019	0.0008	0.421	0.00059U	0.0030
(ug/L)	85.3	6	0.0014	0.0016	0.0009	0.563	0.00059U	0.0031
	63.5-64.5	6	0.0014	0.0018	0.0014	0.778	0.00065U	0.0046
Total Recoverable Pb	96.0	7	1U	--	--	--	1U	4.15
(ug/L)	85.3	8	1U	--	--	--	1U	3.70
	63.5-64.5	8	1U	--	--	--	1U	5.10
Total Pb	96.0	8	1.04	1.58	1.31	0.833	0.69	4.42
(ug/L)	85.3	8	0.78	1.44	1.35	0.933	0.62	4.30
	63.5-64.5	8	1.27	1.97	1.62	0.823	0.62	5.38
Dissolved Pb	96.0	7	0.219	0.291	0.194	0.666	0.184	0.724
(ug/L)	85.3	7	0.153	0.243	0.248	1.020	0.035	0.788
	63.5-64.5	6	0.187	0.284	0.249	0.877	0.141	0.788
Total Recoverable Zn	96.0	7	70.2	69.8	30.3	0.434	27.5	118
(ug/L)	85.3	8	65.4	66.1	27.9	0.421	33.0	117
	63.5-64.5	8	38.2	51.3	31.3	0.611	23.0	113
Total Zn	96.0	8	86.6	96.9	39.1	0.404	41.7	157
(ug/L)	85.3	8	95.0	95.4	34.0	0.356	43.3	136
	63.5-64.5	8	75.5	84.3	43.7	0.518	40.9	179
Dissolved Zn	96.0	7	70.9	81.8	42.8	0.523	19.3	139
(ug/L)	85.3	7	69.8	88.9	48.6	0.547	22.7	163
	63.5-64.5	7	61.6	59.4	24.3	0.409	20.2	94.3

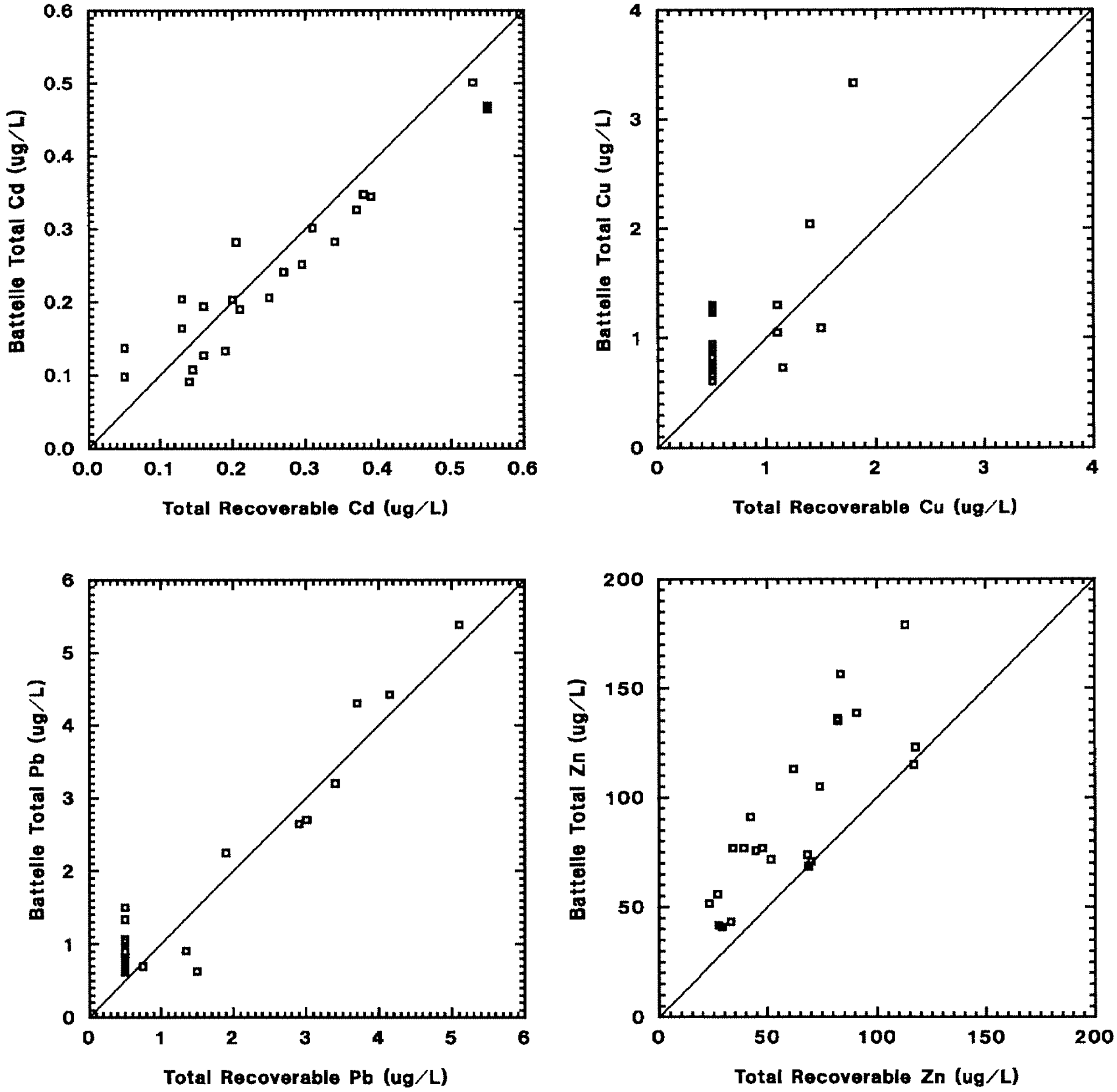

Figure 8. Comparison of Battelle's total with Manchester's total recoverable Cd, Cu, Pb, and Zn

Both methods were able to quantify Zn in most samples and the total Zn measurements by Battelle were on average about 41 percent higher than the total recoverable measurements by Manchester. The results by Manchester are considered to be more accurate for Zn based on analysis of standard reference materials, which showed similar differences between methods. Possible biases in Battelle's Zn measurements would not affect conclusions about violations of water quality criteria for Zn since dissolved Zn was typically higher than the criteria by a much greater amount than the possible bias of 41 percent (Figure 7).

The reason for the differences between methods is not certain. Subtraction of lab method blanks from measurements by Battelle did not significantly improve data accuracy. The sample digestion for the total recoverable method by Manchester was more thorough than the sample preparation for total metals by Battelle but did not generally result in higher metals concentrations.

Dissolved Metals as a Fraction of Total

The fraction of dissolved/total metals was calculated for each pair of dissolved and total measurements of Cd, Cu, Hg, Pb, and Zn by Battelle. Summaries of the calculated dissolved fractions are presented in Figure 9 and Table 6. For metals with criteria for the dissolved fraction (Cd, Cu, Pb, and Zn), the dissolved fractions were typically in the following increasing order: Pb < Cd < Zn < Cu. No significant differences (at a probability level of less than 0.05) between stations or sampling dates were found using Kruskal-Wallis analysis of variance tests (SYSTAT, 1990) for the fractions of dissolved/total Cd, Cu, Pb, or Zn.

The calculated fractions of dissolved/total metals are considered to be accurate even if biases may be present for some reported metals concentrations (e.g., Zn by Battelle). Any biases that may be present in concentration measurements are expected to be the same for both the dissolved and total determinations by Battelle since the laboratory methods were identical. Therefore, the fraction of dissolved/total metals is not expected to be biased even if the underlying concentration measurements are biased. The more rigorous digestion for total recoverable metals by Manchester did not generally yield higher concentrations than the total metals analyses by Battelle. Therefore, the unbiased fractions of dissolved/total metals are expected to adequately represent the fraction of dissolved/total recoverable metals.

Correlations Between Metals and Other Water Quality Variables

Correlations between flow, pH, hardness, total suspended solids (TSS), total organic carbon (TOC), dissolved Cd, dissolved Cu, total Hg, dissolved Pb, dissolved Zn, and fractions of dissolved/total Cd, Cu, Hg, Pb, and Zn were analyzed using the

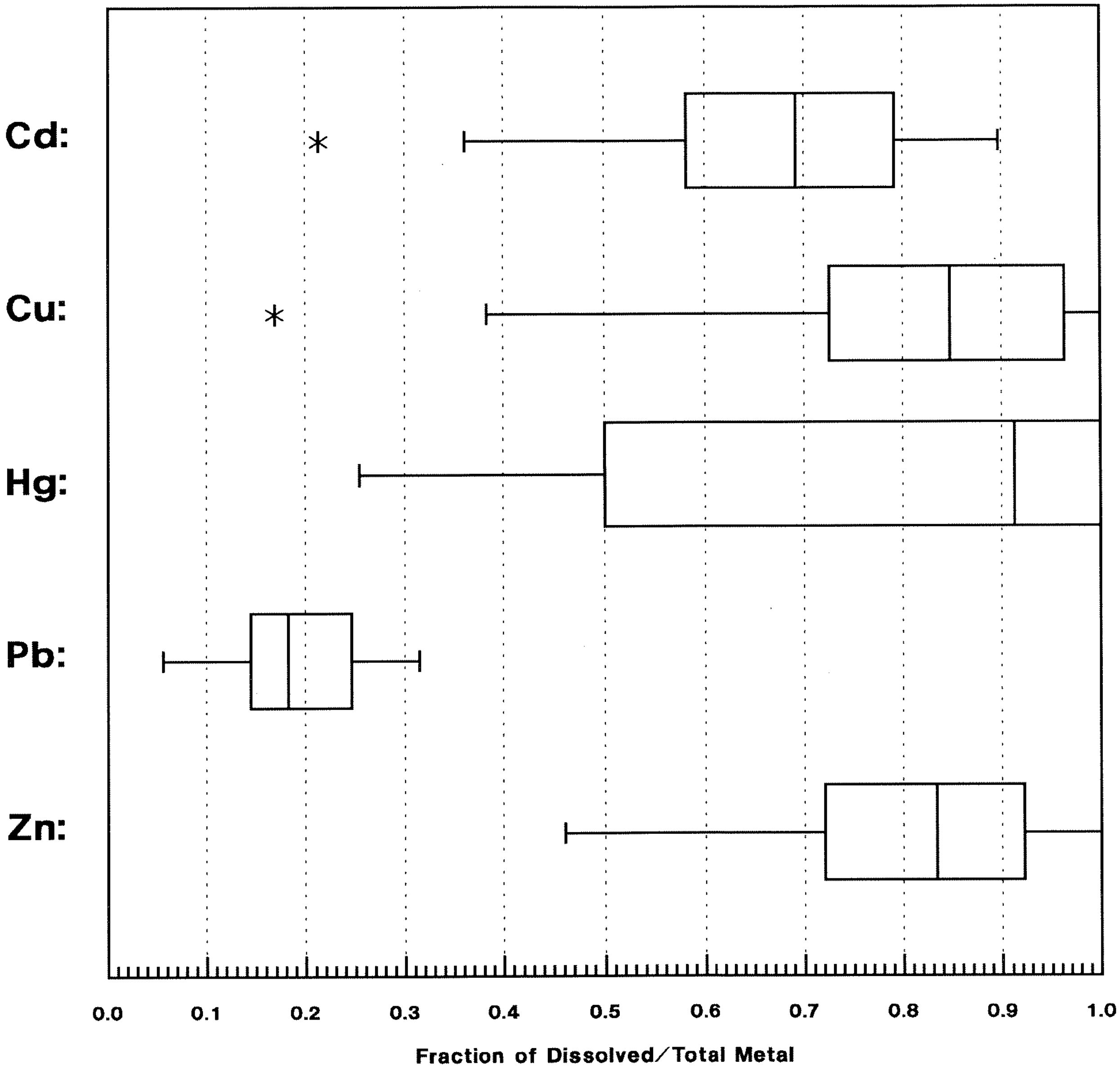

Figure 9. Box plots of the ratio of dissolved/total Cd, Cu, Hg, Pb, and Zn.

Table 6. Summary of fractions of dissolved/total metals in the Spokane River from 28-Jul-92 through 08-Sep-93.

Parameter	Spokane River Mile	Number of Samples	Median	Mean	Standard Deviation	Coefficient of Variation	Minimum	Maximum
Fraction of Dissolved/Total Cd	96.0	7	0.751	0.738	0.120	0.162	0.567	0.897
	85.3	7	0.711	0.689	0.223	0.323	0.213	0.880
	63.5-64.5	7	0.581	0.574	0.124	0.216	0.361	0.748
	63.5-96.0	21	0.692	0.667	0.170	0.254	0.213	0.897
Fraction of Dissolved/Total Cu	96.0	7	0.856	0.891	0.110	0.124	0.720	1.000
	85.3	7	0.866	0.809	0.211	0.261	0.383	1.000
	63.5-64.5	6	0.770	0.710	0.282	0.398	0.169	0.928
	63.5-96.0	20	0.847	0.808	0.211	0.261	0.169	1.000
Fraction of Dissolved/Total Hg	96.0	6	1.000	0.823	0.294	0.357	0.302	1.000
	85.3	6	0.871	0.732	0.290	0.396	0.254	1.000
	63.5-64.5	6	0.963	0.774	0.323	0.417	0.357	1.000
	63.5-96.0	18	0.913	0.776	0.287	0.369	0.254	1.000
Fraction of Dissolved/Total Pb	96.0	7	0.255	0.216	0.075	0.349	0.108	0.292
	85.3	7	0.183	0.179	0.088	0.491	0.056	0.315
	63.5-64.5	6	0.175	0.170	0.056	0.329	0.075	0.226
	63.5-96.0	20	0.183	0.189	0.074	0.391	0.056	0.315
Fraction of Dissolved/Total Zn	96.0	7	0.862	0.805	0.173	0.215	0.462	1.000
	85.3	7	0.930	0.871	0.182	0.209	0.524	1.000
	63.5-64.5	7	0.768	0.688	0.161	0.234	0.494	0.838
	63.5-96.0	21	0.834	0.788	0.181	0.230	0.462	1.000

Spearman rank correlation test (SYSTAT, 1990; Zar, 1974). The Spearman rank correlation coefficients are presented in Table 7. The Spearman analysis gives an indication of the direction of change of possible correlations. However, the significance of each correlation coefficient is probably overestimated in Table 7 due to the large number of variables analyzed. The results in Table 7 are most useful for identifying directions of relationships and are only a screening for possibly significant relationships.

Most metals showed increasing trends with increasing flow. The fraction of dissolved/total metals tended to decrease as TSS increased, which is consistent with other studies (USEPA, 1984). Correlations between metals concentrations and fractions of dissolved/total metals with pH and hardness seemed to be influenced by the correlations between flow, pH, and hardness. TOC did not seem to be significantly correlated with metals concentrations or dissolved fractions.

Although metals concentrations were correlated with flow, water quality criteria for dissolved Zn were exceeded at low and high flows (Figure 10). Criteria for dissolved Cd and Pb were exceeded only at the highest river flows (>15,000 cfs at Spokane) during March and May 1993. Total Hg concentrations tend to increase with flow although the highest concentration was observed when flow was relatively low (<2,000 cfs at Spokane).

Consideration of Phased TMDLs for Cd, Pb, and Zn

Three metals were found to exceed water quality criteria: dissolved Cd, Pb, and Zn. TMDLs for Cd, Pb, and Zn are proposed to meet the requirements of Section 303(d) of the federal Clean Water Act. TMDLs for Cu and Hg are not considered necessary at this time because water quality standards appear to be met and these metals will not be retained on the proposed 1994 Section 303(d) list.

The water quality standards for Cd, Pb, and Zn are not met primarily because of excessive concentrations coming from sources upstream of the state line. The state of Idaho and the USEPA have jurisdiction and the responsibility to regulate sources in Idaho which contribute to conditions in Washington. A problem assessment and interim water quality improvement plan have been completed for the most significant sources in the South Fork Coeur d'Alene River in Idaho (Martin, 1993). The major sources of Cd, Pb, and Zn are nonpoint from historical mining practices for extraction of lead, silver, and zinc. Reductions in metals loading, if they occur, are expected to be gradual. Demonstration projects for an interim remediation plan are in progress to provide data for a final remediation plan. Significant reductions in total loading to the Spokane River may not occur for many years and there is presently no way to predict if Washington's water quality criteria will be met at the state line.

Table 7. Spearman rank correlation coefficients (shaded values indicate possibly significant correlations at a probability of .05 for n=17).

	Flow	pH	Hardness	TSS	TOC
pH	-0.61				
Hardness	-0.58	0.09			
TSS	0.38	-0.21	-0.15		
TOC	0.31	-0.14	-0.45	0.16	
Dissolved Cd	0.77	-0.44	-0.66	0.23	0.25
Dissolved Cu	0.02	-0.07	0.03	-0.52	0.05
Total Hg	0.74	-0.43	-0.43	0.62	-0.01
Dissolved Pb	0.66	-0.12	-0.66	0.54	0.34
Dissolved Zn	0.75	-0.53	-0.37	0.23	-0.26
Dissolved/Total Cd	0.27	-0.15	-0.39	-0.49	0.19
Dissolved/Total Cu	0.02	-0.04	-0.08	-0.27	-0.34
Dissolved Total Hg	-0.05	0.17	-0.11	0.09	-0.26
Dissolved/Total Pb	-0.19	0.20	-0.04	-0.52	-0.01
Dissolved/Total Zn	0.66	-0.47	-0.44	0.22	0.07

NOTE: Significance of each correlation should be interpreted with caution and may be over-estimated (may be falsely indicated as significant).

The significance level was calculated based on a bivariate population and does not account for the number of variables that were correlated.

Correlation coefficients can range from -1 to +1. Negative values indicate that one variable decreases as the other increases.

Positive correlation coefficients indicate that both variables increase and decrease together.

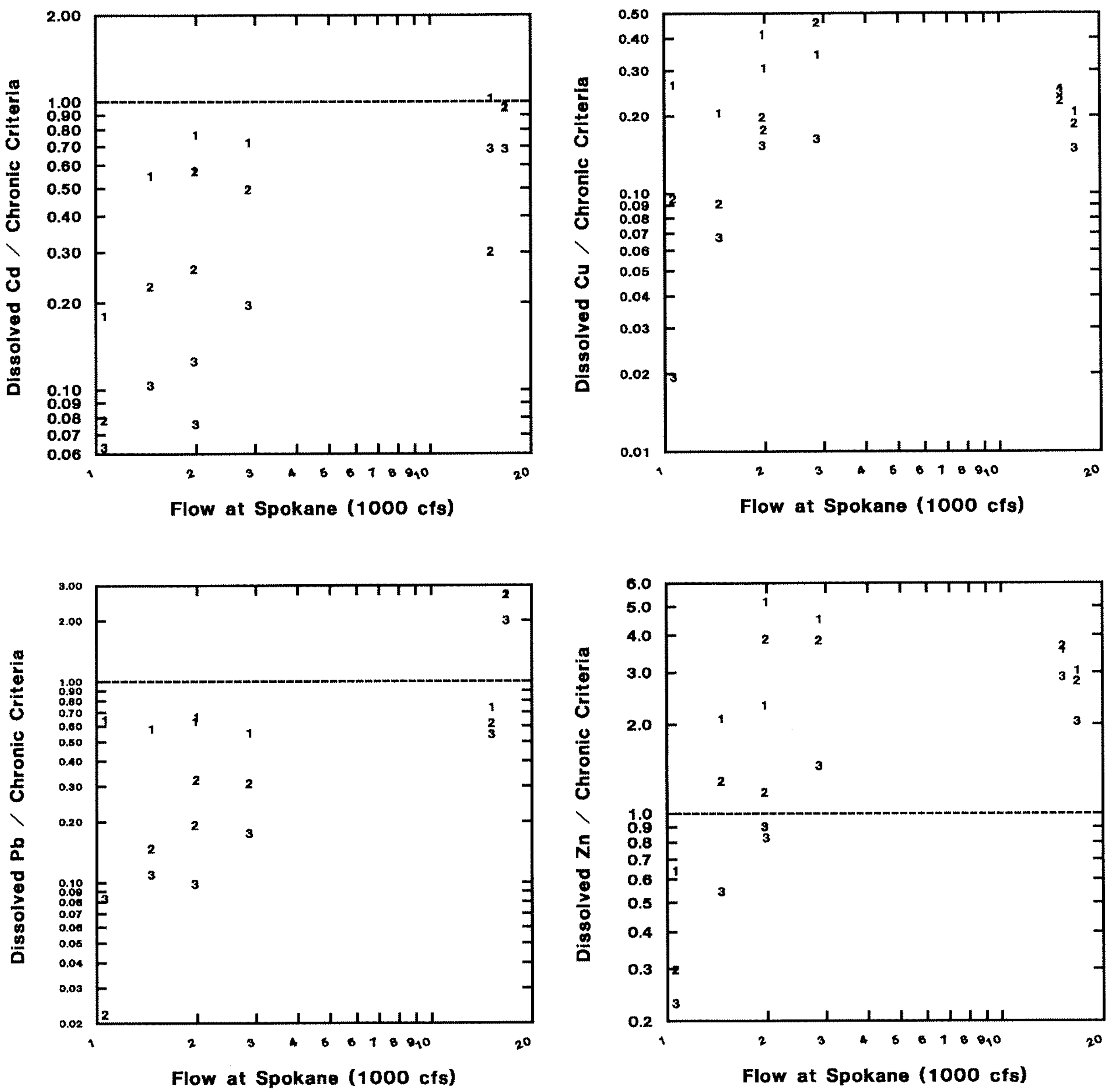

Figure 10. Dissolved Cd, Cu, Pb, and Zn as a fraction of chronic criteria versus flow at Spokane. The plotting symbols identify sample stations (1= river mile 96.0; 2= river mile 85.3; 3= river mile 63.5-64.5).

The USEPA and the state of Idaho need to apply Washington's water quality standards at the state line for development of TMDLs, waste load allocations (WLAs) for point sources, and load allocations (LAs) for nonpoint sources in Idaho. Progress in reducing loads of metals in Idaho should be monitored. Estimates of background loading to the Spokane River from Idaho may be reduced in the future if data show that remediation activities are successful.

A seasonal strategy is proposed for phased TMDLs for Cd, Pb, and Zn in Washington's segments of the Spokane River because of significant seasonal patterns of concentration and criteria. Highest concentrations are generally observed during spring snow melt which typically peaks in April or May. The proposed high and low-flow seasons for establishing phased TMDLs, LAs, and WLAs for metals are as follows:

- A high-flow season of March through June was selected to bracket the period of highest flows during spring snow melt; and

- A low-flow season of July through February was selected to bracket lower flows during summer, fall, and winter.

The river was divided into three reaches between river miles 58 and 96.5 for consideration of loading capacity for metals. The divisions between reaches were selected to define local regions of similar river flows, hardness, and metals concentrations as influenced by surface and groundwater inflows. The three reaches were defined as follows based on general river hydrology presented by Patmont *et al.*, 1985: river miles 58-78, 78-88, and 88-96.5.

A phased TMDL strategy is proposed to allow for adjustments of LAs and WLAs as remediation efforts are monitored and progress is documented (USEPA, 1991a). A phased approach to TMDLs is required when the TMDL involves both nonpoint and point sources and the point source WLAs are based on LAs for which nonpoint source controls need to be implemented. Under the phased approach the allocations are based on estimates which use available information, but monitoring for collection of new data is required.

Dissolved Cd, Pb, and Zn currently exceed water quality standards because of high concentrations from upstream nonpoint sources in Idaho. The observed concentrations of Cd, Pb, and Zn during 1987 through 1994 are considered representative of expected background conditions for establishing initial LAs and WLAs as part of a phased TMDL. Initial LAs and WLAs would be based on existing conditions in the river. USEPA and Idaho should provide a schedule of loading controls and monitoring designed to meet criteria at the border with Washington. LAs and WLAs would be adjusted if monitoring data demonstrate reductions in loading from Idaho or if reductions could be confidently predicted.

Three alternatives are proposed for evaluating initial phased WLAs for NPDES dischargers:

- Alternative A: For metals with background concentrations greater than the water quality standards, require phased WLAs that maintain effluent concentrations for point sources at or below background concentrations in the river;
- Alternative B: For metals with background concentrations less than the water quality standards, calculate WLAs to meet water quality standards at acute and chronic mixing zone boundaries as allowed under Chapter 173-201A-100 WAC; or
- Alternative C: For metals with background concentrations greater than the water quality criteria, require NPDES discharges to meet water quality criteria prior to discharge to the river.

The choice of whether to apply Alternative A or B depends on background concentrations of metals relative to criteria. Alternative C would be the most restrictive and would result in metals in effluent that are significantly lower than concentrations in the river, which would probably provide insignificant benefit to the river compared with Alternative A because point sources are a minor part of the total river flow. The following sections provide detailed recommendations for application of the alternatives.

Phased WLAs for Alternative A

Phased WLAs under Alternative A would not cause an increase in concentrations of dissolved Cd, Pb, or Zn in the Spokane River from point sources. Two methods are proposed for deriving phased WLAs for NPDES dischargers when background concentrations exceed chronic or acute criteria: 1) require highest effluent concentrations not to exceed the highest background concentrations; and 2) require long-term average effluent concentrations not to exceed long-term average background concentrations. Consideration of both methods is recommended. The two methods may not differ significantly because natural river flows are many times higher than effluent flows and metals concentrations of NPDES or background sources would be similar for either method. If effluent variability is assumed to be about the same magnitude or greater than variability in the river, then WLAs based on highest concentrations in the river can result in long-term average effluent concentrations that do not exceed long-term average background concentrations in the river.

Ecology policy for calculating water quality-based effluent limits using EPA's statistical methods involves using a 99 percent probability basis for evaluating long-term average concentrations (section VI-3.3.7 of Ecology, 1993). Defining the phased WLAs for Cd, Pb, and Zn for Alternative A as the 99th percentiles of background concentrations is consistent with Ecology policies for the probability-basis for permit limit derivation, and would achieve long-term average effluent concentrations that do not exceed concentrations in the river on average if effluent variability is equal to or greater than background variability.

USEPA recommends that permit limits for NPDES dischargers should be expressed as total recoverable and the fraction of dissolved/total recoverable metals in the ambient river should be used to translate between criteria for dissolved metal and permit limits for total recoverable metals (USEPA, 1993). Since the background concentrations of dissolved Cd, Pb, and Zn in the river are proposed as the phased WLAs, then background total recoverable Cd, Pb, and Zn concentrations in the river would be the most appropriate measurement to translate the criteria for dissolved metals to permit limits for total recoverable metals. Therefore, the phased TMDLs for Cd, Pb, and Zn are proposed for total recoverable metals based on observed concentrations. The background concentrations of total recoverable Cd, Pb, and Zn, which are proposed for initial estimates of phased WLAs, are presented in Table 8.

The proposed daily maximum concentrations were estimated as the 99th percentiles of background concentrations during each season. The 99th percentiles for Cd and Pb were based on the log-normal distribution, while Zn was based on the normal distribution (99th percentiles were estimated as means plus 2.326 times the standard deviations; a log transformation was used for Cd and Pb. Decisions to use normal or log-normal distributions were based on graphical comparisons of probability plots using SYSTAT). Seasonal averages were estimated as the means of river concentrations during each season. Data were used from Ecology's ambient monitoring station 54A120 (at river mile 66) and stations 57A150 and 57A190 pooled (at river miles 96 and 100.7) collected from water years 1987 through 1992 (Appendix B). Data collected from 1987-1992 were considered to be accurate based on quality assurance analyses conducted by Ecology (Hopkins, 1994). For the low flow season, data from station 54A120 was assumed to represent river miles 58-88, and stations 57A150 and 57A190 were assumed to represent river miles 88-96.5. Data from all three stations were pooled to estimate TMDLs for the high flow season because there were no significant differences between stations.

If Alternative A is applied for the phased WLAs for NPDES dischargers, then concentrations of Cd, Pb, and Zn in the river are not expected to be increased by NPDES dischargers. For the purpose of calculating effluent limits for NPDES dischargers using Ecology and EPA guidelines (Ecology,1993; Box 5-2 of USEPA, 1991b), the proposed daily maximum WLA could be considered equivalent to an acute WLA (WLA_{ac} in Box 5-2 of USEPA, 1991b), and the proposed seasonal average WLA could be considered equivalent to a seasonal long-term average effluent concentration (LTA in Box 5-2 of USEPA 1991b).

Table 8. Background concentrations of total recoverable Cd, Pb, and Zn in the Spokane River proposed as initial estimates of phased WLAs.

	Total Recoverable Cd (μg/L)		Total Recoverable Pb (μg/L)		Total Recoverable Zn (μg/L)	
	Daily Max (1)	Seasonal Average (2)	Daily Max (1)	Seasonal Average (2)	Daily Max (1)	Seasonal Average (2)
High Flow Season (March-June)						
River Mile 58-96.5	1.44	0.62	27.3	4.9	172	97
Low Flow Season (July-February)						
River Mile 88-96.5	0.77	0.32	5.4	1.9	148	75
River Mile 58-88	0.50	0.23	5.1	1.7	125	52

1) equivalent to WLA_{ac} in Box 5-2 of USEPA (1991) for derivation of NPDES permit limits.

2) equivalent to LTA in Box 5-2 of USEPA (1991) for derivation of NPDES permit limits.

WLAs for Alternatives B and C

Concentrations of Cd, Cu, Hg, Pb, and Zn were detected at levels which would affect permissible effluent limits if mixing zones are allowed under Chapter 173-201A-100 WAC. Table 9 presents statistical summaries of river hardness, metals criteria, background metals concentrations, fractions of dissolved/total metals, and river flows which could be used to develop water quality-based permit limits for Cd, Cu, Hg, Pb, and Zn.

The data in Table 9 can be used to estimate WLAs for NPDES dischargers for Alternatives B and C using the following mass balance equation:

$$\text{WLA} = [\ (\text{WQC} * \text{DF}) - (\text{CA} * (\text{DF} - 1))\ ] / \text{FRACTION} \qquad \text{(equation 1)}$$

where:

WLA = acute or chronic waste load allocation for total recoverable metals;
WQC = acute or chronic water quality criteria for dissolved Cd, Cu, Pb, or Zn or total recoverable Hg;
DF = allowable dilution factor at acute or chronic mixing zone boundary (reciprocal of effluent volume fraction);
CA = ambient background concentration of dissolved Cd, Cu, Pb, or Zn or total recoverable Hg (or WQC if it is less than CA for Cd, Cu, Hg, Pb, or Zn);
FRACTION = fraction of dissolved/total recoverable Cd, Cu, Pb, or Zn (or 1.0 for total recoverable Hg).

For Alternative C, the mass-balance equation simplifies to the following:

$$\text{WLA} = \text{WQC} / \text{FRACTION} \qquad \text{(equation 2).}$$

The WLAs for individual NPDES dischargers under Alternative B will vary depending on the water quality criteria and dilution factors at the discharge location. Dilution factors will depend on available river flows, which are presented in Table 10 for USGS measurement sites and locations of major NPDES dischargers.

The critical conditions presented in Tables 9 and 10 are intended to represent a reasonable worst case as recommended in Ecology and EPA guidelines (Ecology, 1991; USEPA, 1991b). The critical conditions for water quality variables were generally estimated as the most restrictive of either seasonal 10th or 90th percentiles or confidence limits of data distributions as explained in Table 9. Critical conditions for river flows were estimated as the seasonal 7-day-average low flows with a recurrence interval of once every 20 years (7Q20) as explained in Table 10.

Table 9. Critical conditions for calculating water quality-based limits for Cd, Cu, Hg, Pb, and Zn for NPDES dischargers to the Spokane River.

	High Flow Season (March-June)			Low Flow Season (July-February)		
River Miles of Segment:	58-78	78-88	88-96.5	58-78	78-88	88-96.5
Total Hardness (mg/L as CaCO3) (1):	54	36	20	81	59	20
Chronic Criteria for trace metals (ug/L) (2):						
Dissolved Cd	0.60	0.44	0.28	0.83	0.65	0.28
Dissolved Cu	6.0	4.3	2.6	8.5	6.5	2.6
Total Recoverable Hg	0.012	0.012	0.012	0.012	0.012	0.012
Dissolved Pb	1.00	0.60	0.28	1.67	1.12	0.28
Dissolved Zn	56.0	39.7	24.1	79.0	60.4	24.1
Acute Criteria for trace metals (ug/L) (2):						
Dissolved Cd	1.69	1.07	0.55	2.67	1.87	0.55
Dissolved Cu	8.5	5.8	3.4	12.5	9.3	3.4
Total Recoverable Hg	2.4	2.4	2.4	2.4	2.4	2.4
Dissolved Pb	25.6	15.3	7.2	42.9	28.7	7.2
Dissolved Zn	61.9	43.9	26.7	87.2	66.7	26.7
Background concentration of trace metals (ug/L) (3):						
Dissolved Cd	0.40	0.40	0.40	0.13	0.28	0.31
Dissolved Cu	0.88	0.88	0.88	1.8	1.6	1.2
Total Recoverable (4) Hg	0.0037	0.0037	0.0037	0.0032	0.0020	0.0017
Dissolved Pb	0.97	0.97	0.97	0.20	0.29	0.24
Dissolved Zn	111	111	111	80.9	164	144
Fraction of dissolved/total recoverable (3):						
Cd	0.883	0.883	0.883	0.742	0.864	0.908
Cu	0.861	0.861	0.861	1.000	1.000	1.000
Pb	0.186	0.186	0.186	0.237	0.334	0.332
Zn	1.000	1.000	1.000	0.882	1.000	0.942

1) Estimated 10th %tiles at critical river flows based on ambient monitoring data from Oct-84 to Sep-93 at stations 54A120 (located at river mile 66) and stations 57A150 and 57A190 pooled (river miles 96 and 100.7) (Appendix B).
Hardness at 54A120 was signficantly correlated with river flow. Therefore, a regression equation was developed (Appendix C) to predict hardness from flow (r^2 = 0.88). The lower 90 percent confidence limit (1-tailed) of predicted hardness at the seasonal 7Q20 flows was used to estimate critical conditions for hardness at 54A120, which was assumed to represent river miles 58-78.
The regression equation to estimate hardness from flow at Ecology station 54A120 is as follows (lower 90% prediction limit, 1-tail):

[Hardness at 54A120, mg/L as CaCO3] = 1295 * [Flow at 54A120, cfs] ^ (-0.4103)

Hardness at Ecology station 57A120 (river mile 85.3) was related to hardness at station 54A120 (river mile 66) by a regression (Appendix C) of data collected during water year 1973 (r^2=0.89). Predicted hardness at 57A120 from the regression equation was assumed to represent river miles 78-88. The regression equation to predict hardness at 57A120 from hardness at 54A120 was as follows:

[Hardness at 57A120, mg/L as CaCO3] = 10 ^ [1.135 + 0.007834 * (Hardness at 54A120, mg/L as CaCO3)]

Hardness at stations 57A150 and 57A190 (river miles 96 and 100.7) was not correlated with flow.
Therefore, hardness from river mile 88 to the state line at 96.5 was assumed to be represented by the 10th percentiles of seasonal data from stations 57A150 and 57A190.

2) WAC 173-201A-040.

3) Seasonal 90th %tiles of Jul-92 to Sep-93 data. For the high flow season, all stations were pooled.
For the low flow season, the station at river mile 96.0 was assumed to represent the segment from river mile 88-96.5,
the station at river mile 85.3 was assumed to represent the segment from river mile 78-88,
and the stations at river mile 63.5-64.5 were assumed to represent the segment from river mile 58-78.
Fractions of dissolved/total recoverable metals were estimated by fractions of dissolved/total measurements by Battelle.

4) background concentration of total recoverable Hg estimated as 90%tile of total Hg measurements by Battelle.

Table 10. Critical conditions of flow in the Spokane River during high and low flow seasons at USGS stations and at locations of NPDES dischargers.

Location	Station	Record Used (Water Year)	High Flow Season 7Q20 (1) Mar-Jun (cfs)	Low Flow Season 7Q20 (1) Jul-Feb (cfs)
USGS GAGING STATIONS:				
Spokane River near Post Falls, ID (river mile 100.7)	12419000	1948-92	921	105
Spokane River above Liberty Lake bridge near Otis Orchard, WA (river mile 93.9)	12419500	1950-83	1130	75.3
Spokane River at Spokane (river mile 72.9)	12422500	1948-92	1850	651
Hangman Creek at Spokane (enters the Spokane River at river mile 72.4)	12424000	1948-92	9.3	2.6
ESTIMATED FLOWS AT NPDES DISCHARGE LOCATIONS:				
City of Liberty Lake Sewage Treatment Plant (river mile 92.7) (2)			1130	75.3
Spokane Industrial Park, Kaiser, Inland Empire Paper Company (river mile 82-87) (3)			1610	404
City of Spokane Advanced Waste Treatment Plant (river mile 67.6) (4)			2260	853

1) low 7-day average flow with a recurrence interval of 20 years (7Q20), estimated using Log Pearson type III frequency factor method with WQHYDRO (Aroner, 1992).

2) represented by USGS station 12419500.

3) estimated by subtracting net groundwater inflow above station 12422500 (RM 85.3-72.9) of 246 cfs (Patmont et al., 1985) from daily flows at station 12422500. The Log Pearson type III frequency factor method was then used to estimate 7Q20 low flows from the synthesized record of daily flows.

4) estimated by adding daily flows at USGS 12422500 and 12424000 with estimated groundwater inflow of 200 cfs (Carey, 1990; Bernhardt, 1985). Log Pearson type III frequency factor method was then used to estimate 7Q20 low flows from the synthesized record of daily flows.

Hardness is significantly correlated with flow at Ecology stations downstream from approximately river mile 88. Hardness progressively increases in the river proceeding downstream as groundwater inflows represent increasing fractions of the total river flow. Hardness is greatest during the low flow season and decreases as surface water inputs increase. The critical conditions for hardness were estimated based on predicted hardness at the seasonal 7Q20 low flows using regression analysis of ambient monitoring data as presented in Table 9 and Appendix C. The critical conditions represent a balance of low flows available for dilution coinciding with relatively high hardness, which tends to relax criteria for Cd, Cu, Pb, and Zn.

The sensitivity of loading capacity of the river to varying river flows and hardness was tested using the regression equations presented in Appendix C. Loading capacities of Cd, Pb, Cu, and Zn in the river (i.e., the product of river flows and water quality criteria) were found to increase as flow increases even though the criteria for metals concentrations decreases with river flow. Therefore, regression estimates of hardness at seasonal low flows are assumed to provide a protective and accurate prediction of conditions of flow and hardness that can occur simultaneously in the river.

Recommended Approach for Determining WLAs for Cd, Cu, Hg, Pb, and Zn

Tables 8, 9, and 10 present data for evaluating WLAs for NPDES dischargers. The recommended methods for determining phased WLAs are as follows:

- Alternative A: For metals with background concentrations greater than the water quality standards, use Table 8 to represent daily maximum WLAs and seasonal long-term average effluent concentrations and calculate permit limits using the method in Box 5-2 of USEPA (1991b); or

- Alternative B: For metals with background concentrations less than the water quality standards, use data in Tables 9 and 10 to calculate WLAs to meet water quality standards at acute and chronic mixing zone boundaries using equation 1. If the resulting WLA is less than the background concentration presented in Table 8, then the existing background concentration in Table 8 can be used to define the WLA (*i.e.*, WLAs may be based on Table 8 if background concentrations meet the water quality criteria and are greater than WLAs derived from Equation 1).

The choice of whether to apply Alternative A or B depends on background concentrations of metals relative to criteria. Background concentrations of dissolved Cu and total Hg were not found to exceed criteria. Background concentrations of dissolved Cd, Pb, and Zn were found to exceed water quality standards as follows:

- Dissolved Cd exceeded standards at river mile 96 during the high flow season (Table 4). Variability of dissolved Cd at river mile 96 also suggests that background concentrations can exceed standards during the low flow season (Table 9).

- Dissolved Pb exceeded standards at river miles 64.5, 85.3, and 96 during the high flow season (Table 4). Variability of dissolved Pb at river mile 96 also suggests that background concentrations can exceed standards during the low flow season (Table 9).

- Dissolved Zn exceeded standards at river miles 64.5, 85.3, and 96 during the high flow and low flow seasons.

Based on comparisons of background concentrations with water quality criteria, the alternatives for estimating phased WLAs for NPDES dischargers are recommended in Table 11.

Summary and Conclusions

- Water quality standards for Cd, Pb, and Zn are not met in the Spokane River primarily because of excessive concentrations coming from sources upstream of the state line. The USEPA and the state of Idaho have jurisdiction and responsibility to regulate sources in Idaho which contribute to conditions in Washington. The major sources of Cd, Pb, and Zn are nonpoint from historical mining practices for extraction of lead, silver, and zinc. Reductions in metals loading, if they occur, are expected to be gradual. Significant reductions in total loading to the Spokane River may not occur for many years and there is presently no way to predict if Washington's water quality criteria for protection of aquatic life will be met at the state line.

- The USEPA and the state of Idaho are required to apply Washington's water quality standards at the state line for development of TMDLs, WLAs, and LAs in Idaho. Progress in reducing loads of metals in Idaho should be monitored by reviewing USEPA's and the state of Idaho's activities and collecting data in Washington. Estimates of background loading to the Spokane River from Idaho may be reduced in the future if data show that remediation activities are successful. The Department of Ecology should maintain monitoring stations at the state line (river mile 96) and Riverside State Park (river mile 66) for dissolved and total recoverable Cd, Pb, and Zn, and hardness. Ambient monitoring data should be periodically reviewed to assess trends in loading from Idaho and phased WLAs should be revised if significant reductions are documented.

Table 11. Recommended alternatives for estimating phased WLAs for NPDES dischargers. (Alternative A: assume background concentrations exceed criteria and use Table 8 to determine WLAs; Alternative B: assume background concentrations are less than criteria and use the greater of WLAs in Table 8 or application of data in Tables 9 and 10 with equation 1).

	River Mile 58-78	River Mile 78-88	River Mile 88-96.5
High Flow Season (March-June)			
Cd	B	B	A
Cu	B	B	B
Hg	B	B	B
Pb	A	A	A
Zn	A	A	A
Low Flow Season (July-February)			
Cd	B	B	A
Cu	B	B	B
Hg	B	B	B
Pb	B	B	A
Zn	A	A	A

- Concentrations of dissolved Cd, Cu, Pb, and Zn typically decreased relative to criteria proceeding from upstream to downstream stations. This occurred mainly because of increases in hardness, which resulted in increases in metals criteria proceeding downstream, and decreases in metals concentrations from dilution with groundwater inflows. Concentrations relative to criteria also varied seasonally, with highest values typically associated with highest river flows during winter and spring.

- Dissolved Cd exceeded standards at river mile 96 during the high flow season. Variability of dissolved Cd at river mile 96 also suggests that background concentrations can exceed standards during the low flow season.

- Dissolved Pb exceeded standards at river miles 64.5, 85.3, and 96 during the high flow season. Variability of dissolved Pb at river mile 96 also suggests that background concentrations can exceed standards during the low flow season.

- Dissolved Zn exceeded standards at river miles 64.5, 85.3, and 96 during the high flow and low flow seasons.

- For metals with criteria for the dissolved fraction (Cd, Cu, Pb, and Zn), the fractions of dissolved/total metals were typically in the following increasing order: Pb < Cd < Zn < Cu. No significant differences between stations or sampling dates were found for the fractions of dissolved/total Cd, Cu, Pb, or Zn.

- Most metals showed increasing trends with increasing flow. Although metals concentrations were correlated with flow, water quality criteria for dissolved Zn were exceeded at low and high flows. Criteria for dissolved Cd and Pb were exceeded only at the highest river flows (>15,000 cfs at Spokane) during March and May 1993. Concentrations of dissolved Cu were not significantly correlated with flow. Total Hg concentrations tend to increase with flow although the highest concentration was observed when flow was relatively low (<2,000 cfs at Spokane).

- A seasonal strategy is proposed for TMDLs for Cd, Pb, and Zn in Washington's segments of the Spokane River because of significant seasonal patterns of concentration and criteria. The proposed high and low-flow seasons for establishing TMDLs and WLAs for metals are as follows: a high-flow season of March through June was selected to bracket the period of highest flows during spring snow melt; and a low-flow season of July through February was selected to bracket lower flows during summer, fall, and winter.

- The river was divided into three reaches between river miles 58 and 96.5 for consideration of TMDLs. The divisions between reaches were selected to define local regions of similar river flows, hardness, and metals concentrations as influenced by surface and groundwater inflows. The three reaches were defined as follows: river miles 58-78, 78-88, and 88-96.5.

- A combination of two alternative methods are recommended for evaluating phased WLAs for NPDES dischargers for Cd, Cu, Hg, Pb, and Zn:

  - For metals with background concentrations greater than the water quality standards, consider daily maximum WLAs as estimated 99th percentiles of existing background concentrations during each season, and seasonal long-term average concentrations in effluent not to exceed seasonal averages in the river.

  - For metals with background concentrations less than the water quality standards, calculate WLAs to meet water quality standards at acute and chronic mixing zone boundaries using reasonable worst case estimates of ambient conditions.

- USEPA and the state of Idaho should manage NPDES permits consistent with a phased TMDL to meet Washington's water quality criteria at the border. NPDES dischargers in Idaho should not be allowed to increase concentrations of Cd, Pb, or Zn in the river at the border. For metals which are currently meeting criteria (*e.g.*, Cu and Hg), WLAs for NPDES dischargers in Idaho should equitably share the loading capacity of the river with dischargers in Washington and should not be allowed to use the entire loading capacity before the river enters Washington.

- USEPA and the state of Idaho should develop a schedule for the installation and evaluation of point and nonpoint source control measures for reducing Cd, Pb, and Zn concentrations as part of a phased TMDL. Data collection, assessment of water quality standards attainment at the Washington border, and appropriate predictive modeling efforts should also be scheduled. The schedule for installation and implementation of control measures and their subsequent evaluation should include descriptions of the types of controls, expected pollutant reductions, and the time frame within which water quality standards are expected to be met at the Washington border including a schedule for re-evaluation of control adequacy.

Acknowledgements

Several people contributed valuable and much appreciated work during this project. Art Johnson contributed significant portions of the methods sections and assisted in field sampling. Bob Cusimano assisted on field sampling. Bill Kammin (Manchester) provided review of data quality and technical guidance on analytical methods. Eric Crecelius (Battelle) provided consultation for data quality evaluations. Bill Ehinger and Dave Hallock provided advice on creating graphics. Brad Hopkins provided and advised on use of Ecology ambient monitoring data for metals. Barbara Tovrea provided word processing and report formatting. Reviewers included Steve Butkus, Dale Davis, Mark Hicks, Will Kendra, and Ken Merrill from the Department of Ecology's Water Quality and EILS Programs.

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APPENDIX A

Data from July 1992 through September 1993 sampling

APPENDIX A.

Data from July, 1992 through September, 1993 sampling.

A.1	Spokane River metals data
A.2	Analyses of standard reference materials for Cd, Cu, Pb, and Zn.
A.3	Analyses of standard reference materials for Hg.
A.4	Results of field and method blanks for Battelle's Cd, Cu, Hg, Pb, and Zn analyses.
A.5	Spokane River ancillary data.

Appendix A.1: Spokane River metals data (all units ug/L).

File APNDX-A1.WK1; Revised 07-Apr-94

Sample Collection Date	Spokane River Mile	Sample Collection Time	Manchester Total Recov Cd	Battelle Total Cd	Battelle Dissolved Cd		Manchester Total Recov Cu	Battelle Total Cu	Battelle Dissolved Cu		Manchester Total Recov Hg	Battelle Total Hg	Battelle Dissolved Hg	Manchester Total Recov Pb	Battelle Total Pb	Battelle Dissolved Pb		Manchester Total Recov Zn	Battelle Total Zn	Battelle Dissolved Zn	
28-Jul-92	96.0	1910	0.12 P	0.11	0.062		1.8 J	0.74	1.01		0.05 U	0.00102 J	0.00127 J	1.4 P	0.942	0.233		29	45	19.6	
28-Jul-92	85.3	1735	0.14 P	0.091	0.063		1.4 J	2.04	0.782		0.05 U	0.00104 J	0.00093 J	1.5 P	0.628	0.035		33	43.3	22.7	
28-Jul-92	63.5	1600	0.1 U	0.098	0.058		1.5 J	1.09	0.184		0.05 U	0.00086 J	0.00093 J	1 U	0.896	0.163		29	40.9	20.2	
28-Jul-92	96.0	1930	0.17 P	0.105	0.06		1 UJ	0.719	0.677		0.05 U	0.00085 J	0.00091 J	1.3 P	0.873	0.268		26	38.4	18.9	
24-Sep-92	96.0	800		0.216				0.903			0.05 U				1.21				99.2		
24-Sep-92	85.3	1100	0.13 P	0.204			1.1 P	1.3			0.05 U			1 U	1.062			62	113		
24-Sep-92	64.5	1300	0.1 U	0.137			1 U	1.25			0.05 U			1 U	1.5			23	51.6		
24-Sep-92	96.0	1000		0.199				1.34			0.05 U				1.12				93.2		
25-Nov-92	96.0	848	0.29 P	0.241	0.215		1 U	0.656	1.11		0.05 U	0.00052 J	0.00209 J	1 P	0.582	0.184 B		81.6 B	147	131	CA
25-Nov-92	85.3	1000	0.27 P	0.241	0.194		1 U	0.909	1.73		0.05 U	0.00046 J	0.00227 J	1 U	0.786	0.153 B		82.3 B	135	135	CA
25-Nov-92	64.5	1112	0.2 P	0.203	0.118		1.1 P	1.05	0.974		0.05 U	0.00122 J	0.00160 J	1 U	1.03	0.173 B		73.9 B	105	80.6	CA
25-Nov-92	96.0	910	0.3 P	0.262	0.236		1 U	0.881	0.922		0.05 U	0.00071 J	0.00105 J	1 U	0.806	0.194 B		100 B	130	118	CA
27-Jan-93	96.0	850	0.34 P	0.309	0.239		1 U	0.685	0.656		0.1 U	0.00147 J	0.00209 J	1 U	0.806	0.19 B		83.4	119	156	CA
27-Jan-93	85.3	955	0.31 P	0.301	0.265		1 U	0.744	0.794		0.1 U	0.00198 J	0.00178 J	1 U	0.664	0.209 B		82.1	136	163	CA
27-Jan-93	64.5	1100	0.19 P	0.133	0.048		1.8 P	3.33	22.5 R	CA	0.1 U	0.00414 J	0.00462 J	1.9 P	2.25	2.25 R	C	42.3	91.1	48.6	
27-Jan-93	96.0	910	0.34 P	0.256	0.23		1 U	0.631	1.1		0.1 U	0.00137 J	0.00145 J	1 U	0.692	0.247		83.6	194	122	CA
31-Mar-93	96.0	700	0.55 P	0.481	0.37	C	1 U	0.94	0.86		0.05 U	0.00208 B	0.00178 B	3 P	2.46	0.33		117	122	107	CA
31-Mar-93	85.3	800	0.55 P	0.464	0.099		1 U	0.82	0.71		0.05 U	0.00354 B	0.00177 B	3 P	2.7	0.23 B		117	115	107	CA
31-Mar-93	64.5	900	0.53 P	0.501	0.251		1 U	1.23	0.86		0.05 U	0.00365 B	0.00132 B	3.4 P	3.2	0.24 B		113	179	94.3	CA
31-Mar-93	96.0	715	0.55 P	0.456	0.321		1 U	0.94	0.75		0.05 U	0.00270 B	0.00125 B	2.8 P	2.83	0.24 B		118	124	105	CA
25-May-93	96.0	1615	0.38 P	0.347	0.25		1 U	0.74	0.51		0.05 U	0.00171 J	0.00366 B	4 P	4.3	0.681	C	70	69.3	72.4	CA
25-May-93	85.3	1705	0.37 P	0.326	0.271		1 U	0.67	0.49		0.05 U	0.00175 JB	0.00311 B	3.7 P	4.3	0.788	C	68.8	68.5 B	69.3	CA
25-May-93	64.5	1515	0.39 P	0.344	0.233		1 U	0.67	0.48		0.05 U	0.00166 J	0.00385 B	5.1 P	5.38	0.788	C	68.2	73.9	61.6 B	CA
25-May-93	96.0	1630	0.38 P	0.347	0.271	C	1 U	0.69	0.52		0.05 U	0.00185 B	0.00228 B	4.3 P	4.54	0.766	C	70.3	72.4	69.3	CA
11-Aug-93	96.0	1450	0.26 P	0.214	0.159		1 U	1.37 B	1.09 B		0.05 U	0.00097 B	0.00059 UB	1 U	0.758	0.187 B		49.7	82.4	57.3	CA
11-Aug-93	85.3	1400	0.21 P	0.19	0.135		1 U	1.23 B	1 B		0.05 U	0.00116 B	0.00059 UB	1 U	0.624	0.148 B		39 P	77	55.5	CA
11-Aug-93	64.5	1243	0.16 P	0.127	0.095		1 U	1.28 B	1.18 B		0.086 PR	0.00091 B	0.00065 UB	1 U	0.624	0.141 B		34 P	77	64.5	
11-Aug-93	96.0	1510	0.24 P	0.198	0.167		1 U	1.23 B	1.09 B		0.05 U	0.00090 B	0.00054 UB	1 U	0.68	0.18 B		45.6	71.6	57.3	CA
08-Sep-93	96.0	1420	0.21 P	0.31	0.177		1 U	0.74	0.6		0.0035 P	0.00124 B	0.00357 B	1 U	1.49	0.19 B		52.2	67.8	59.8	CA
08-Sep-93	85.3	1330	0.16 P	0.194	0.134		1 U	0.61	0.53		0.0037 P	0.00111 B	0.00094 B	1 U	0.78	0.14 B		44.5	75.7	69.8	CA
08-Sep-93	64.5	1230	0.13 P	0.164	0.091		1 U	0.74	0.61		0.002 U	0.00150 B	0.00139 B	1 U	0.9	0.2 B		27 P	55.8	45.8	
08-Sep-93	96.0	1440	0.2 P	0.254	0.159		1 U	0.68	0.57		0.002 U	0.00198 B	0.00208 B	1 U	1.18	0.19 B		50.9	75.7	51.8	CA

Data Qualifier

U = the analyte was not detected at or above the reported result
B = the analyte was also found in the analytical blank at a level which indicates the sample may have been contaminated
J = the analyte was positively identified and the reported value is an estimate
P = the value was above the instrument detection limit but below the quantitation limit
R = outlier; data rejected
C = the value exceeds the chronic aquatic life criteria
CA = the value exceeds the chronic and acute aquatic life criteria

Appendix A.2: Analyses of standard reference materials for Cd, Cu, Pb, and Zn (ug/L).
File SRM.WK1\TAB1 07-Apr-94

Standard Reference Material		Sample Set	Manchester Total Recov-erable Cd	Battelle Total Copre-cipitated Cd	Manchester Total Recov-erable Cu	Battelle Total Copre-cipitated Cu	Manchester Total Recov-erable Pb	Battelle Total Copre-cipitated Pb	Manchester Total Recov-erable Zn	Battelle Total Copre-cipitated Zn
SLRS-2	(blind)	Jul-92	0.1 U	0.048	3.8 P	4.08	1 U	0.186	13 P	8.43
"	"	Sep-92								
"	"	Nov-92		0.06		3.42		0.235		4.95
"	"	Jan-93		0.038		3.37		0.18		4.8 B
"	"	Mar-93	0.1 U	0.032	2.2 P	2.51	1 U	0.15 B	4 U	3.38 B
"	"	May-93	0.1 U	0.033 B	2.3 P	2.74	1 U	0.149 J	4 U	2.52 J
"	"	Sep-93	0.1 U	0.048	3.1 P	3.84	1 U	0.21 B	4 U	169 R
SLRS-2	(not blind)	Jul-93		0.048		3.09		0.175		3.92
"	"	"		0.046		2.92		0.175		4.51
"	"	Sep-92/Jan-93		0.049		3.8		0.163		4.26
"	"	"		0.051		3.96		0.173		4.39
"	"	"		0.049		3.75		0.19		4.42
"	"	"		0.044		3.75		0.19		4.23
"	"	"		0.038		3.63				4.55
"	"	Mar-93		0.035		3.23		0.18		4.26
"	"	"				3.06				
"	"	May-93		0.038		3		0.192		4.24
"	"	"		0.038		2.37		0.181		
"	"	Aug-93		0.036		3.83		0.19		3.86
"	"	"		0.032		3.74		0.201		3.86
"	"	Sep-93		0.039		3.72		0.18		4.49
"	"	"				3.76				
SLRS-2 Certified Values:			0.028 ± 0.004		2.76 ± 0.17		0.129 ± 0.011		3.33 ± 0.15	
NIST 1643c	(blind)	Jul-92	11.9	11.6	24.6 J	26	39.3	31.7	89.5	81.7
"	"	Sep-92	12.1	16.2	18.8	31	37.9	41.3	74.8	122
"	"	Nov-92	12.6	13.4	21	26	36.6	37.3	119 B	136
"	"	Jan-93	13	12.6	19	25.9	38.2	36.6	64	134
"	"	Mar-93	13.2	11.7	18.7	23.7	37	34.7	72.8	86.7
"	"	May-93	12.8	51.6 R	18.1	21.8	39.6	35.7	69.7	100
"	"	Sep-93	13.9	8.35	24.1	19.8	33.3	24.6	73.4	183
NIST 1643c Certified Values:			12.2 ± 1.0		22.3 ± 2.8		35.3 ± 0.9		73.9 ± 0.9	

Data qualifiers defined in Appendix Table A.1

Appendix A.3: Analyses of standard reference materials for Hg (ug/L).
File SRM.WK1\TAB2 07-Apr-94

			Battelle Total Hg
NIST 1643b(not blind)		Jul-92	1444
"	"	Sep-92/Jan-93	1549
"	"	"	1338
"	"	"	706
"	"	"	786
"	"	"	1157
"	"	"	1568
"	"	"	1462
"	"	"	1548
"	"	"	1604
"	"	"	1759
"	"	"	1355
"	"	Mar-93	1682
"	"	"	1417
"	"	"	1456
"	"	"	1740
"	"	May-93	1522
"	"	"	1464
"	"	Aug-93	1476
"	"	Sep-93	1501
NIST 1643b Certified Values:			1520 ± 40

Data qualifiers defined at end in Appendix Table A.1

Appendix A.4: Results of field and method blanks for Battelle's Cd, Cu, Hg, Pb and Zn analyses.
File BLANKS.WK1\TAB1
Revised: 07-Apr-94

Sample Set	Blank Type	Cd	Cu	Hg	Pb	Zn
FIELD BLANKS:						
Jul-92	Bottle	0.005	0.058	--	0.035	0.98
"	Filter	0.006	0.095	--	0.035	0.78
Nov-92	Bottle	0.001	0.076	--	0.031	0.90
"	Filter	0.001	1.8	--	0.031	1.2
Mar-93	Bottle	0.001	0.016	--	0.040	1.3
"	Filter	0.001	0.016	--	0.030	1.8
Aug-93	Bottle	0.004	0.59UB	0.00069UB	0.032UB	0.40UB
"	Filter	0.014	0.55UB	0.00059UB	0.028UB	0.45UB
Sep-93	Bottle	0.004	0.041	0.00093B	0.034	0.61
"	Filter	0.005	0.038	0.00114B	0.029U	0.76
LAB METHOD BLANKS:						
Jul-92		0.005	0.037	0.00084	0.035U	0.882
"		0.006	0.042	--	0.035U	0.98
"		0.004	0.047	--	0.035U	0.98
Sep-92/Jan-93		0.001U	0.024	0.00180	0.02U	1.05
"		0.002	0.048	0.00172	0.02	0.75
"		0.001U	0.042	0.00149	0.03U	0.81
"		0.002U	0.038	0.00143	0.03U	0.65
"		0.003	0.033U	--	--	0.81
Mar-93		0.001	0.012U	0.00102	0.03	0.96
"		0.002	0.012U	0.00115	0.022U	0.8
"		0.001	0.02	0.00117	0.03	0.96
"		0.001	0.016	--	0.03	0.96
"		0.001	0.02	--	0.03	1.1
May-93		0.001U	0.017U	0.00122	0.032U	0.38
"		0.001U	0.017U	0.00178	0.032	0.38
"		0.001U	0.017U	--	0.032U	0.29
Aug-93		0.001U	0.64	0.00082	0.032	0.45
"		--	0.56	--	--	--
Sep-93		0.003	0.041	0.00108	0.029U	0.61
"		0.009	0.14U	0.00100	0.18	15.9
"		--	1.10U	--	0.75	--

U = the analyte was not detected at or above the reported result
B = the analyte was also found in the analytical blank at a level that indicates the sample may have been contaminated.

Appendix A.5: Spokane River ancillary data.

File APNDX-A1.WK1; Revised 08-Mar-94

Sample Collection Date	Spokane River Mile	Sample Collection Time	Temp-erature (deg C)	pH (s.u.)	Specific Cond-uctance (umho/cm @ 25C)	Alk-alinity (mg/L as CaCO3)	Total Hardness (mg/L as CaCO3)	Total Susp. Solids (mg/L)	Total Diss. Solids (mg/L)	Total Organic Carbon (mg/L)	Nitrate+ Nitrite Nitrogen (mg/L as N)	Diss. Chloride (mg/L)	Diss. Sulfate (mg/L)	Diss. Calcium (ug/L)	Diss. Magnesium (ug/L)	Diss. Potassium (ug/L)	Diss. Sodium (ug/L)
28-Jul-92	96.0	1910	23.9	9.12	57.4	21.5	23.5	3 B	32	1.8	0.05 U	0.76	5	5980	1700	480 P	2090
28-Jul-92	85.3	1735	18.5	8.46	156	68.9	77.5	1 UB	111	1.3	0.344	1	9.5	17100	7130	1200	2810
28-Jul-92	63.5	1600	19.1	8.4	204	83	92	2 B	112	1.6	0.594	4.8	12.8	22300	8300	1700	6400
28-Jul-92	96.0	1930			57.1	21.4	28.1	1 UB	32		0.05 U	0.77	5	5980	1690	500 P	2050
24-Sep-92	96.0	800	16	7.96	59	21.5	22.6	1	49	1.5	0.028	0.68	5	6170	1760	650 P	2050
24-Sep-92	85.3	1100	14.9	8.27	88.7	36.9	42.2	2	89	1.4	0.132	0.77	6.5	9920	3570	740 P	2290
24-Sep-92	64.5	1300	14.7	8.41	157	64.5	69.4	2	135	1.4	0.479	3	10.1	16600	6470	1400	4710
24-Sep-92	96.0	1000			57.9	21.6	26.5	2	58	1.5	0.028	0.68	5	6200	1770	450 P	2010
25-Nov-92	96.0	848	6.5		57.3	22.3	23.6	1 U	35	1.3	0.021	0.63	5.1	6250	1790	720 P	1800
25-Nov-92	85.3	1000	6.1	7.85	75.4	30.4	31.1	1 U	45	1.4	0.086	0.65	5.8	8220	2770	830 P	1950
25-Nov-92	64.5	1112	6.3	7.56	126	50.4	53.6	1	78	1.3	0.441	2.1	7.9	13400	4950	990 P	3780
25-Nov-92	96.0	910			57.3	22	23	1 U	45	1.3	0.02	0.61	5	6270	1800	420 P	1780
27-Jan-93	96.0	850	2.3	8.47	60.6	22.5	22.4	1	27	1.3	0.046	0.93	5.6	6360	1870	810 P	2040
27-Jan-93	85.3	955	3	7.35	89.3	36.1	38.4	1	61	1.2	0.16	0.93	6.8	9500	3490	990 P	2190
27-Jan-93	64.5	1100	3.4	7.39	140	52.3	57.1	36	133	2.3	1.08	3.4	8.6	13700	5180	2100 P	4680
27-Jan-93	96.0	910			60.5	22.4	22.8	1	45	1.2	0.047	0.93	5.6	6330	1870	850 P	2060
31-Mar-93	96.0	700	3	8.01	61.2	22.9	24.7	3	114 J	1.9	0.034	0.62	6.1	6530	1950	730 P	1830
31-Mar-93	85.3	800	3.2	7.83	61.1	23.2	24.9	4	62 J	1.7	0.034	0.63	6.2	7230	2220	880 P	2270
31-Mar-93	64.5	900	3.8	7.56	69.8	25.8	28.5	8	67 J	1.8	0.166	0.96	6.6	7260	2220	910 P	2280
31-Mar-93	96.0	715	3.1	7.9	61.2	23	26.3 J	3	45 J	1.9	0.033	0.62	6.1	6480	1930	880 P	1810
25-May-93	96.0	1615	14	7.58	48.4	19.1	19.1	2	52	2.4	0.01 U	0.45	4	4990	1500	650 P	1520
25-May-93	85.3	1705	14	7.68	51	20.2	20.6	2	41	2.9	0.024	0.45	4	5250	1630	750 P	1530
25-May-93	64.5	1515	14.4	7.86	64	24.8	26	4	45	2	0.121	0.86	4.6	6610	2150	800 P	1930
25-May-93	96.0	1630			48.5	19.2	19.3	2	64 J	2.5	0.011	0.45	4	4950	1490	670 P	1500
11-Aug-93	96.0	1450	22.9	8.4	51	20.2	21	1 U	44	2.6	0.036	0.6	4.4	5280	1510	810 J	1660
11-Aug-93	85.3	1400	20	8.38	94	29.6	44	1	146	2.1	0.189	0.79	6.3	10100	3830	850 J	2030
11-Aug-93	64.5	1243	18.4	7.33	162	65.3	72	1	113	2.2	0.796	3.1	10.1	16900	6620	1400 J	4360
11-Aug-93	96.0	1510			51	20.2	20	1 U	86	2.7	0.036	0.59	4.4	5310	1520	660 J	1660
08-Sep-93	96.0	1420	21.2	7.93	54	20.7	23	2	69	1.8	0.058	0.81	4.9	5690	1630	750 P	1890
08-Sep-93	85.3	1330	17.7	8.17	113	47.6	52	2	84	1.5	0.284	1	7.5	12000	4740	1300 P	2310
08-Sep-93	64.5	1230	16.2	8.46	193	79.6	87	2	130	1.8	1.05	3.6	11.1	21900	8140	1600 P	4820
08-Sep-93	96.0	1440			54	20.7	22	2	84	1.8	0.059	0.8	4.9	5580	1600	780 P	1850

Data Qualifier:

U = the analyte was not detected at or above the reported result
B = the analyte was also found in the analytical blank at a level which indicates the sample may have been contaminated
J = the analyte was positively identified and the reported value is an estimate
P = the value was above the instrument detection limit but below the quantitation limit
R = outlier; data rejected

APPENDIX B

Ecology ambient monitoring data

APPENDIX B.

Ecology ambient monitoring data.

B.1 Ecology metals data from the Spokane River, stations 54A120, 57A150, and 57A190, January 1987 through 1992.

B.2 Spokane River hardness data, October, 1983 through September, 1993.

B.3 Comparison of hardness at Ecology stations 54A120 and 57A145, water year 1973.

Appendix B.1. Ecology metals data from the Spokane River.
File SPOMET2.WK1 Revised 26-Apr-94

Station	Date	Time	Total Recoverable Cu (ug/L)	Total Recoverable Pb (ug/L)	Total Recoverable Zn (ug/L)	Total Recoverable Cd (ug/L)
Spokane River at Riverside Park (RM 66.0)						
54A120	13-Jan-87	1400	1.0 K	5.0 K	35.0	0.20 K
54A120	10-Feb-87	1400	-99.0	-99.0	-99.0	-99.00
54A120	17-Mar-87	1445	3.0	25.0	135.0	0.90
54A120	14-Apr-87	1410	1.0 U	1.0 U	112.0	0.40
54A120	05-May-87	1430	5.0 U	1.0 U	83.0	0.50
54A120	07-Jul-87	1500	5.0	1.0 U	36.0	0.20 U
54A120	04-Aug-87	1425	5.0 K	5.0 K	22.0	0.20 K
54A120	08-Sep-87	1505	6.0	1.0 U	14.0	0.20
54A120	06-Oct-87	1355	12.0	1.0 U	23.0	0.20 K
54A120	03-Nov-87	1355	5.0 K	1.0 K	23.0	0.20 K
54A120	08-Dec-87	1410	5.0	1.0 U	54.0	0.20 U
54A120	12-Jan-88	1335	1.0	1.0 K	52.0	0.40
54A120	02-Feb-88	1415	2.0	1.0 K	63.0	0.20
54A120	08-Mar-88	1450	2.0	1.0 K	102.0	0.50
54A120	05-Apr-88	1440	7.0	1.0 K	110.0	0.80
54A120	03-May-88	1335	1.0 K	4.0	100.0	0.60
54A120	07-Jun-88	1450	1.0	1.0 K	80.0	1.10
54A120	05-Jul-88	1505	1.0 U	1.0 U	47.0	0.20 U
54A120	02-Aug-88	1320	2.0 U	3.0 U	-99.0	0.10 K
54A120	13-Sep-88	1455	-99.0	1.7	-99.0	0.40
54A120	04-Oct-88	1505	2.0 U	1.8	51.0	0.20 U
54A120	07-Nov-88	1410	2.0 K	2.5	49.0	-99.00
54A120	06-Dec-88	1455	2.0 K	1.5	99.0	0.31
54A120	03-Jan-89	1445	16.0	1.0	81.0	0.20 K
54A120	07-Feb-89	1355	2.3	1.5	70.0	0.27
54A120	07-Mar-89	1445	36.0	24.3	111.0	0.39
54A120	04-Apr-89	1455	3.0 V	1.5	108.0	0.35
54A120	02-May-89	1445	2.0 K	-99.0	106.0	0.42
54A120	06-Jun-89	1510	2.0 K	2.2 V	69.0	0.51
54A120	05-Jul-89	1505	4.0 U	1.3	32.0	0.20 V
54A120	08-Aug-89	1450	4.0 K	2.0	24.0	0.23
54A120	05-Sep-89	1415	4.0 U	1.3	28.0 V	0.24 V
54A120	03-Oct-89	1415	2.0 K	1.7	143.0	0.20 K
54A120	07-Nov-89	1405	4.3 U	1.1	55.0	0.20 U

V=possibly blank contaminated; K or U=below detection limit; -99=missing data

Appendix B.1. Ecology metals data from the Spokane River.
File SPOMET2.WK1 Revised 26-Apr-94

Station	Date	Time	Total Recov-erable Cu (ug/L)	Total Recov-erable Pb (ug/L)	Total Recov-erable Zn (ug/L)	Total Recov-erable Cd (ug/L)
54A120	05-Dec-89	1410	2.0 K	1.9 J	94.0	-99.00
54A120	09-Jan-90	1455	2.5 J	6.5	99.0	0.47 J
54A120	06-Feb-90	1440	2.2 J	2.7 J	104.0	0.40 J
54A120	06-Mar-90	1435	2.0 K	6.1	106.0	0.55 J
54A120	03-Apr-90	1520	2.0 K	-99.0	134.0	0.63 J
54A120	08-May-90	1330	2.0 K	4.7 V	97.0	0.86
54A120	05-Jun-90	1445	5.0 K	3.8 J	9.0 J	0.46 J
54A120	10-Jul-90	1305	5.0 K	1.8 J	38.0	0.22 J
54A120	07-Aug-90	1335	5.0 K	1.6 J	26.0 J	0.20 J
54A120	04-Sep-90	1250	2.0 K	1.6 V	23.0	0.14 V
54A120	09-Oct-90	1300	6.9 V	1.3 V	35.0	0.13 V
54A120	06-Nov-90	1305	4.2 V	1.3 V	49.0	0.24 V
54A120	04-Dec-90	1320	2.0 K	1.5 V	102.0	-99.00 V
54A120	08-Jan-91	1355	2.0 K	2.2 V	91.0	0.13 V
54A120	05-Feb-91	1430	2.0 K	4.0 V	94.0	0.45 V
54A120	05-Mar-91	1345	8.8 J	7.9	119.0	0.82
54A120	02-Apr-91	1315	2.0 K	-99.0	104.0	0.44 J
54A120	07-May-91	1325	-99.0	-99.0	93.0	-99.00
54A120	04-Jun-91	1315	-99.0	-99.0	71.0 V	-99.00
54A120	09-Jul-91	1525	-99.0	-99.0	66.0	-99.00
54A120	06-Aug-91	1500	-99.0	-99.0	41.0	-99.00
54A120	03-Sep-91	1530	3.0 K	1.2 V	22.0 V	-99.00
54A120	08-Oct-91	1640	-99.0	-99.0	-99.0	-99.00
54A120	05-Nov-91	1550	-99.0	-99.0	-99.0	-99.00
54A120	03-Dec-91	1540	-99.0	-99.0	-99.0	-99.00
54A120	07-Jan-92	1620	-99.0	-99.0	-99.0	-99.00
54A120	04-Feb-92	1550	-99.0	-99.0	-99.0	-99.00
54A120	03-Mar-92	1530	-99.0	-99.0	-99.0	-99.00
54A120	07-Apr-92	1620	-99.0	-99.0	-99.0	-99.00
54A120	05-May-92	1525	-99.0	-99.0	-99.0	-99.00
54A120	02-Jun-92	1610	-99.0	-99.0	-99.0	-99.00
54A120	07-Jul-92	1640	-99.0	-99.0	-99.0	-99.00
54A120	04-Aug-92	1640	-99.0	-99.0	-99.0	-99.00
54A120	09-Sep-92	1605	-99.0	-99.0	-99.0	-99.00
54A120	06-Oct-92	1515	-99.0	-99.0	-99.0	-99.00

V=possibly blank contaminated; K or U=below detection limit; -99=missing data

Appendix B.1. Ecology metals data from the Spokane River.
File SPOMET2.WK1 Revised 26-Apr-94

Station	Date	Time	Total Recov-erable Cu (ug/L)	Total Recov-erable Pb (ug/L)	Total Recov-erable Zn (ug/L)	Total Recov-erable Cd (ug/L)
54A120	03-Nov-92	1550	-99.0	-99.0	-99.0	-99.00
54A120	02-Dec-92	1525	-99.0	-99.0	-99.0	-99.00
54A120	05-Jan-93	1345	-99.0	-99.0	-99.0	-99.00
54A120	02-Feb-93	1515	-99.0	-99.0	-99.0	-99.00
54A120	02-Mar-93	1530	-99.0	-99.0	-99.0	-99.00
54A120	06-Apr-93	1520	-99.0	-99.0	-99.0	-99.00
54A120	04-May-93	1655	-99.0	-99.0	-99.0	-99.00
54A120	08-Jun-93	1605	-99.0	-99.0	-99.0	-99.00
54A120	06-Jul-93	1600	-99.0	-99.0	-99.0	-99.00
54A120	03-Aug-93	1555	-99.0	-99.0	-99.0	-99.00
54A120	07-Sep-93	1535	-99.0	-99.0	-99.0	-99.00
54A120	05-Oct-93	1420	-99.0	-99.0	-99.0	-99.00
54A120	02-Nov-93	1415	-99.0	-99.0	-99.0	-99.00
54A120	07-Dec-93	1420	-99.0	-99.0	-99.0	-99.00
54A120	04-Jan-94	1420	-99.0	-99.0	-99.0	-99.00
54A120	08-Feb-94	1420	-99.0	-99.0	-99.0	-99.00
Spokane River at Stateline Bridge (RM 96.0)						
57A150	05-Dec-90	0720	-99.0	-99.0	-99.0	-99.00
57A150	09-Jan-91	0730	2.9 V	3.7 V	107.0	0.21 V
57A150	06-Feb-91	0710	2.0 K	4.6 V	121.0	0.52
57A150	06-Mar-91	0700	2.0 K	4.3 J	120.0	0.69
57A150	03-Apr-91	0710	2.0 K	-99.0	116.0	0.51
57A150	08-May-91	0720	-99.0	-99.0	94.0	-99.00
57A150	05-Jun-91	0645	-99.0	-99.0	135.0	-99.00
57A150	10-Jul-91	0700	-99.0	-99.0	70.0	-99.00
57A150	07-Aug-91	0645	-99.0	-99.0	66.0	-99.00
57A150	04-Sep-91	0705	3.0 K	2.5 V	69.0 V	0.30 V
57A150	09-Oct-91	0705	-99.0	-99.0	-99.0	-99.00
57A150	06-Nov-91	0710	3.0 K	2.7 P	105.0	0.46 P
57A150	04-Dec-91	0710	-99.0	-99.0	101.0	0.33 V
57A150	08-Jan-92	0710	3.0 K	1.0 K	93.0	0.74 V
57A150	05-Feb-92	0715	-99.0	-99.0	-99.0	-99.00
57A150	04-Mar-92	0645	-99.0	-99.0	-99.0	-99.00

V=possibly blank contaminated; K or U=below detection limit; -99=missing data

Appendix B.1. Ecology metals data from the Spokane River.

File SPOMET2.WK1 Revised 26-Apr-94

Station	Date	Time	Total Recov-erable Cu (ug/L)	Total Recov-erable Pb (ug/L)	Total Recov-erable Zn (ug/L)	Total Recov-erable Cd (ug/L)
57A150	08-Apr-92	0645	-99.0	-99.0	-99.0	-99.00
57A150	06-May-92	0630	-99.0	-99.0	-99.0	-99.00
57A150	03-Jun-92	0635	-99.0	-99.0	-99.0	-99.00
57A150	08-Jul-92	0640	-99.0	-99.0	-99.0	-99.00
57A150	05-Aug-92	0610	-99.0	-99.0	-99.0	-99.00
57A150	10-Sep-92	0640	-99.0	-99.0	-99.0	-99.00
57A150	07-Oct-92	0700	-99.0	-99.0	-99.0	-99.00
57A150	04-Nov-92	0643	-99.0	-99.0	-99.0	-99.00
57A150	03-Dec-92	0730	-99.0	-99.0	-99.0	-99.00
57A150	06-Jan-93	0750	-99.0	-99.0	-99.0	-99.00
57A150	03-Feb-93	0700	-99.0	-99.0	-99.0	-99.00
57A150	03-Mar-93	0620	-99.0	-99.0	-99.0	-99.00
57A150	07-Apr-93	0645	-99.0	-99.0	-99.0	-99.00
57A150	05-May-93	0730	-99.0	-99.0	-99.0	-99.00
57A150	09-Jun-93	0805	-99.0	-99.0	-99.0	-99.00
57A150	07-Jul-93	0700	-99.0	-99.0	-99.0	-99.00
57A150	04-Aug-93	0710	-99.0	-99.0	-99.0	-99.00
57A150	08-Sep-93	0710	-99.0	-99.0	-99.0	-99.00
57A150	05-Oct-93	0920	-99.0	-99.0	-99.0	-99.00
57A150	02-Nov-93	0925	-99.0	-99.0	-99.0	-99.00
57A150	07-Dec-93	0930	-99.0	-99.0	-99.0	-99.00
57A150	04-Jan-94	0940	-99.0	-99.0	-99.0	-99.00
57A150	08-Feb-94	0945	-99.0	-99.0	-99.0	-99.00
57A150	08-Mar-94	0940	-99.0	-99.0	-99.0	-99.00

Spokane River near Post Falls Idaho (RM 100.7)

57A190	14-Jan-87	0800	1.0 K	5.0 K	67.0	0.20 K
57A190	11-Feb-87	0730	-99.0	-99.0	-99.0	-99.00
57A190	18-Mar-87	0820	1.0 K	14.0	142.0	0.80
57A190	15-Apr-87	0705	1.0 U	1.0 U	127.0	0.40
57A190	06-May-87	0800	5.0 U	1.0 U	97.0	0.90
57A190	03-Jun-87	0650	1.0 U	5.0 U	100.0	0.70
57A190	08-Jul-87	0735	5.0 U	1.0 U	69.0	0.20 U

V=possibly blank contaminated; K or U=below detection limit; -99=missing data

Appendix B.1. Ecology metals data from the Spokane River.
File SPOMET2.WK1 Revised 26-Apr-94

Station	Date	Time	Total Recov-erable Cu (ug/L)	Total Recov-erable Pb (ug/L)	Total Recov-erable Zn (ug/L)	Total Recov-erable Cd (ug/L)
57A190	05-Aug-87	0740	5.0	5.0 K	55.0	0.20 K
57A190	09-Sep-87	0800	3.0	1.0 U	45.0	0.20
57A190	07-Oct-87	0730	5.0	1.0 U	52.0	0.20 K
57A190	04-Nov-87	0745	5.0 K	1.0 K	54.0	0.20 K
57A190	09-Dec-87	0740	14.0	1.0 U	98.0	0.20 U
57A190	13-Jan-88	0745	1.0	1.0 K	80.0	0.20 K
57A190	03-Feb-88	0735	2.0	1.0 K	108.0	0.40
57A190	09-Mar-88	0740	1.0 K	1.0 K	113.0	0.60
57A190	06-Apr-88	0610	3.0	1.0 K	127.0	0.60
57A190	04-May-88	0645	1.0 K	1.0 K	108.0	0.30
57A190	08-Jun-88	0710	1.0 U	1.0 K	90.0	1.50
57A190	06-Jul-88	0715	1.0 U	1.0 U	78.0	0.20 U
57A190	03-Aug-88	0720	7.0	3.0 U	-99.0	0.10 K
57A190	14-Sep-88	0705	-99.0	1.4	-99.0	0.30
57A190	05-Oct-88	0720	2.0 U	1.0 U	78.0	0.40
57A190	08-Nov-88	0720	2.0 K	1.0 K	102.0	0.33
57A190	07-Dec-88	0715	2.0 K	1.8	110.0	0.50
57A190	04-Jan-89	0705	3.0 K	2.5	110.0	0.20
57A190	08-Feb-89	0720	2.0 U	1.6	108.0	0.32
57A190	08-Mar-89	0735	3.9 V	3.9	114.0	0.34
57A190	05-Apr-89	0725	2.0 K	1.9	121.0	-99.00
57A190	03-May-89	0715	2.0 K	-99.0	116.0	0.46
57A190	07-Jun-89	0800	2.0 K	2.4 V	8.0 V	0.39
57A190	06-Jul-89	0715	4.0 U	1.8	64.0	-99.00 V
57A190	09-Aug-89	0720	4.0 K	2.6	57.0	-99.00
57A190	06-Sep-89	0735	4.0 U	1.6	56.0	0.24 V
57A190	04-Oct-89	0715	2.0 K	1.0 K	59.0	0.21
57A190	08-Nov-89	0705	4.8 U	1.0 U	83.0	0.26
57A190	06-Dec-89	0720	2.0 K	5.6	140.0	0.70
57A190	10-Jan-90	0735	2.0 K	2.9 J	129.0	0.53 J
57A190	07-Feb-90	0735	2.0 K	3.9 J	121.0	0.52 J
57A190	07-Mar-90	0720	2.0 K	7.4	134.0	0.57 J
57A190	04-Apr-90	0750	3.0 J	-99.0	505.0	1.80
57A190	09-May-90	0735	2.0 K	4.3 V	96.0	0.52
57A190	06-Jun-90	0730	5.0 K	3.2 J	96.0	0.42 J

V=possibly blank contaminated; K or U=below detection limit; -99=missing data

Appendix B.1. Ecology metals data from the Spokane River.
File SPOMET2.WK1 Revised 26-Apr-94

Station	Date	Time	Total Recov-erable Cu (ug/L)	Total Recov-erable Pb (ug/L)	Total Recov-erable Zn (ug/L)	Total Recov-erable Cd (ug/L)
57A190	11-Jul-90	0710	5.0 K	1.7 J	73.0	-99.00 J
57A190	08-Aug-90	0745	5.0 K	1.5 J	56.0	0.24 J
57A190	05-Sep-90	0655	2.0 K	1.5 V	51.0	0.23 V
57A190	10-Oct-90	0725	3.9 V	1.7 V	65.0	0.24 V
57A190	07-Nov-90	0720	2.3 V	1.2 V	9.0 V	0.37 V

V=possibly blank contaminated; K or U=below detection limit; -99=missing data

Appendix B.2. Spokane River hardness data, Oct-83 to Sep-93.

File WY8493.WK1 Revised 26-Apr-94

Station	Spokane River Mile	Date	Time	Hardness (mg/L as CaCO3)	Flow (cfs)
54A120	66.0	25-Oct-83	1500	65	2420
54A120	66.0	29-Nov-83	1505	63	5390
54A120	66.0	20-Dec-83	1505	52	5380
54A120	66.0	17-Jan-84	1350	56	6040
54A120	66.0	07-Feb-84	1320	40	8480
54A120	66.0	06-Mar-84	1355	44	6580
54A120	66.0	10-Apr-84	1335	36	12100
54A120	66.0	08-May-84	1335	40	11500
54A120	66.0	12-Jun-84	1345	999999	17000
54A120	66.0	10-Jul-84	1530	68	3420
54A120	66.0	14-Aug-84	1410	92	1650
54A120	66.0	11-Sep-84	1545	68	2280
54A120	66.0	09-Oct-84	1350	84	2290
54A120	66.0	13-Nov-84	1410	56	3220
54A120	66.0	11-Dec-84	1435	44	4470
54A120	66.0	15-Jan-85	1415	68	2500
54A120	66.0	05-Feb-85	1430	76	1820
54A120	66.0	12-Mar-85	1450	80	3340
54A120	66.0	02-Apr-85	1400	36	8410
54A120	66.0	07-May-85	1430	25	20600
54A120	66.0	11-Jun-85	1400	22	17500
54A120	66.0	13-Aug-85	1425	110	1050
54A120	66.0	17-Sep-85	1435	99	2480
54A120	66.0	22-Oct-85	1430	63	2350
54A120	66.0	19-Nov-85	1450	49	5630
54A120	66.0	10-Dec-85	1450	48	4570
54A120	66.0	14-Jan-86	1425	68	2230
54A120	66.0	11-Feb-86	1455	40	6780
54A120	66.0	11-Mar-86	1440	34	24100
54A120	66.0	15-Apr-86	1535	50	13700
54A120	66.0	13-May-86	1430	46	10400
54A120	66.0	10-Jun-86	1440	50	4460
54A120	66.0	08-Jul-86	1500	110	1160
54A120	66.0	12-Aug-86	1450	120	918
54A120	66.0	09-Sep-86	1525	110	879
54A120	66.0	21-Oct-86	1445	999999	2640
54A120	66.0	04-Nov-86	1440	999999	3180

999999 = missing data

Appendix B.2. Spokane River hardness data, Oct-83 to Sep-93.
File WY8493.WK1 Revised 26-Apr-94

Station	Spokane River Mile	Date	Time	Hardness (mg/L as CaCO3)	Flow (cfs)
54A120	66.0	09-Dec-86	1330	51	4000
54A120	66.0	13-Jan-87	1400	61	3240
54A120	66.0	10-Feb-87	1400	55	3340
54A120	66.0	17-Mar-87	1445	34	14500
54A120	66.0	14-Apr-87	1410	42	11000
54A120	66.0	05-May-87	1430	37	15800
54A120	66.0	07-Jul-87	1500	80	1940
54A120	66.0	04-Aug-87	1425	110	1100
54A120	66.0	08-Sep-87	1505	85	1280
54A120	66.0	06-Oct-87	1355	74	1490
54A120	66.0	03-Nov-87	1355	84	1500
54A120	66.0	08-Dec-87	1410	58	2430
54A120	66.0	12-Jan-88	1335	60	2290
54A120	66.0	02-Feb-88	1415	69	2010
54A120	66.0	08-Mar-88	1450	58	4570
54A120	66.0	05-Apr-88	1440	27	10100
54A120	66.0	03-May-88	1335	41	11100
54A120	66.0	07-Jun-88	1450	38	6000
54A120	66.0	05-Jul-88	1505	70	1870
54A120	66.0	02-Aug-88	1320	110	750
54A120	66.0	13-Sep-88	1455	77	1270
54A120	66.0	04-Oct-88	1505	79	1370
54A120	66.0	07-Nov-88	1410	60	2340
54A120	66.0	06-Dec-88	1455	40	4150
54A120	66.0	03-Jan-89	1445	60	3390
54A120	66.0	07-Feb-89	1355	57	2790
54A120	66.0	07-Mar-89	1445	48	4830
54A120	66.0	04-Apr-89	1455	29	12800
54A120	66.0	02-May-89	1445	28	21500
54A120	66.0	06-Jun-89	1510	30	11600
54A120	66.0	05-Jul-89	1505	62	2710
54A120	66.0	08-Aug-89	1450	103	919
54A120	66.0	05-Sep-89	1415	96	1250
54A120	66.0	03-Oct-89	1415	58	2140
54A120	66.0	07-Nov-89	1405	68	1800
54A120	66.0	05-Dec-89	1410	44	5400
54A120	66.0	09-Jan-90	1455	38	7850

999999 = missing data

Appendix B.2. Spokane River hardness data, Oct-83 to Sep-93.

File WY8493.WK1 Revised 26-Apr-94

Station	Spokane River Mile	Date	Time	Hardness (mg/L as CaCO3)	Flow (cfs)
54A120	66.0	06-Feb-90	1440	48	6080
54A120	66.0	06-Mar-90	1435	38	7650
54A120	66.0	03-Apr-90	1520	29	11600
54A120	66.0	08-May-90	1330	26	16200
54A120	66.0	05-Jun-90	1445	22	24100
54A120	66.0	10-Jul-90	1305	62	3260
54A120	66.0	07-Aug-90	1335	103	1360
54A120	66.0	04-Sep-90	1250	98	302
54A120	66.0	09-Oct-90	1300	73	1820
54A120	66.0	06-Nov-90	1305	51	3480
54A120	66.0	04-Dec-90	1320	29	16000
54A120	66.0	08-Jan-91	1355	45	4900
54A120	66.0	05-Feb-91	1430	39	6410
54A120	66.0	05-Mar-91	1345	29	19100
54A120	66.0	02-Apr-91	1315	38	7250
54A120	66.0	07-May-91	1325	31	12900
54A120	66.0	04-Jun-91	1315	43	12900
54A120	66.0	09-Jul-91	1525	45	5280
54A120	66.0	06-Aug-91	1500	72	2360
54A120	66.0	03-Sep-91	1530	121	1680
54A120	66.0	08-Oct-91	1640	999999	2150
54A120	66.0	05-Nov-91	1550	999999	2180
54A120	66.0	03-Dec-91	1540	999999	2870
54A120	66.0	07-Jan-92	1620	999999	3260
54A120	66.0	04-Feb-92	1550	999999	6510
54A120	66.0	03-Mar-92	1530	999999	10100
54A120	66.0	07-Apr-92	1620	999999	7030
54A120	66.0	05-May-92	1525	999999	7340
54A120	66.0	02-Jun-92	1610	999999	2710
54A120	66.0	07-Jul-92	1640	999999	1440
54A120	66.0	04-Aug-92	1640	999999	1000
54A120	66.0	09-Sep-92	1605	999999	594
54A120	66.0	06-Oct-92	1515	999999	1600
54A120	66.0	03-Nov-92	1550	999999	2530
54A120	66.0	02-Dec-92	1525	999999	2870
54A120	66.0	05-Jan-93	1345	999999	2310
54A120	66.0	02-Feb-93	1515	999999	2810

999999 = missing data

Appendix B.2. Spokane River hardness data, Oct-83 to Sep-93.

File WY8493.WK1 Revised 26-Apr-94

Station	Spokane River Mile	Date	Time	Hardness (mg/L as CaCO3)	Flow (cfs)
54A120	66.0	02-Mar-93	1530	999999	2320
54A120	66.0	06-Apr-93	1520	999999	17500
54A120	66.0	04-May-93	1655	999999	19300
54A120	66.0	08-Jun-93	1605	999999	6000
54A120	66.0	06-Jul-93	1600	999999	3860
54A120	66.0	03-Aug-93	1555	999999	2340
54A120	66.0	07-Sep-93	1535	999999	1400
57A190	100.7	26-Oct-83	920	19	1960
57A190	100.7	30-Nov-83	910	39	4620
57A190	100.7	21-Dec-83	800	36	4820
57A190	100.7	18-Jan-84	730	36	5440
57A190	100.7	08-Feb-84	715	28	6820
57A190	100.7	07-Mar-84	750	36	5900
57A190	100.7	11-Apr-84	825	36	11200
57A190	100.7	09-May-84	840	84	11200
57A190	100.7	13-Jun-84	820	46	15300
57A190	100.7	11-Jul-84	815	32	2460
57A190	100.7	15-Aug-84	815	27	670
57A190	100.7	12-Sep-84	830	44	1730
57A190	100.7	10-Oct-84	855	36	1810
57A190	100.7	14-Nov-84	910	44	2780
57A190	100.7	12-Dec-84	840	44	4100
57A190	100.7	16-Jan-85	905	32	1630
57A190	100.7	06-Feb-85	850	40	1600
57A190	100.7	13-Mar-85	830	36	2220
57A190	100.7	03-Apr-85	655	40	7240
57A190	100.7	08-May-85	825	21	19300
57A190	100.7	12-Jun-85	835	999999	16300
57A190	100.7	14-Aug-85	810	23	873
57A190	100.7	18-Sep-85	805	999999	2240
57A190	100.7	23-Oct-85	810	23	1830
57A190	100.7	20-Nov-85	830	51	4440
57A190	100.7	11-Dec-85	815	999999	4110
57A190	100.7	15-Jan-86	805	34	1650

999999 = missing data

Appendix B.2. Spokane River hardness data, Oct-83 to Sep-93.
File WY8493.WK1 Revised 26-Apr-94

Station	Spokane River Mile	Date	Time	Hardness (mg/L as CaCO3)	Flow (cfs)
57A190	100.7	12-Feb-86	835	39	6620
57A190	100.7	12-Mar-86	810	37	22900
57A190	100.7	16-Apr-86	815	26	12600
57A190	100.7	14-May-86	810	999999	9070
57A190	100.7	11-Jun-86	830	20	4000
57A190	100.7	09-Jul-86	755	39	1420
57A190	100.7	13-Aug-86	715	41	325
57A190	100.7	10-Sep-86	730	28	320
57A190	100.7	22-Oct-86	830	999999	2310
57A190	100.7	05-Nov-86	735	999999	2960
57A190	100.7	10-Dec-86	730	32	3890
57A190	100.7	14-Jan-87	800	28	2470
57A190	100.7	11-Feb-87	730	23	2800
57A190	100.7	18-Mar-87	820	32	13700
57A190	100.7	15-Apr-87	705	38	11600
57A190	100.7	06-May-87	800	46	15500
57A190	100.7	03-Jun-87	650	30	3230
57A190	100.7	08-Jul-87	735	31	1900
57A190	100.7	05-Aug-87	740	27	576
57A190	100.7	09-Sep-87	800	29	1160
57A190	100.7	07-Oct-87	730	25	884
57A190	100.7	04-Nov-87	745	28	1160
57A190	100.7	09-Dec-87	740	30	2160
57A190	100.7	13-Jan-88	745	30	1720
57A190	100.7	03-Feb-88	735	15	1510
57A190	100.7	09-Mar-88	740	41	4860
57A190	100.7	06-Apr-88	610	27	10900
57A190	100.7	04-May-88	645	29	10400
57A190	100.7	08-Jun-88	710	21	5960
57A190	100.7	06-Jul-88	715	25	1020
57A190	100.7	03-Aug-88	720	26	621
57A190	100.7	14-Sep-88	705	29	1080
57A190	100.7	05-Oct-88	720	29	1080
57A190	100.7	08-Nov-88	720	28	2180
57A190	100.7	07-Dec-88	715	20	4060
57A190	100.7	04-Jan-89	705	30	2920
57A190	100.7	08-Feb-89	720	26	2610

999999 = missing data

Appendix B.2. Spokane River hardness data, Oct-83 to Sep-93.
File WY8493.WK1 Revised 26-Apr-94

Station	Spokane River Mile	Date	Time	Hardness (mg/L as CaCO3)	Flow (cfs)
57A190	100.7	08-Mar-89	735	37	2030
57A190	100.7	05-Apr-89	725	25	12700
57A190	100.7	03-May-89	715	25	21300
57A190	100.7	07-Jun-89	800	27	11900
57A190	100.7	06-Jul-89	715	31	11700
57A190	100.7	09-Aug-89	720	38	477
57A190	100.7	06-Sep-89	735	23	1120
57A190	100.7	04-Oct-89	715	24	1910
57A190	100.7	08-Nov-89	705	22	2140
57A190	100.7	06-Dec-89	720	30	11300
57A190	100.7	10-Jan-90	735	25	9800
57A190	100.7	07-Feb-90	735	24	5240
57A190	100.7	07-Mar-90	720	25	7500
57A190	100.7	04-Apr-90	750	24	14400
57A190	100.7	09-May-90	735	20	16400
57A190	100.7	06-Jun-90	730	17	24100
57A190	100.7	11-Jul-90	710	21	2480
57A190	100.7	08-Aug-90	745	24	695
57A190	100.7	05-Sep-90	655	23	395
57A190	100.7	10-Oct-90	725	23	1470
57A190	100.7	07-Nov-90	720	23	2980
57A150	96.0	05-Dec-90	720	24	15600
57A150	96.0	09-Jan-91	730	23	4500
57A150	96.0	06-Feb-91	710	23	5730
57A150	96.0	06-Mar-91	700	23	17100
57A150	96.0	03-Apr-91	710	23	6840
57A150	96.0	08-May-91	720	22	13000
57A150	96.0	05-Jun-91	645	23	13500
57A150	96.0	10-Jul-91	700	20	4550
57A150	96.0	07-Aug-91	645	20	1950
57A150	96.0	04-Sep-91	705	21	749
57A150	96.0	09-Oct-91	705	999999	1910
57A150	96.0	06-Nov-91	710	20	2150
57A150	96.0	04-Dec-91	710	21	2600
57A150	96.0	08-Jan-92	710	999999	3030
57A150	96.0	05-Feb-92	715	22	6810
57A150	96.0	04-Mar-92	645	999999	10400

999999 = missing data

Appendix B.2. Spokane River hardness data, Oct-83 to Sep-93.

File WY8493.WK1 Revised 26-Apr-94

Station	Spokane River Mile	Date	Time	Hardness (mg/L as CaCO3)	Flow (cfs)
57A150	96.0	08-Apr-92	645	999999	6890
57A150	96.0	06-May-92	630	999999	5050
57A150	96.0	03-Jun-92	635	999999	2530
57A150	96.0	08-Jul-92	640	999999	1150
57A150	96.0	05-Aug-92	610	999999	647
57A150	96.0	10-Sep-92	640	999999	237
57A150	96.0	07-Oct-92	700	999999	1440
57A150	96.0	04-Nov-92	643	999999	2030
57A150	96.0	03-Dec-92	730	999999	3260
57A150	96.0	06-Jan-93	750	999999	2070
57A150	96.0	03-Feb-93	700	999999	2280
57A150	96.0	03-Mar-93	620	999999	1820
57A150	96.0	07-Apr-93	645	999999	18000
57A150	96.0	05-May-93	730	999999	18600
57A150	96.0	09-Jun-93	805	999999	5700
57A150	96.0	07-Jul-93	700	999999	4050
57A150	96.0	04-Aug-93	710	999999	1230
57A150	96.0	08-Sep-93	710	999999	1160

999999 = missing data

Appendix B.3: Comparison of hardness at Ecology stations 54A120 and 57A145, WY 1973 (sorted by 54A120)
File HARDHARD.WK1
06-Apr-94

Date	Hardness (mg/L as CaCO3) at 54A120	Hardness (mg/L as CaCO3) at 57A145
730424	31	23
721227	34	25
730327	35	27
730410	36	27
730313	36	26
721212	36	26
730320	37	26
730118	37	27
730612	41	27
730222	44	32
730925	48	33
730227	49	31
730626	52	33
730912	53	33
721010	58	35
721119	58	39
721031	61	39
730711	65	59
721129	66	41
730821	79	60
730724	96	110
730807	110	72

APPENDIX C

Regression relationships for river hardness and flow

APPENDIX C.

Regression relationships for river hardness and flow.

C.1 Regression analysis of hardness versus flow at Ecology station 54A120.

C.2 Regression of hardness at Ecology station 57A145 versus 54A120.

Appendix C.1. Regression of hardness and flow for station 54A120 (HARDREGR.WK1, 07-Apr-94)

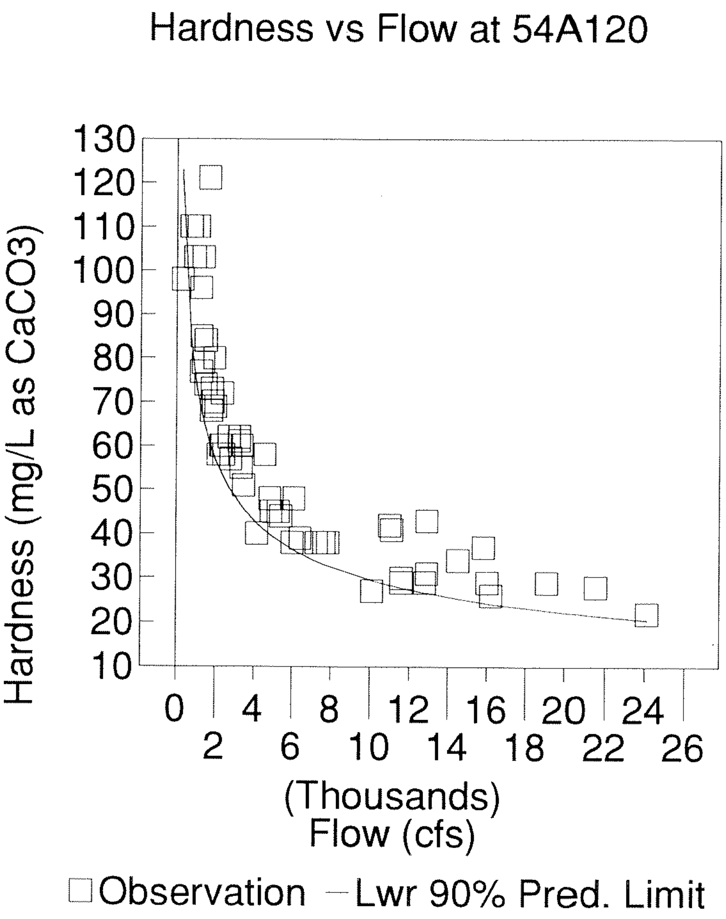
Data from Oct-83 to Sep-93 sorted by flow	Log base 10 [Flow (cfs)]	Log base 10 [Hardness (mg/L as CaCO3)]			
	Xi	Yi	XiYi	Xi^2	Yi^2
	2.480006	1.991226	4.938254	6.150434	3.964981
	2.875061	2.041392	5.869129	8.265977	4.167284
	2.963315	2.012837	5.964671	8.781238	4.051513
	3.041392	2.041392	6.208676	9.250069	4.167284
	3.096910	1.982271	6.138915	9.590851	3.929399
	3.103803	1.886490	5.855296	9.633597	3.558847
	3.107209	1.929418	5.995109	9.654753	3.722657
	3.133538	2.012837	6.307303	9.819066	4.051513
	3.136720	1.897627	5.952325	9.839015	3.600988
	3.173186	1.869231	5.931420	10.06911	3.494027
	3.176091	1.924279	6.111686	10.08755	3.702850
	3.225309	2.082785	6.717626	10.40261	4.337994
	3.255272	1.832508	5.965315	10.59679	3.358088
	3.260071	1.863322	6.074565	10.62806	3.471972
	3.271841	1.845098	6.036868	10.70494	3.404386
	3.287801	1.903089	6.256982	10.80964	3.621751
	3.303196	1.838849	6.074079	10.91110	3.381365
	3.330413	1.763427	5.872944	11.09165	3.109678
	3.359835	1.778151	5.974295	11.28849	3.161821
	3.369215	1.778151	5.990975	11.35161	3.161821
	3.372912	1.857332	6.264619	11.37653	3.449684
	3.385606	1.763427	5.970272	11.46232	3.109678
	3.432969	1.792391	6.153225	11.78527	3.212667
	3.445604	1.755874	6.050049	11.87218	3.083096
	3.510545	1.785329	6.267480	12.32392	3.187402
	3.513217	1.792391	6.297062	12.34269	3.212667
	3.523746	1.740362	6.132596	12.41678	3.028862
	3.530199	1.778151	6.277229	12.46230	3.161821
	3.541579	1.707570	6.047495	12.54278	2.915795
	3.618048	1.602059	5.796330	13.09027	2.566596
	3.659916	1.763427	6.453998	13.39498	3.109678
	3.683947	1.681241	6.193603	13.57146	2.826572
	3.690196	1.653212	6.100678	13.61754	2.733111
	3.722633	1.653212	6.154304	13.85800	2.733111
	3.732393	1.643452	6.134012	13.93076	2.700936
	3.778151	1.579783	5.968661	14.27442	2.495716
	3.783903	1.681241	6.361654	14.31792	2.826572
	3.806858	1.591064	6.056957	14.49216	2.531486
	3.860338	1.579783	6.098498	14.90220	2.495716
	3.883661	1.579783	6.135344	15.08282	2.495716
	3.894869	1.579783	6.153051	15.17000	2.495716
	4.004321	1.431363	5.731640	16.03458	2.048802
	4.041392	1.623249	6.560187	16.33285	2.634938
	4.045322	1.612783	6.524231	16.36463	2.601071
	4.064457	1.477121	6.003697	16.51981	2.181887
	4.064457	1.462397	5.943855	16.51981	2.138607
	4.107209	1.462397	6.006375	16.86917	2.138607
	4.110589	1.633468	6.714518	16.89694	2.668219
	4.110589	1.491361	6.130376	16.89694	2.224159
	4.161368	1.531478	6.373047	17.31698	2.345427
	4.198657	1.568201	6.584341	17.62872	2.459256
	4.204119	1.462397	6.148096	17.67462	2.138607
	4.209515	1.414973	5.956351	17.72001	2.002149
	4.281033	1.462397	6.260574	18.32724	2.138607
	4.332438	1.447158	6.269723	18.77002	2.094266
	4.382017	1.342422	5.882519	19.20207	1.802098
SUM :	201.6389	96.25844	342.3931	736.2885	167.4095
N :	56				
MEAN :	3.600696	1.718900			

Appendix C.1. Regression of hardness and flow for station 54A120 (HARDREGR.WK1, 07-Apr-94)

SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE
TOTAL	1.950829	55	
LINEAR REGRESSION	1.724865	1	1.7248654
RESIDUAL	0.225963	54	0.0041845

Slope (B):	-0.41026
Y intercept:	3.196130
R squared:	0.884170
F Statistic:	412.2020
Std Err of B:	0.020207
Std Err of Y estimate:	0.064687

Plot of observed hardness and lower 90% confidence limit of predicted hardness (using 1-tailed t-statistic, probability=0.10) at Station 54A120



Appendix C.2. Regression of hardness at station 57A145 vs 54A120 (HARDREG2.WK1)

Data from Oct-72 to Sep-73 sorted by 54A120	Hardness (mg/L as CaCO3) @ 54A120 (RM 66.0) Xi	Log base 10 [Hardness (mg/L as CaCO3)] @ 57A145 (RM 85.3) Yi	XiYi	Xi^2	Yi^2
	31	1.361727	42.21356	961	1.854302
	34	1.397940	47.52996	1156	1.954236
	35	1.431363	50.09773	1225	2.048802
	36	1.431363	51.52909	1296	2.048802
	36	1.414973	50.93904	1296	2.002149
	36	1.414973	50.93904	1296	2.002149
	37	1.414973	52.35401	1369	2.002149
	37	1.431363	52.96045	1369	2.048802
	41	1.431363	58.68591	1681	2.048802
	44	1.505149	66.22659	1936	2.265476
	48	1.518513	72.88866	2304	2.305884
	49	1.491361	73.07672	2401	2.224159
	52	1.518513	78.96272	2704	2.305884
	53	1.518513	80.48123	2809	2.305884
	58	1.544068	89.55594	3364	2.384146
	58	1.591064	92.28174	3364	2.531486
	61	1.591064	97.05494	3721	2.531486
	65	1.770852	115.1053	4225	3.135916
	66	1.612783	106.4437	4356	2.601071
	79	1.778151	140.4739	6241	3.161821
	96	2.041392	195.9736	9216	4.167284
	110	1.857332	204.3065	12100	3.449684
SUM :	1162	34.06880	1870.080	70390	53.38038
N :	22				
MEAN :	52.81818	1.548582			

SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE
TOTAL	0.622041	21	
LINEAR REGRESSION	0.553323	1	0.553323
RESIDUAL	0.068717	20	0.003435

Slope (B):	0.007834
Y Intercept:	1.134788
R squared:	0.889528
F Statistic:	161.0423
Std Err of B:	0.000617
Std Err of Y estimate:	0.058616