**WASHINGTON STATE
DEPARTMENT OF
ECOLOGY**

Applying Metals Criteria to Water Quality-Based Discharge Limits

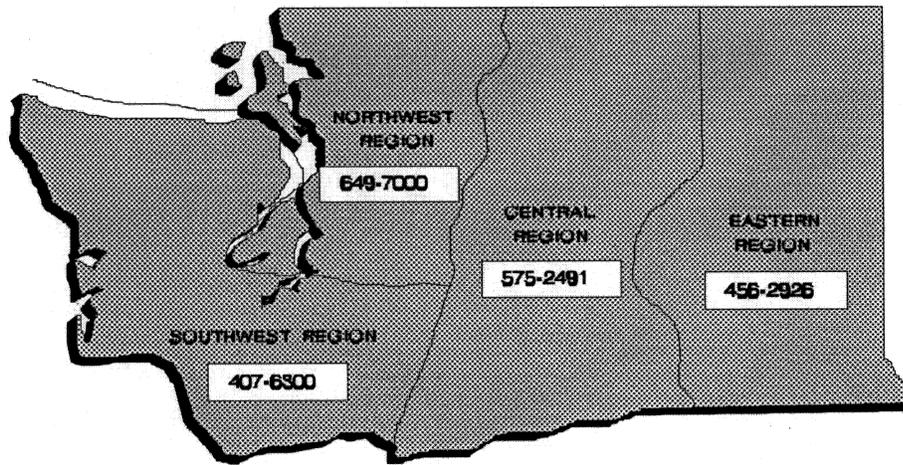## Empirical Models of the Dissolved Fraction of Cadmium, Copper, Lead, and Zinc

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Empirical Models of the Dissolved Fraction
of Cadmium, Copper, Lead, and Zinc

by
Greg Pelletier

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Abstract

This report compares the results of recently collected metals data in the state of Washington with models for metals partitioning that are advocated by EPA. New models were also developed using data from rivers in Washington. Technical guidance for permit managers is proposed to support water quality-based permitting for metals under the National Pollutant Discharge Elimination System (NPDES).

The EPA screening models were found to poorly represent data from rivers in Washington. Dissolved fractions of Cd, Cu, and Zn were under-estimated, and the dissolved fraction of Pb was over-estimated by the EPA models. Under-estimation of the dissolved fraction of metals could lead to exceedence of the water quality criteria in NPDES permitting. These results indicate that the EPA models should not be used to estimate fractions of dissolved metals in Washington's rivers. The poor performance of the EPA models for Cd, Cu, Pb, and Zn also suggests that the EPA models for other metals should not be used.

Empirical models from data in Washington were developed and proposed as an interim measure in NPDES permitting until site-specific data are available. Dissolved fractions of Cu and Zn were found to be significantly correlated with total suspended solids. Regression equations were developed to allow prediction of dissolved fractions of Cu and Zn from total suspended solids with a margin of safety to account for data variability. Dissolved fractions of Cd and Pb were found to be poorly correlated with other water quality variables. Estimated 90th and 95th percentiles of dissolved Cd and Pb fractions from available state-wide data were proposed for use in NPDES permitting in the absence of site-specific data.

Introduction

The state of Washington has adopted criteria for dissolved metals for the protection of aquatic life. When water quality criteria are expressed as the dissolved form of a metal, there is a need to translate between the dissolved and total recoverable forms (EPA, 1993) because regulations for the National Pollutant Discharge Elimination System (NPDES) require that limits for metals in permits be stated as total recoverable in most cases (40 CFR §122.45(c)). In addition, Total Maximum Daily Loads (TMDL) for toxic metals must consider the following:

- determination of the dissolved metal concentration in order to demonstrate attainment of the water quality standards, and

- conversion of the dissolved criteria to total recoverable for mass balance and to meet requirements of NPDES permitting.

EPA recommends using one of three approaches for translating dissolved criteria to total recoverable permit limits (EPA, 1993):

- measure fractions of dissolved/total recoverable metals from the discharge location to translate between dissolved and total recoverable concentrations;

- assume that all of the metal is present in the dissolved form; or

- use historical data for total suspended solids in receiving waterbodies and estimate fractions of dissolved/total recoverable metals from empirical models presented in EPA technical guidance documents (EPA, 1984; EPA, 1985).

The third approach is recommended as an interim measure until sufficient data are collected to implement the first approach. The second approach is generally considered to be too conservative. The major limitation of the third approach is lack of confidence in the EPA models due to quality assurance problems with the original data (EPA, 1993). EPA suggests that although this approach may not provide an accurate estimate of the dissolved fraction, the bias may be conservative (*i.e.* dissolved fractions may be over-estimated). However, recent work in estuaries by Sung (1995) demonstrates that the EPA models do not always provide conservative estimates.

The Department of Ecology has recently collected data from rivers throughout the state of Washington using ultra-clean sampling and analytical methods (Johnson and Hopkins, 1991; Johnson, 1994; Pelletier, 1994; Cusimano, 1996; Erickson, 1996; Hopkins, 1996). The Ecology data can be used to compare with the EPA models or to develop models that are applicable to rivers in Washington for translating between dissolved and total recoverable metals concentrations.

This report compares the results of recently collected metals data in the state of Washington with models for metals partitioning that are advocated by EPA. New models were also developed using data from rivers in Washington. Technical guidance for permit managers is also proposed to support water quality-based permitting for metals under NPDES.

Objectives

- Compare the results of EPA's recommended empirical models of dissolved metals partitioning with recent Ecology data from rivers in the state of Washington.

- Develop a new model or models to translate between the dissolved and total recoverable forms of metals from existing data collected from rivers in Washington.

- Summarize findings in a technical report which will provide guidance to permit managers on water quality-based permitting for metals under NPDES.

Another original objective of the study was to evaluate the feasibility and possible utility of developing watershed-specific empirical models for NPDES permit management. The limited amount of available data did not allow this objective to be addressed in this study.

Project Benefits and Relationship to the NPDES Program

EPA's NPDES regulations require that limits for metals in permits be stated as total recoverable in most cases (40 CFR §122.45(c)). The present project provides technical guidance for managers of NPDES permits for translating criteria for dissolved metals into permit limits for total recoverable metals. The present project also provides guidance on use of appropriate models to evaluate partitioning of dissolved and total recoverable metals in rivers in Washington. The methods developed in the present project may be incorporated into Ecology's Permit Writer's Manual (Ecology, 1994), which describes procedures used for developing NPDES permits.

Methods

Metals Partitioning Models

Many toxic substances, including metals, have a tendency to leave the dissolved phase and attach to suspended solids. The partitioning of toxics between the solid and dissolved phase is often expressed as a function of a pollutant-specific partition coefficient and the concentration of solids. This relationship is usually modeled as a linear partitioning equation (EPA, 1984; EPA, 1985; EPA, 1993) as shown in equation 1 and Table 1.

$$C_d = C_T / (1 + K_p * TSS * 10^{-6})$$ equation 1

where

C_d = dissolved phase metal concentration
C_T = total metal concentration
TSS = total suspended solids concentration (mg/L)
K_p = partition coefficient (liter/kilogram) = $K_{po}TSS^{\alpha}$ (Table 1).

Table 1. Linear partition coefficients for metals in streams (EPA, 1985; Kinerson, 1996.)

	K_{po}	α
Arsenic	0.48×10^6	-0.73
Cadmium	4.00×10^6	-1.13
Chromium	3.36×10^6	-0.93
Copper	1.04×10^6	-0.74
Lead	2.8×10^6	-0.8
Mercury	2.91×10^6	-1.14
Nickel	0.49×10^6	-0.57
Zinc	1.25×10^6	-0.70

Ambient factors influencing metal partitioning are usually assumed to remain constant with distance in a river. This assumption is often valid under the low flow conditions typically used as design flows for permitting of metals (EPA, 1993). In steady-state modeling, metals releases may be assumed to remain fairly constant with time.

The empirical models recommended by EPA may be used to estimate the partition coefficient (K_p) from ambient data for total suspended solids. Ecology data can be used to compare with EPA's empirical models or to develop partitioning models that are more representative of conditions in rivers in Washington.

An alternative simplified model for prediction of dissolved metals concentration was also considered (Thomann and Mueller, 1987):

$$C_d = f_d \, C_T \qquad \text{equation 2}$$

where f_d is the fraction of total metals present in the dissolved form. Ambient fractions of dissolved metals (f_d) are referred to as *translators* between dissolved and total recoverable criteria for metals in EPA guidance.

The principal method of model development was linear regression (Zar, 1984). Regression analysis was used to evaluate the relationship between f_d and TSS. EPA's empirical models were compared with observed data from rivers in Washington using graphical presentations. Models for estimating partitioning of dissolved metals in the absence of site-specific data were recommended based on either EPA's proposed models or models developed from regional data.

Geographical Location and Environmental Problems Addressed

This project addresses state-wide application of metals criteria in NPDES permitting in Washington. The results of this project will help to prevent violation of water quality criteria for metals from NPDES dischargers, and will protect against potential toxicity to aquatic life. Existing data collected by the Department of Ecology from rivers throughout the state were used for the project.

Data Collection Methods, Quality, and Availability

The measurement of trace metals at ambient levels has been the subject of increased emphasis in recent years (EPA, 1995a). Measurement of ambient levels of trace metals near the water quality criteria requires quantification at levels that may be hundreds of times lower than the most commonly used methods. Also, recent USGS and EPA studies strongly indicate that rigorous steps must be taken in order to prevent contamination during collection and analysis of samples for trace metals (Windom *et al.*, 1991; EPA, 1992).

The Department of Ecology has recently collected data from rivers throughout the state of Washington using ultra-clean sampling and analytical methods (Johnson and Hopkins, 1991; Johnson, 1994; Pelletier, 1994; Cusimano, 1996; Erickson, 1996; Hopkins, 1996). Rigorous quality control was applied to the collection and analysis of trace metals for these studies to prevent contamination during collection and analysis.

The availability of reliable data with paired measurements of dissolved and total or total recoverable trace metals from a cross-section of sampling sites throughout the state is limited to copper, cadmium, lead, and zinc samples from the waterbodies shown in Figure 1 and Table 2. Data compiled for this project are presented in Appendix A. Because of the relatively small number of samples with measurable dissolved and total recoverable metals, the development of empirical models for individual waterbodies was not explored. Data from all waterbodies were pooled to explore relationships between fractions of dissolved metals and other water quality parameters to develop state-wide empirical models. Data for development of empirical models was restricted to observations above the detection limits for both dissolved and total or total recoverable metals. The diverse water quality characteristics of the available sample locations provided a wide range of conditions representative of variability in rivers in the state of Washington.

Table 2. Sampling locations for studies of low-level metals in rivers of Washington.

Waterbody	Investigator	Laboratory for Metals[1]
Columbia River	Johnson and Hopkins, 1991	Battelle
Gibbons Creek	Erickson, 1995	MEL
Green River	Johnson, 1994	Battelle
Puyallup River	Johnson, 1994	Battelle
Snohomish River	Johnson, 1994	Battelle
	Cusimano, 1996	MEL
Spokane River	Pelletier, 1994	Battelle
Yakima River	Johnson, 1994	Battelle

[1]Battelle: Battelle Marine Sciences Laboratory, Sequim, WA; MEL: Manchester Environmental Laboratory

Quality assurance procedures during sample collection and analysis generally included careful attention to the major elements identified by EPA (1995b and 1995c), including: special cleaning procedures for sample containers and filter units, grab sample collection directly into pre-cleaned sample containers, field filtration with laboratory-cleaned filter units, field and laboratory blanks, standard reference materials, and field and laboratory duplicate samples. Quality assurance procedures and results are documented in individual project plans and reports for each study. Staff at Ecology's Manchester Environmental Laboratory (MEL) -- either the lab director or the supervisor of the metals analysis section -- prepared written quality assurance reviews, which evaluated the validity and usefulness of all metals data used in this study. Where applicable, EPA Contract Laboratory Program requirements were followed during all studies.

Cd, Cu, Pb, and Zn were analyzed in filtered and unfiltered samples. Field measurements were also obtained for temperature and pH, and laboratory measurements by MEL were made for specific conductance, total hardness, total suspended solids (TSS), and total organic carbon (TOC). Two methods were used to analyze unfiltered samples for metals during different studies: *total* and *total recoverable*. The measurement of *total* metals by Battelle Marine Sciences Laboratory was the preferred low-level method until the Manchester Environmental Laboratory had completed development of a low-level method for *total recoverable* metals in
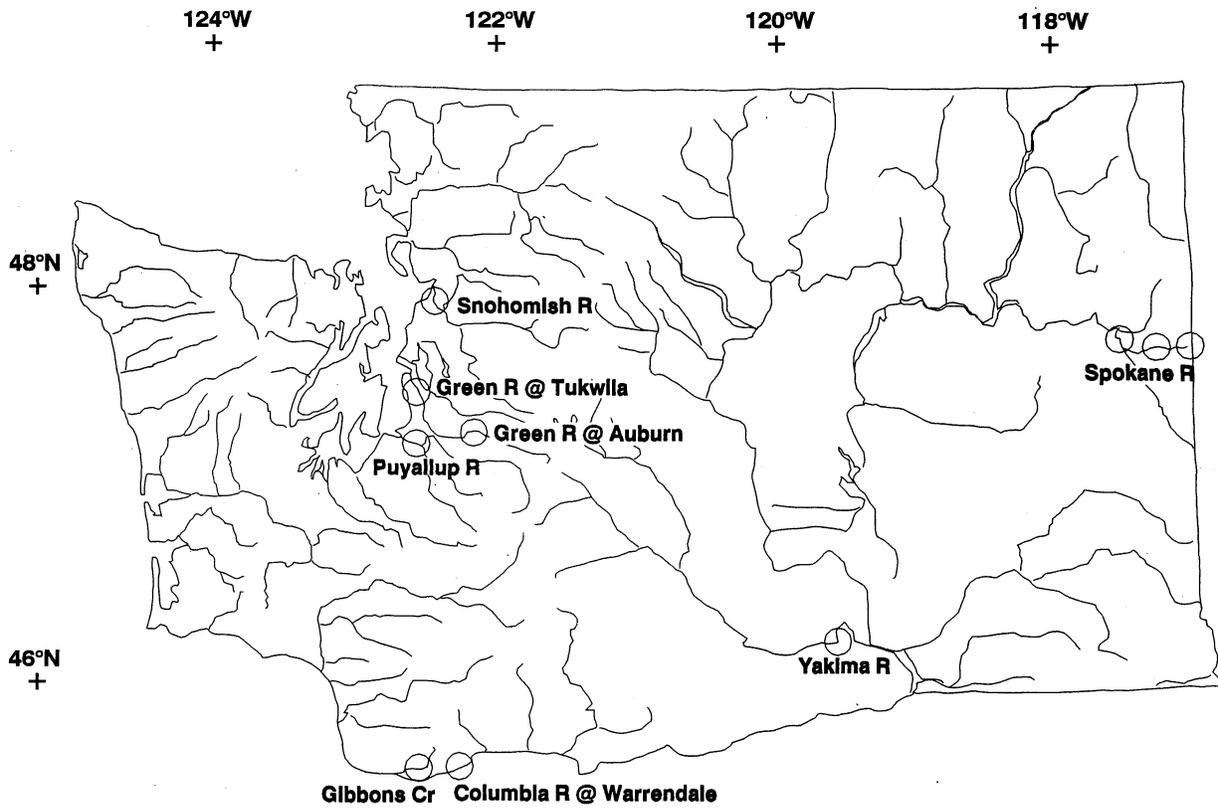
Figure 1. Sampling locations for studies of low-level metals in Washington.

1994. 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 prior to 1994. Dissolved Cd, Cu, and Pb by Battelle were also determined after coprecipitation. Analyses for total and total recoverable metals were considered to be equivalent for the purposes of this study.

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.

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 mm 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.

Laboratory analysis by Manchester Environmental Laboratory

Dissolved metals were analyzed by MEL using inductively coupled plasma mass spectrometry (ICP-MS) with a modified version of EPA Method 200.8. Total recoverable metals were analyzed by MEL using a microwave-assisted digestion (EPA Method 202.2) and ICP-MS, GFAA, or ICP, depending on the detection limits needed. All lab analyses by MEL were conducted using approved standard methods as documented by Kammin (1994).

Freshwater Aquatic Life Criteria for Metals in Washington

Water quality criteria to protect aquatic life (established in WAC 173-201A-040) apply to the dissolved fraction for Cd, Cu, Pb, and Zn. The equations in Table 3 are specified in the November 25, 1992 revision of WAC 173-201A-040 to calculate chronic (four-day average not to be exceeded more than once every three years) and acute criteria (one-hour average not to be exceeded more than once every three years) from total hardness (mg/L as $CaCO_3$).

The first term in each criterion equation in Table 3 is a *conversion factor*, which converts the original total recoverable criteria to dissolved criteria (*e.g.*, 0.865 is the *conversion factor* for Cd). The *conversion factors* are a measure of the fraction of total metal in the dissolved phase during the toxicity tests used to develop the criteria. The fractions of metals in the dissolved and

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particulate phases are dependent on water chemistry. Because of the differences between chemical properties of the waters used during toxicity tests compared with typical ranges in water chemistry in ambient waters, there is no reason to expect that the *conversion factors* can be used to estimate the fraction of metal that would be in the dissolved phase in ambient waters.

Table 3. Fresh water criteria for dissolved Cd, Cu, Pb, and Zn.

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

EPA has recently developed new *conversion factors* for dissolved criteria which are different from the values adopted in WAC 173-201A-040. The new criteria for dissolved metals, which were proposed by EPA in an interim final rule (IFR; Federal Register, May 4, 1995, Volume 60, Number 86; 40 CFR Part 131), and which Ecology intends to adopt into the state water quality standards during the current triennial review, are presented in Table 4.

Table 4. EPA's IFR criteria for dissolved Cd, Cu, Pb, and Zn, which Ecology intends to adopt in the current triennial review of the state water quality standards.

	chronic dissolved	acute dissolved
Cadmium	$[1.101672-((\ln(hardness))(.041838))]*$ $[e^{(0.7852[\ln(hardness)]-3.490)}]$	$[1.136672-((\ln(hardness))(.041838))]* [e^{(1.128[\ln(hardness)]-3.828)}]$
Copper	$0.96[e^{(0.8545[\ln(hardness)]-1.465)}]$	$0.96[e^{(0.9422[\ln(hardness)]-1.464)}]$
Lead	$[1.46203-((\ln(hardness))(.145712))]*$ $[e^{(1.273[\ln(hardness)]-4.705)}]$	$[1.46203-((\ln(hardness))(.145712))]*$ $[e^{(1.273[\ln(hardness)]-1.460)}]$
Zinc	$0.986[e^{(0.8473[\ln(hardness)]+0.7614)}]$	$0.978[e^{(0.8473[\ln(hardness)]+0.8604)}]$

Ambient fractions of dissolved metals, f_d in equation 2, are referred to as *translators* between dissolved and total recoverable criteria in EPA guidance. Ecology's current policy for conversion of the dissolved criteria to total recoverable criteria for NPDES permitting, in the absence of site-specific data for ambient *translators*, is to divide the dissolved criteria by the criteria *conversion factors*, which yields total recoverable criteria (Table 5).

Ecology's policy for conversion of the dissolved criteria to total recoverable criteria for NPDES permitting in the absence of site-specific data or models for ambient translators is not planned to change after adoption of the IFR criteria for dissolved metals. Therefore, the default criteria for total recoverable metals in NPDES permitting, in the absence of ambient translators, will be the equations in Table 5.

Table 5. Default criteria for total recoverable Cd, Cu, Pb, and Zn in the absence of site-specific dissolved/total recoverable translators.

	chronic total recoverable	acute total recoverable
Cadmium	$e^{(0.7852[\ln(\text{hardness})]-3.490)}$	$e^{(1.128[\ln(\text{hardness})]-3.828)}$
Copper	$e^{(0.8545[\ln(\text{hardness})]-1.465)}$	$e^{(0.9422[\ln(\text{hardness})]-1.464)}$
Lead	$e^{(1.273[\ln(\text{hardness})]-4.705)}$	$e^{(1.273[\ln(\text{hardness})]-1.460)}$
Zinc	$e^{(0.8473[\ln(\text{hardness})]+0.7614)}$	$e^{(0.8473[\ln(\text{hardness})]+0.8604)}$

Results and Discussion

Summary Statistics for Metals Data from Rivers in Washington

Table 6 presents a summary of the state-wide data for low-level dissolved and total metals concentrations, dissolved fractions of metals, and ancillary water quality variables (pH, hardness, conductivity, total organic carbon, and total suspended solids). The data represent a wide range of conditions throughout the state. Summaries of water quality variables by waterbody are presented in Figures 2, 3, and 4.

Correlations Between Dissolved Fractions of Metals and Other Variables

Correlation between ratios of dissolved/total metals and other water quality variables were evaluated by calculating Spearman rank correlation coefficients (SYSTAT, 1993). Correlations between dissolved fractions of metals and total suspended solids were most significant (Table 7). In general, the dissolved fraction of metals decreases as total suspended solids increases, which is consistent with partitioning theory and previous findings by EPA (EPA, 1984; EPA, 1985). The actual significance of estimated correlation coefficients is difficult to quantify because of the large number of variables that were analyzed. Correlations between other variables and dissolved metals fractions were generally weaker than for total suspended solids.

Table 6. Summary of water quality for waterbodies included in the state-wide metals database.

	Number of Samples	Minimum	Maximum	Median	Mean	Standard Deviation	Coefficient of Variation
pH	99	6.8	9.1	7.7	7.8	0.54	7.0%
Hardness (mg/L as CaCO3)	102	12.1	412	45.9	79.8	74.9	93.9%
Conductivity (uS)	112	25.0	850	123	173	143	82.9%
Total Organic Carbon (mg/L)	97	0.5	9.1	1.8	2.5	1.82	72.6%
Total Suspended Solids (mg/L)	88	0.5.	1970	6.0	40.2	215	535%
Dissolved Metals (ug/L)							
Cd	104	<0.005	0.35	0.03	0.055	0.070	127%
Cu	102	<0.05	3.4	0.53	0.78	0.60	77.8%
Pb	85	<0.015	0.79	0.062	0.11	0.15	132%
Zn	85	0.17	163	1.3	20.4	38.0	187%
Total and Total Recoverable Metals (ug/L)							
Cd	112	<0.007	0.50	0.05	0.091	0.10	113%
Cu	112	0.285	43	0.84	2.4	6.3	263%
Pb	94	<0.07	5.4	0.40	0.81	1.1	131%
Zn	94	0.165	179	4.6	28.4	42.7	150%
Fractions of Dissolved/Total Metals (1)							
Cd	26	0.213	1	0.684	0.661	0.193	30.0%
Cu	60	0.032	1	0.659	0.679	0.252	39.0%
Pb	17	0.030	1	0.123	0.158	0.224	132%
Zn	31	0.074	1	0.639	0.649	0.279	45.4%

1) Only data which were above the detection limit and were unqualified were included for determination of fractions of dissolved/total metals. The arcsine transformation was used to estimate means of ratios of dissolved/total metals.

Comparison of EPA's Partitioning Models With Data from Washington

The EPA screening models described by equation 1 were used to estimate the fractions of dissolved metals from measured total suspended solids for comparison with measured fractions of dissolved metals. The EPA models were found to poorly represent the measured fractions of dissolved metals for Washington's rivers (Figure 5). The dissolved fractions for Cd, Cu, and Zn were grossly under-estimated by the EPA models, and Pb was generally over-estimated. Under-estimation of the dissolved fraction of metals for NPDES permits could lead to exceedence of the water quality criteria. These results indicate that the EPA models should not be used to estimate fractions of dissolved metals in Washington's rivers.
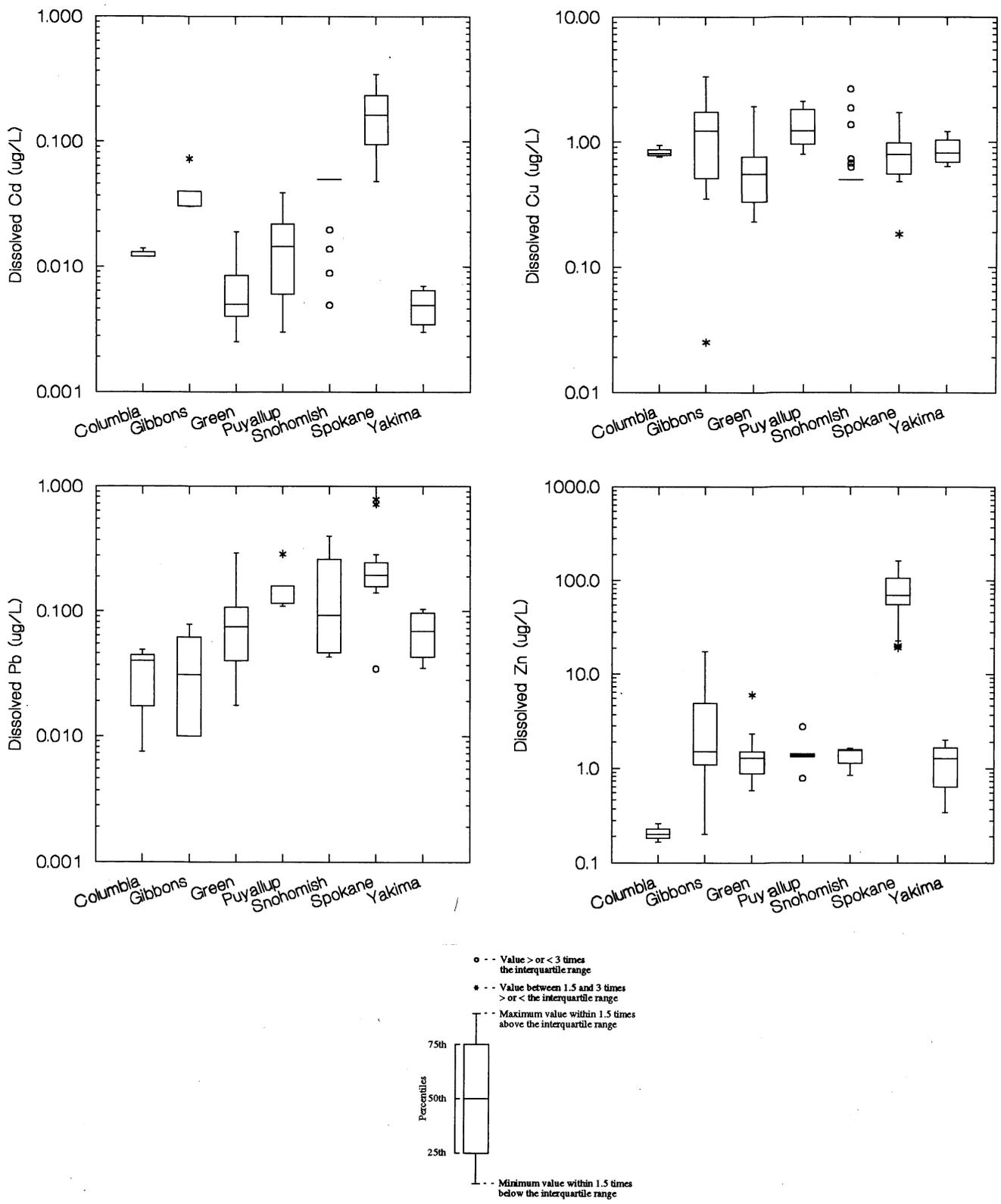
Figure 2. Box plots of dissolved Cd, Cu, Pb, and Zn concentrations by waterbody.
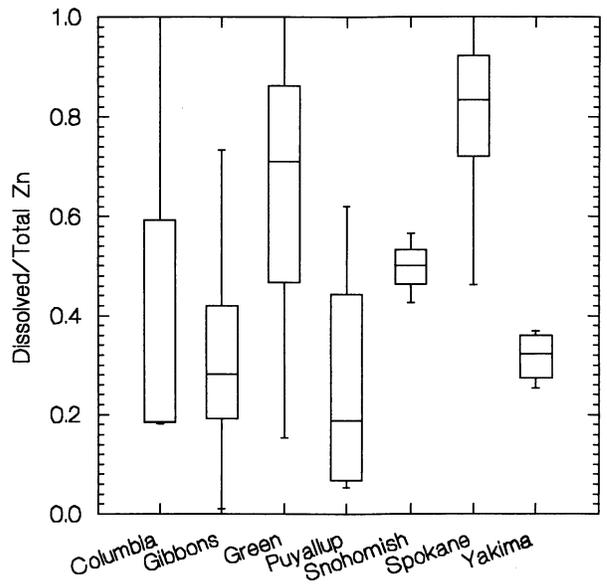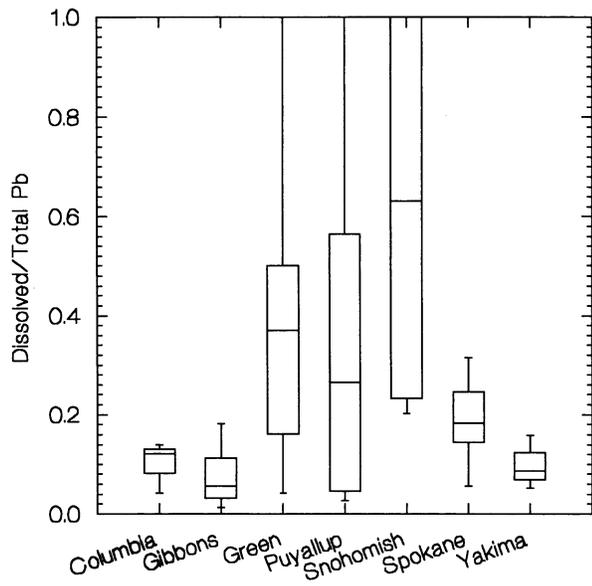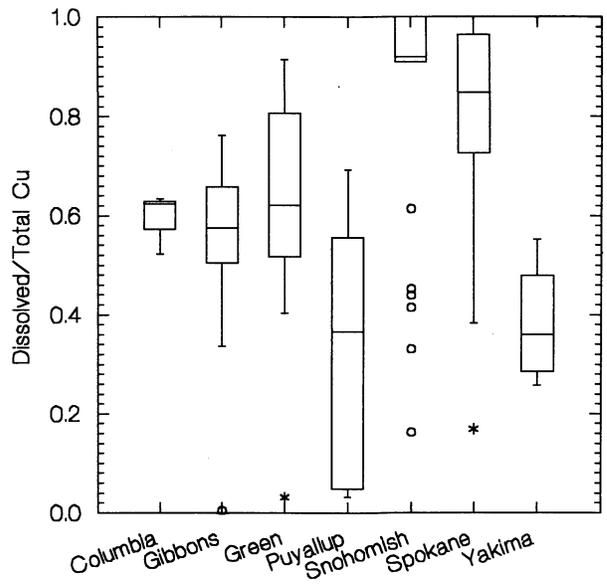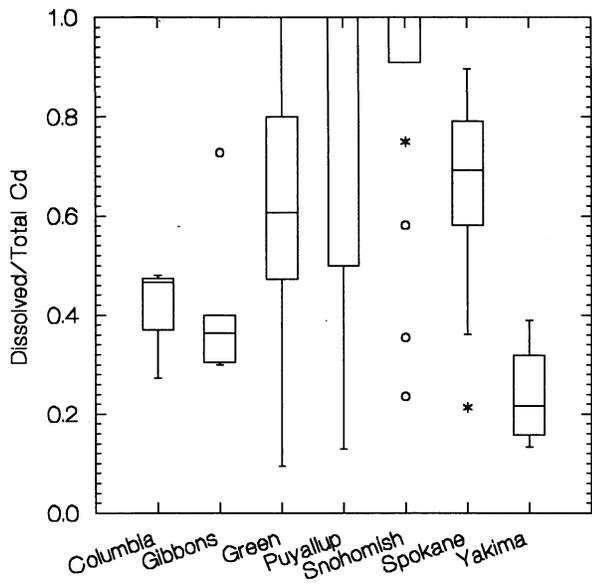
Figure 3. Box plots of fractions of dissolved Cd, Cu, Pb, and Zn by waterbody.
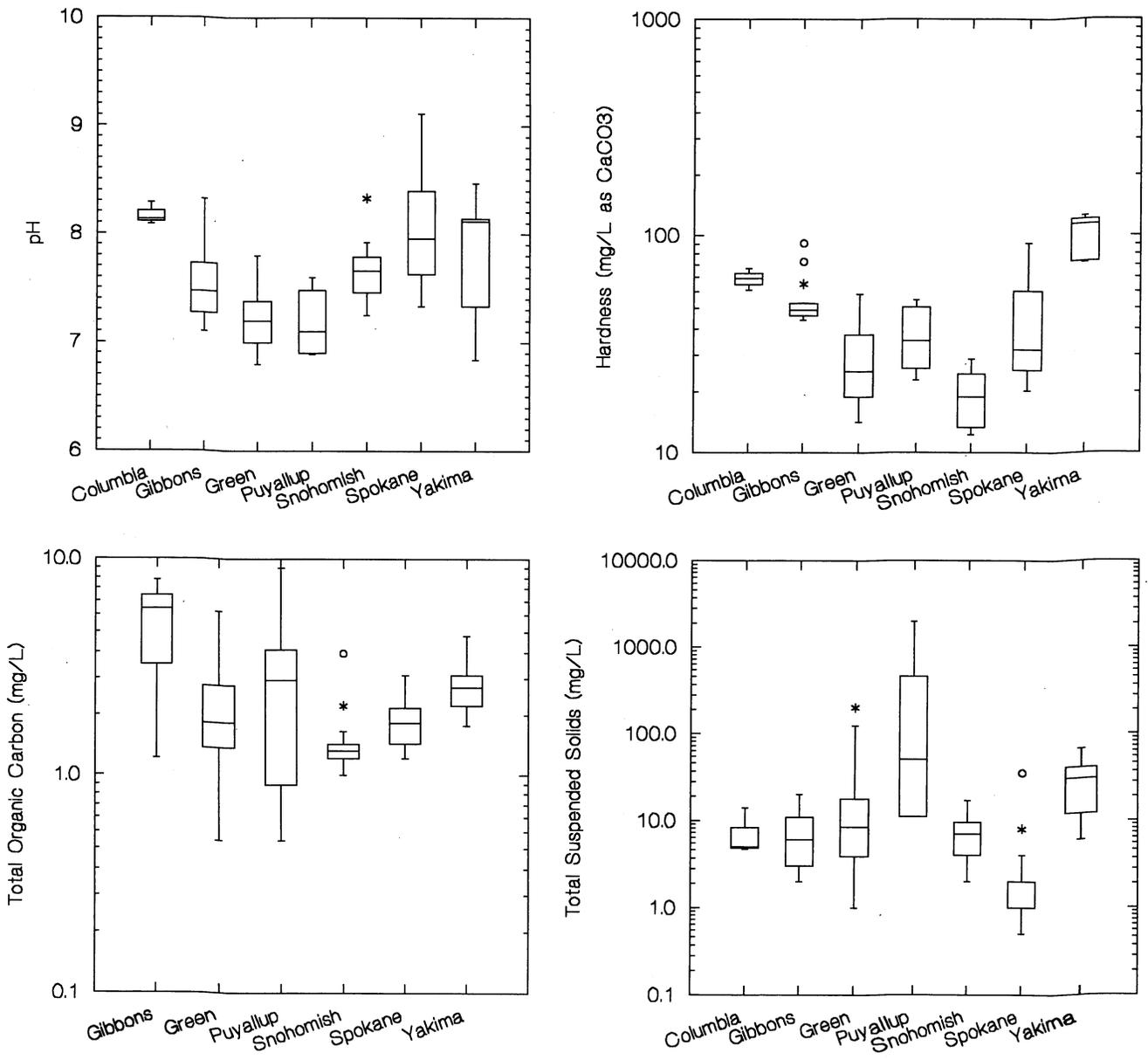
Figure 4. Box plots of pH, hardness, total organic carbon, and total suspended solids by waterbody.

Table 7. Spearman rank correlation coefficients (bold values indicate possibly significant correlations at a probability of 0.05 for n=53 samples.)

	Total Suspended Solids	Total Organic Carbon	Hardness	pH
Total Organic Carbon	**0.50**			
Hardness	0.12	0.07		
pH	**-0.52**	-0.19	0.09	
Ratio of Dissolved/Total Cd	**-0.43**	**-0.45**	**-0.29**	0.04
Ratio of Dissolved/Total Cu	**-0.67**	**-0.40**	**-0.33**	**0.34**
Ratio of Dissolved/Total Pb	**-0.32**	**-0.29**	**-0.51**	0.02
Ratio of Dissolved/Total Zn	**-0.59**	**-0.43**	**-0.39**	0.26

Note: Correlation coefficients can range from -1 to 1. Negative values indicate that one variable decreases as the other increases, positive indicates that variables increase and decrease together. The significance of each correlation should be interpreted with caution and 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.

Empirical Models based on Data from Rivers in Washington

Linear Regression and Univariate Models.

Linear regression was used to develop empirical models for fractions of dissolved metals. Dissolved fractions of metals were assumed to be dependent on total suspended solids for the linear regression analysis. Including other water quality parameters as independent variables (e.g., pH, hardness, organic carbon) did not improve the regressions, as measured by the r^2 and standard error of the estimate. Therefore, in consideration of consistency with prior studies by EPA, simplicity of empirical models, and goodness of fit, TSS was considered to be adequate as the sole independent variable in the regressions. A log-transformation was used to normalize the data for the regressions for simplicity and also because of goodness-of-fit compared with un-transformed data and arcsine transformation. The resulting regressions are shown in Figure 6.
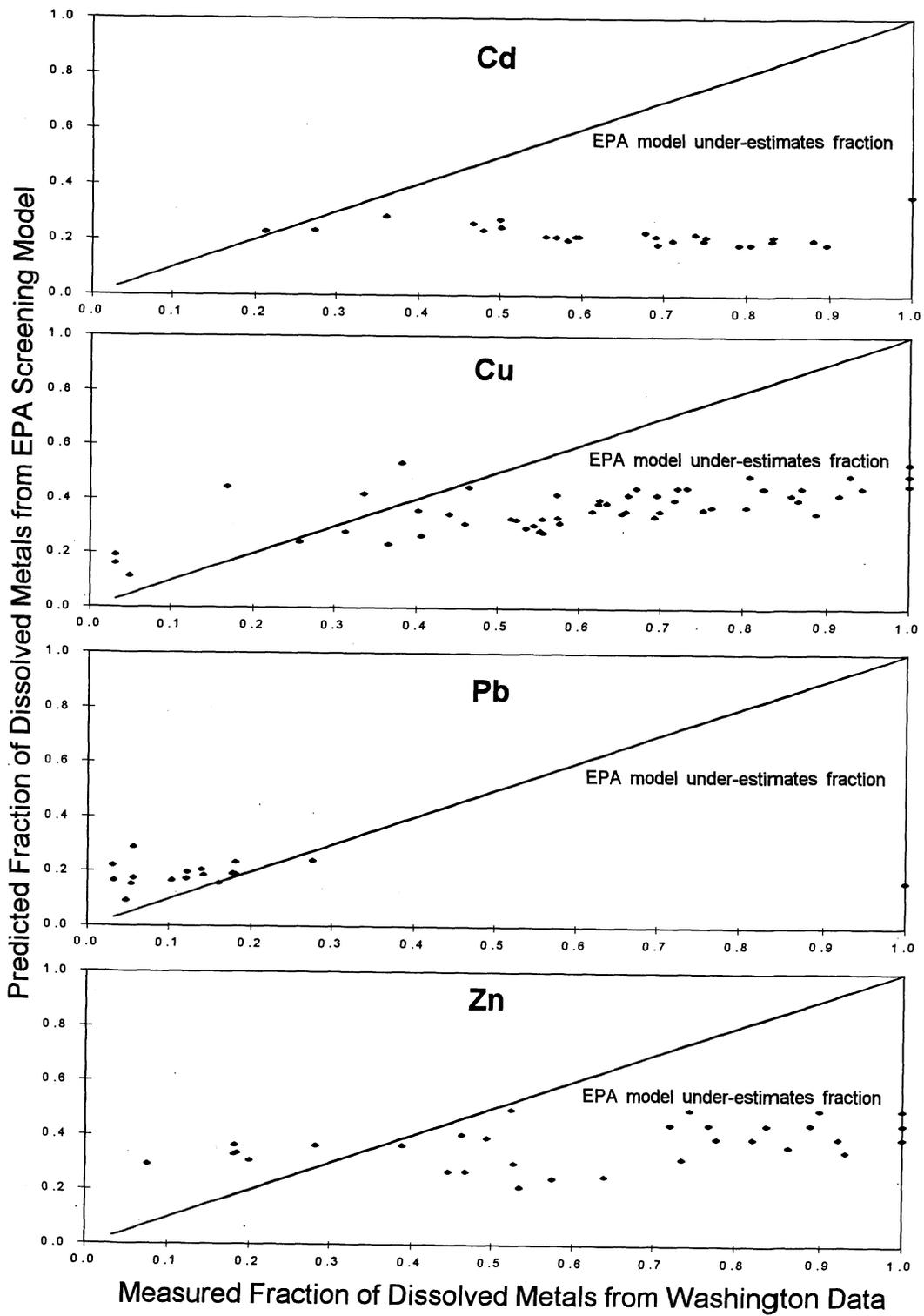
Figure 5. Comparison of observed fractions of dissolved/total metals with the EPA screening models.
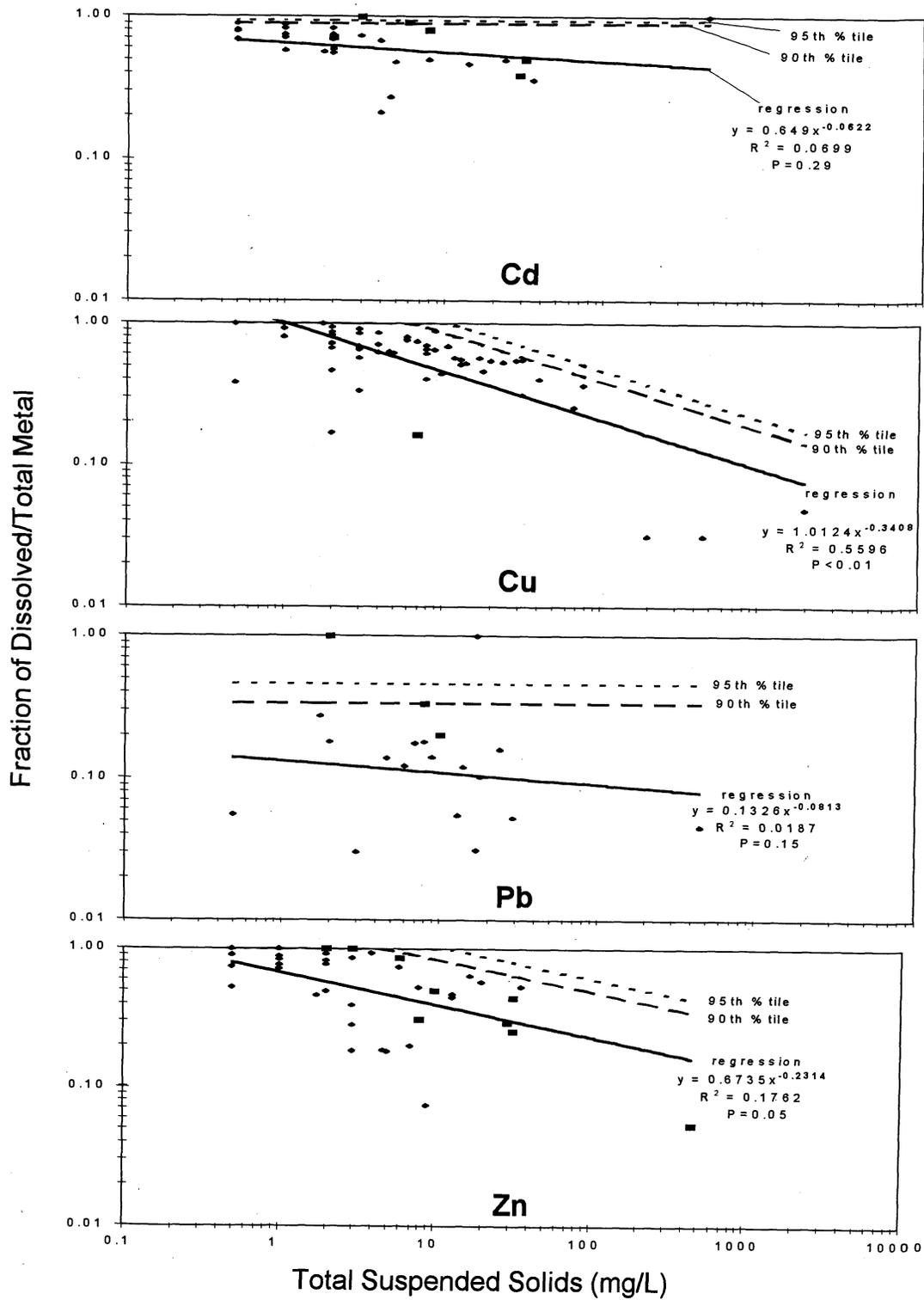
Figure 6. Fractions of dissolved/total metals versus total suspended solids in rivers of Washington (squares are qualified data, which were not included in the regression.)

Regression coefficients for Cd and Pb were not found to be significant, which suggests that dissolved fractions are not dependent on total suspended solids for these metals. The regressions for Cu and Zn were found to be significant, which suggests that the linear regressions could be useful as an empirical model to estimate dissolved fractions for these metals. The regressions for Cu and Zn explain about 56% and 18% of the total variance. Therefore, a large portion of the variability for Cu and Zn, and all of the variability for Cd and Pb, is attributed to unknown sources. Regression results are not recommended for empirical models for Cd and Pb due to the insignificance of the regression coefficients.

Recommended Models for Estimating Dissolved Fractions of Metals.

Variability is an important consideration for selection of appropriate empirical models for application to NPDES permitting. Use of estimated mean values from regression models or univariate analysis could lead to frequent under-estimation of dissolved fractions given the relatively large variability of the data. Empirical models should contain an adequate factor of safety to provide confidence that the estimated fractions of dissolved metals are not under-estimated. The Department of Ecology recommends the use of 10th or 90th percentiles (whichever is more restrictive) from the critical seasonal period for selection of critical conditions for input variables in steady-state modeling for water quality-based permitting. If data are not stratified by season, then the 5th or 95th percentiles are recommended for use as the critical condition.

For Cd and Pb, the 90th and 95th percentiles were estimated by applying the appropriate z-statistics ($z=1.282$ for the 90th percentile and 1.645 for the 95th percentile) to the mean and standard deviation of the transformed fractions of dissolved metals (log-transformation for Cd and arcsine-transformation for Pb, Figure 7).

For Cu and Zn, the 90th and 95th percentiles are shown as approximate upper prediction limits of the regression equations (Figure 6). The 90th and 95th percentile prediction intervals were approximated based on the following equations:

$$Y_{log} = \beta_0 + \beta_1 X_{log} + t_{\alpha(1),n-2} S_{y.x}[1+1/n+((X_{i,log}-X_{bar,log})^2/((n-1)*S_{x,log}^2))]^{0.5} \qquad \text{equation 3}$$

where Y_{log} and X_{log} are the log-transformed dissolved fraction of metals and total suspended solids, β_0 and β_1 are the intercept and slope from the regression, t is the t-statistic (1-tailed for upper prediction interval at probability level of 1-α), n is the number of samples for the regression, $X_{i,log}$ is the value of X_{log} for which Y_{log} is predicted, $X_{bar,log}$ is the mean of the log-
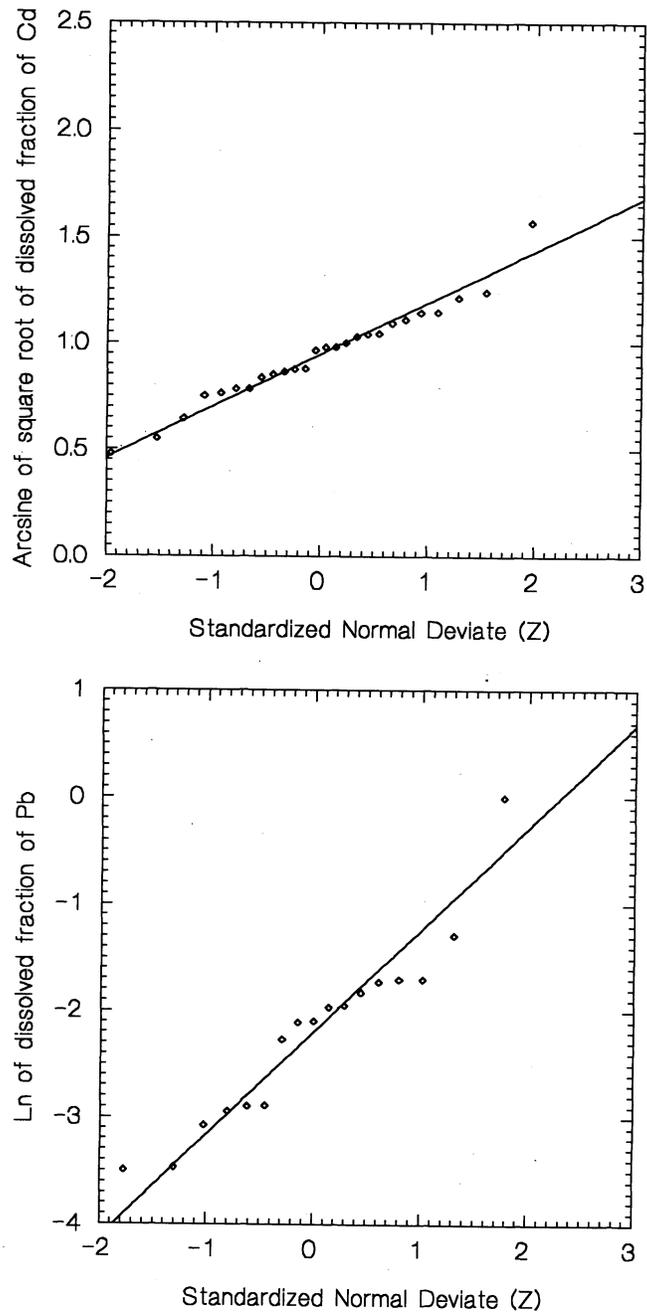
Figure 7. Probability plots of transformed fractions of dissolved Cd and Pb.

transformed total suspended solids, $S_{x,log}^2$ is the variance of the log-transformed total suspended solids, and $S_{y.x}$ is the standard error of the estimate from the regression. Equation 3 was simplified to the equation for a power curve by approximation as follows:

$$Y = aX^b$$

equation 4

where Y = the dissolved fraction of metals, X = total suspended solids (mg/L), a=antilog(β_0+ $zS_{y.x}$), z= 1.282 for the 90th percentile and 1.645 for the 95th percentile, and b=β_1 (z is approximately equal to the t-statistic for large values of n, and the square root term in equation 3 is approximately equal to 1).

The recommended estimates for 90th and 95th percentiles of the dissolved fractions of Cd, Cu, Pb, and Zn are shown in Table 8. The 90th percentiles are recommended when other input data (*e.g.* TSS and hardness) are stratified by season and 95th percentiles are recommended when data are not stratified by season or when no TSS data are available. Estimates for Cd and Pb are based on univariate distributions because of the finding of no significant regression with TSS. Estimates for Cu and Zn are based on the regression equations. A value of f_d=1 is recommended in Table 8 for TSS values below which the upper prediction limits of the regression equations for Cu and Zn return $f_d \geq 1$ because the dissolved fraction cannot exceed 100 percent of the total metals concentration.

Table 8. Recommended estimates of the 90th and 95th percentiles of ambient dissolved fractions (f_d) of Cd, Cu, Pb, and Zn based on data from rivers in Washington (regressions assume TSS in mg/L). Conversion factors from Table 3 are shown for comparison.

	90th percentile of f_d	95th percentile of f_d	Conversion Factor from Table 3
Cd	0.898	0.943	0.89-1.0[1]
Cu	if TSS<6.7 mg/L: 1 if TSS $\geq$ 6.7 mg/L: 1.91*TSS$^{-0.341}$ if no TSS: 0.968	if TSS<11.4 mg/L: 1 if TSS $\geq$ 11.4 mg/L: 2.29*TSS$^{-0.341}$ if no TSS: 0.996	0.96
Pb	0.340	0.466	0.73-0.99[1]
Zn	if TSS<4.9 mg/L: 1 if TSS $\geq$ 4.9 mg/L: 1.44*TSS$^{-0.231}$ if no TSS: 0.965	if TSS<12.5 mg/L: 1 if TSS $\geq$ 12.5 mg/L: 1.79*TSS$^{-0.231}$ if no TSS: 0.996	0.978 (acute) 0.986 (chronic)

[1]The conversion factor is dependent on hardness (Table 4). The range for hardness of 25-150 mg/L as $CaCO_3$ is shown.

Application to NPDES Permits

The empirical models for estimating the dissolved fractions of Cd, Cu, Pb, and Zn may be used to translate dissolved criteria for metals into total recoverable permit limits for effluent. The following procedure is recommended for derivation of permit limits using the empirical models for ambient dissolved fractions of metals.

- *Step 1: Calculate the acute and chronic criteria for dissolved metals from the equations in Table 3 or Table 4.* The 10th percentile of hardness from seasonally stratified data or 5th percentile from unstratified data is recommended for critical conditions. Table 4 represents the new criteria for dissolved metals which were proposed by EPA, and which Ecology intends to adopt into the state water quality standards during the current triennial review. *[For example, the 10th percentile hardness during the critical season may be 25 mg/L as $CaCO_3$. Therefore, the acute and chronic water quality criteria for dissolved Cu from Table 4 would be 4.61 µg/L and 3.47 µg/L.]*

- *Step 2: Calculate the ambient dissolved fraction (f_d) of Cd, Cu, Pb, or Zn from the equations in Table 8.* The 10th percentile of TSS from seasonally stratified data or 5th percentile from unstratified data is recommended for critical conditions. *[For example, the 10th percentile TSS during the critical season may be 10 mg/L. Therefore, the equation for the 90th percentile of the dissolved fraction of Cu would result in $f_d = 1.91 * 10^{-0.341} = 0.871$.]*

- *Step 3: Calculate the acute and chronic waste load allocations (WLA) for effluent total recoverable metals.*

    If the background metals are measured as dissolved metals (CB_{dis}), then equation 5 should be used as follows to calculate acute and chronic WLAs for total recoverable metals:

$$WLA = [(WQC_{dis} * DF) - (CB_{dis} * (DF - 1))] / f_d \qquad \text{equation 5}$$

    where WQC_{dis} are acute and chronic water quality criteria for dissolved metals (Step 1 from Table 4), DF are acute and chronic dilution factors at the mixing zone boundary, and f_d is the fraction of dissolved metals (Step 2 from Table 8). The background concentration of dissolved metals (CB_{dis}) should be the estimated 90th percentile during the critical season, or the 95th percentile if the data are not seasonally stratified.

    If the background metals are measured as total recoverable metals (CB_{trec}), then equation 6 is recommended to estimate the acute and chronic WLAs for total recoverable metals as follows:

$$WLA = [(WQC_{dis} * DF) / f_d] - [CB_{trec} * (DF - 1)] \qquad \text{equation 6}$$

[For example: if the acute and chronic DF are 10 and 30, and the 90th percentile of CB_{trec} is 2 µg/L, then, from equation 6, the acute WLA for total recoverable Cu = [(4.61*10)/0.871]-[2*(10-1)] = 35 µg/L, and the chronic WLA for total recoverable Cu = [(3.47*30)/0.871]-[2*(30-1)] = 62 µg/L.]

- *Step 4: Calculate the daily maximum and monthly average permit limits for total recoverable metals from the acute and chronic WLAs using the procedures described in the Permit Writer's Manual.* Water quality-based effluent limits are calculated by the two-value WLA process as described by EPA (1991) and Ecology (1994). A spreadsheet for calculating permit limits is available from Ecology's home page on the Internet World Wide Web (http://www.wa.gov/ecology/).

Conclusions and Recommendations

- The EPA screening models to predict the dissolved fraction of metals (EPA 1993, 1985, and 1984) were found to poorly represent data from rivers in Washington. The EPA models were found to under-estimate the dissolved fraction for Cd, Cu, and Zn, and over-estimate the dissolved fraction for Pb. Under-estimation of the dissolved fraction of metals could lead to exceedence of the water quality criteria in NPDES permitting. These results indicate that the EPA models should not be used to estimate fractions of dissolved metals in Washington's rivers. The poor performance of the EPA models for Cd, Cu, Pb, and Zn also suggests that the EPA models for other metals should not be used.

- Sufficient data are available from rivers in Washington to develop empirical models for prediction of dissolved fractions of Cd, Cu, Pb, and Zn. Empirical models from data in Washington may be used to predict dissolved fractions for use in NPDES permitting when site-specific metals data are not available. The proposed models should be considered an interim measure until site-specific data are available.

- Dissolved fractions of Cu and Zn were found to be significantly correlated with total suspended solids. Regression equations were developed to allow prediction of dissolved fractions of Cu and Zn from total suspended solids with a margin of safety to account for data variability.

- Dissolved fractions of Cd and Pb were found to be poorly correlated with other water quality variables. Estimated 90th and 95th percentiles of available state-wide data were proposed for use in NPDES permitting in the absence of site-specific data.

- Data from future studies by Ecology's Ambient Monitoring Program or other Ecology investigations may be useful for developing empirical models for other metals or refining the models for the present metals. Dissolved and total recoverable measurements are necessary if the data are to be used for developing or refining the regression models. In addition, future low-level metals studies by Ecology should generally include measurement of total suspended solids for possible use in regression analysis.

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Appendix A. Low-level metals database from rivers in Washington

Appendix A. Low-level metals database from rivers in Washington.

Ecology Investigator	Waterbody	Investigator's Station Code	Date	Temperature (deg C)	pH	Specific Conductance (uS @ 25C)	Alkalinity (mg. es CaCO3)	Total Hardness (mg. es CaCO3)	Total Suspended Solids (mg/L)	Total Organic Carbon (mg/L)	Total Recoverable Cd (ug/L)	Total Cd (ug/L)	Dissolved Cd (ug/L)	Total Recoverable Cu (ug/L)	Total Cu (ug/L)	Dissolved Cu (ug/L)	Total Recoverable Pb (ug/L)	Total Pb (ug/L)	Dissolved Pb (ug/L)	Total Recoverable Zn (ug/L)	Total Zn (ug/L)	Dissolved Zn (ug/L)
Peleier	Spokane R	RM96.0	28-Jul-92	23.9	9.1	57	21	26	1.8	1.8		0.108	0.081		0.730	0.844		0.908	0.251		41.7	19.3
Peleier	Spokane R	RM96.0	24-Sep-92	16.0	8.0	58	21	25	1.5	1.5		0.208	0.226		1.12	1.02		1.17	0.189 B		96.2	125
Peleier	Spokane R	RM96.0	25-Nov-92	6.5	8.5	57	22	23	0.5	1.3		0.252	0.235		0.769	0.878		0.694	0.219 B		139	125
Peleier	Spokane R	RM96.0	27-Jan-93	2.3	8.0	61	22	23	3.0	1.9		0.283	0.346		0.658	0.805		0.749	0.285 B		157	139
Peleier	Spokane R	RM96.0	31-Mar-93	3.1	7.6	61	23	26	2.0	2.5		0.469	0.261		0.94	0.515 B		2.65	0.724 B		123	106
Peleier	Spokane R	RM96.0	25-May-93	14.0	8.4	48	20	19	0.5	2.7		0.347	0.163		0.715	1.09 B		4.42	0.184 B		70.9	70.9
Peleier	Spokane R	RM96.0	11-Aug-93	22.9	8.5	51	20	21	2.0	1.8		0.206	0.168		1.3	0.585		0.719	0.19 B		77	57.3
Peleier	Spokane R	RM96.0	8-Sep-93	21.2	8.3	54	23	23	0.5	1.3		0.282	0.063		0.71	0.782		1.34	0.035		71.8	55.8
Peleier	Spokane R	RM96.3	28-Jul-92	18.5	8.3	156	69	78	0.5	1.3		0.091			2.04			0.628			43.3	22.7
Peleier	Spokane R	RM96.3	24-Sep-92	14.9	8.3	89	37	31	0.5	1.4		0.204	0.194		1.3	1.73		1.06	0.153 B		113	135 B
Peleier	Spokane R	RM96.3	25-Nov-92	6.1	7.9	75	30	31	0.5	1.2		0.241	0.265		0.909	0.794		0.786	0.209 B		135	163 B
Peleier	Spokane R	RM96.3	27-Jan-93	3.0	7.3	89	36	38	4.0	1.2		0.301	0.099		0.744	0.71		0.664	0.23 B		138	107 B
Peleier	Spokane R	RM96.3	31-Mar-93	3.2	7.8	61	23	25	1.0	1.7		0.464	0.271		0.82	0.49		2.7	0.788 B		115	69.3
Peleier	Spokane R	RM96.3	11-Aug-93	20.0	7.8	51	30	44	2.0	2.1		0.326	0.135		0.67	0.53		4.3	0.148 B		68.5 B	55.5
Peleier	Spokane R	RM96.3	8-Sep-93	14.0	8.4	94	48	52	2.0	1.5		0.19	0.134		0.61	0.184		0.624	0.163		77	69.8
Peleier	Spokane R	RM63.5-64.5	8-Aug-93	17.7	8.4	113	83	92	2.0	1.6		0.194	0.058		1.09			0.78			40.9	20.2
Peleier	Spokane R	RM63.5-64.5	28-Jul-92	19.1	8.4	204	55	92	2.0	1.4		0.098	0.118		1.25	0.974		0.898	0.173 B		51.6	80.6
Peleier	Spokane R	RM63.5-64.5	24-Sep-92	14.7	7.6	126	50	54	1.0	1.3		0.137	0.048		1.05			1.5			105	48.6
Peleier	Spokane R	RM63.5-64.5	25-Nov-92	6.3	7.9	140	52	57	36.0	2.3		0.203	0.251		3.33	0.86		1.03	0.24 B		91.1	94.3
Peleier	Spokane R	RM63.5-64.5	27-Jan-93	3.4	7.9	70	26	29	1.0	1.8		0.133	0.233		1.23	0.48		2.25	0.788 B		179	61.6 B
Peleier	Spokane R	RM63.5-64.5	15-May-93	14.4	7.9	64	65	72	4.0	2.0		0.344	0.095		0.67	1.18		3.2	0.141 B		73.9	64.5
Peleier	Spokane R	RM63.5-64.5	8-Sep-93	18.4	7.3	162	65	72	1.0	2.2		0.127	0.091		1.28	0.61		5.38	0.2 B		77	45.8
Peleier	Spokane R	RM63.5-64.5	5-Sep-93	16.2	8.5	193	80	87	2.0	1.8		0.164	0.008		0.74	0.331		0.624	0.035		55.8 B	0.882
JohnsonHopkins	Green R Auburn	09A150	28-Jul-92	15.8	7.2	58	25	24	3.0	0.5	J	0.007	0.008 J	J	0.362		J	0.035	J	0.784	0.882
JohnsonHopkins	Green R Auburn	09A150	24-Sep-92	14.4	7.2	57	26	29	5.0	1.6	B	0.005	0.005 B	B	0.464 B	0.766	B	0.133	0.0615 B	B	0.98 B	1.31 B
JohnsonHopkins	Green R Auburn	09A150	25-Nov-92	6.0	6.9	40	16	15	9.0	1.6	B	0.007	0.005 B		0.863	0.441	B	0.1425	0.0805 B	B	1.725	1.265 B
JohnsonHopkins	Green R Auburn	09A150	27-Jan-93	3.0	7.2	35	13	22	200.0	5.7	B	0.0525	0.006 B		14	0.23	B	1.91	0.04 B	B	8.22 B	1.51
JohnsonHopkins	Green R Auburn	09A150	31-Mar-93	5.9	7.2	68	17	15	1.0	1.2	B	0.006	0.003 B		0.285	0.295	B	0.065	0.04 B	B	1.76	0.675 J
JohnsonHopkins	Green R Auburn	09A150	25-May-93	11.7	7.2	41	18	15	2.0	1.2	J	0.0035	0.0025 J	J	0.44	0.62	J	0.0695	0.085 J	J	0.545	1.18 J
JohnsonHopkins	Green R Tukwila	09A080	28-Jul-92	21.0	7.5	155	54	54	2.0	1.5	J	0.012	0.011 J		0.772			0.175	0.035 J		1.37	
JohnsonHopkins	Green R Tukwila	09A080	24-Sep-92	17.0	6.9	137	49	45	123.0	1.5	B	0.011	0.0085 B		0.928	1.12	B	0.284	0.115 B	B	2.03	2.34
JohnsonHopkins	Green R Tukwila	09A080	25-Nov-92	6.1	7.1	60	21	36	13.0	2.5	B	0.0225	0.019 B		2.16	1.93	B	0.508	0.292 B	B	9.12 B	6.02 B
JohnsonHopkins	Green R Tukwila	09A080	27-Jan-93	7.0	7.1	100	32	24	24.0	3.3	B	0.038	0.108 B		3.61	0.598	B	1.81	0.108 B	B	2.87	5.01
JohnsonHopkins	Green R Tukwila	09A080	31-Mar-93	7.6	6.8	67	25	24	12.0	2.7	B	0.009	0.004 B		1.04	0.513	B	0.285	0.0695 J	B	1.91	1.51 J
JohnsonHopkins	Green R Tukwila	09A080	25-May-93	15.5	6.8	192	35	34	8.0	2.1	B	0.005	0.004 J		1.27	0.956	J	0.208	0.116 J	J	25.3	0.588 J
JohnsonHopkins	Puyallup R	10A070	28-Jul-92	16.1	7.5	131	21	50	457.0	0.5		0.038	0.039		30.2			2.51			43.5	1.37 J
JohnsonHopkins	Puyallup R	10A070	24-Sep-92	13.1	7.5	67	20	47	11.0	0.9		0.048	0.022		41.4	1.81		3.23	0.159 B		7.57 B	1.42 B
JohnsonHopkins	Puyallup R	10A070	25-Nov-92	5.3	6.9	61	18	24	78.0	3.8	B	0.0185	0.0145 B		4.94	2.11	B	0.597	0.116 B	B	41.6 B	2.81 B
JohnsonHopkins	Puyallup R	10A070	27-Jan-93	3.5	7.1	54	18	24	11.0	9.1	J	0.0055	0.006 J		43	1.23		4.45	0.11 J	B	8.22	1.33 J
JohnsonHopkins	Puyallup R	10A070	31-Mar-93	11.9	7.1	68	20	22	32.0	2.6	J	0.006	0.003 J		1.16	1.22	J	0.195	0.288 B	B	1.81	0.8 J
JohnsonHopkins	Puyallup R	10A070	25-May-93	13.0	7.1	54	20	22	32.0	2.9		0.008	0.007		2.21			0.266	0.035		4.02	1.18
Hopkins	Yakima R		28-Jul-92	19.4	8.5	279	117	123	29.0	2.5		0.018	0.014		2.02			0.663	0.043		2.2 B	
Hopkins	Yakima R		24-Sep-92	24.7	8.1	308	130	123	12.0	2.0		0.012	0.012		1.01			0.446	0.04		172	
Hopkins	Yakima R		27-Jan-93	5.7	8.1	283	120	119	6.0	4.4		0.01	0.012		2.19	0.89		0.654	0.104		3.74 B	1.38 B
Hopkins	Yakima R		31-Mar-93	10.5	6.8	319	130	75	68.0	2.1		0.045	0.004		2.92	0.75		1.02	0.09 B		5.66 B	1.99 B
Hopkins	Yakima R		25-May-93	18.9	7.3	187	78	76	32.0	2.9		0.022	0.014		2.04	0.64		0.628	0.053		1.34	0.34 J
JohnsonHopkins	Snohomish R	07A090	25-May-93		8.1	194	78	93	8.0	3.7		0.024	0.014		2.87			0.388	0.398		3.45	
Hopkins	Snohomish R	07A090	24-Sep-92		8.3	55	24	43	6.0	1.0		0.022	0.02		0.79	0.744		0.133	0.171		3.82 B	1.63 B
Hopkins	Snohomish R	07A090	27-Jan-93		7.4	44	14	17	18.0	2.1		0.0055	0.009		1.12	0.69		0.133	0.05 B		2.72	1.54 B
Hopkins	Snohomish R	07A090	31-Mar-93		7.4	54	15	13	8.0	2.1		0.018	0.005		2.21	1.23		0.19 B	0.288 B		1.81	0.8 B
Hopkins	Snohomish R	07A090	25-May-93		8.1	142	12	42	10.0	1.6		0.014	0.007		1.45	1.22		0.213	0.035		1.68	1.18 B
JohnsonHopkins	Columbia R	Warrendale	9-Jan-90	5.8	8.3	156		70	14.0	1.2		0.03	0.014	D	1.8	1 D		0.33	0.04		0.33 U	0.33 U
JohnsonHopkins	Columbia R	Warrendale	07-Sep-90	14.0	8.1	131		56	4.7	1.2		0.044	0.012	D	1.2	1 D		0.35	0.049		1.4	0.26
JohnsonHopkins	Columbia R	Warrendale	25-Sep-90	20.0	8.1	159		64	5.0	1.3		0.025	0.012	D	1.3	1 D		0.18	0.015		1.1	0.2
Ericson	Gibbons Cr	RC1	07-Sep-94	20.0	7.3	130	49	48	4.0	1.2	D		0.08	D		0.495	U	0.18	0.02	U		1.2
Ericson	Gibbons Cr	RC1	14-Sep-94	20.1	7.2	130	49	49	3.0	1.3	D		0.08	D 0.793		0.533	U	0.18	0.02	U	3.9 B	1.1
Ericson	Gibbons Cr	RC1-dup	14-Sep-94	8.2	7.1	109	43	43	17.0	6.7	P 0.12 P		0.08	P 0.932		3.28	U	1.09	0.034	U	4.5 B	17.5
Ericson	Gibbons Cr	RC1	29-Nov-94	8.2	8.2	111	45	45	20.0	6.7	0.11 P		0.08	5.7 P		3.2	U	1.16	0.034		27.4	16.6
Ericson	Gibbons Cr	RC1-dup	30-Jan-95	9.5	7.6	112	45	45	6.0	4.0	0.2		0.06	5.88		3.35	U	0.53	0.065	U	28.9	17.1
Ericson	Gibbons Cr	RC1-dup	07-Sep-94	16.1	7.1	180	76	41	6.0	3.9	0.11 P		0.08	4.4		3.69	U	0.36	0.02	U	21	0.4
Ericson	Gibbons Cr	RC2	30-Jan-95	7.0	8.3	118	47	76	3.0	8.0	0.2		0.08	1.24		0.577	U	1.02	0.02	U	8.82	1.9
Ericson	Gibbons Cr	RC2	29-Nov-94	9.0	7.5	128	25	47	3.0	6.0	0.11 P		0.06	3.23		2.13	U	0.3	0.02	U	12.6	4.9
Ericson	Gibbons Cr	RC2	29-Nov-94	20.3	7.4	270	68	93	8.0	6.0	0.2		0.08	1.24		0.35	U	0.33	0.06	U	8.2	1.3
Ericson	Gibbons Cr	RC3	07-Sep-94	6.4	7.9	128	77	44	13.0	7.7	0.2		0.073	1.04		0.388	P 2.7 P	0.33	0.06	P	3.3 B	4.9
Ericson	Gibbons Cr	RC3	30-Nov-94	9.8	7.9	107	44	44	13.0	5.8	0.2		0.08	2.29		1.24		0.65	0.038		11	1.8
Ericson	Gibbons Cr	RC4	07-Sep-94	21.9	7.4	147	24	44	9.0	6.9	0.22 P		0.08	1.9		1.27	U	0.45	0.06	U	24.4	4.9
Ericson	Gibbons Cr	RC4	29-Nov-94	7.2	7.6	103	15	41	18.0	1.5	0.11 P		0.06	1.1 P		0.607	P 1 P	0.65	0.063		3.3 B	1.8 U
Ericson	Gibbons Cr	RC4	30-Jan-95	9.8	7.8	112	12	42	7.0	5.9	0.1 P		0.06	1.1 P		1.42	P 1 P	0.2	0.078		3.9	1.1
Cusimano	Snohomish R	SNO20-388090	14-Sep-93	15.6	7.5	300			13.0	1.4	D 0.1 U		0.1 U	D 1.1 U		1 U	U	0.1 U	U	5.5	1.1 U
Cusimano	Snohomish R	SNO20-388081	14-Sep-93	16.0	8.5	2600			15.0	1.5	D 0.11 U		0.1 U	D 1.2 U		1 U	U	0.11 U	U		1.1 U
Cusimano	Snohomish R	SNO20-388082	14-Sep-93						11.0	1.1	D 0.11 U		0.1 U	D 1.2 U		1 U	U	0.11 U	U		
Cusimano	Snohomish R	STM31-388083	14-Sep-93	16.9	7.5	5300			21.0	0.5	D 0.11 U		0.1 U	D 1.5 U		1 U	U	0.11 U	U		
Cusimano	Snohomish R	STM31-388084	14-Sep-93	16.5	7.5	18200			11.0	1.6	D 0.11 U		0.1 U	D 1.2 U		1 U	U	0.11 U	U		
Cusimano	Snohomish R	EBE23-388085	14-Sep-93	16.0	7.8	147			13.0	1.3	D 0.11 U		0.1 U	D 1.1 U		1 U	U	0.11 U	U		
Cusimano	Snohomish R	EBE23-388086	14-Sep-93						9.0		P 0.11 P		0.1	P 1.5 P		1 P	P	0.21 P	P		
Cusimano	Snohomish R	EBE23-388087	14-Sep-93	16.5	7.7	50	23		29.0	1.2	U 0.11 U		0.1 U	U 1.1 U		1 U	U	0.11 U	U		1.2
Cusimano	Snohomish R	EBE23-388088	14-Sep-93	13.0	7.7	140	27		9.0	1.3	U 0.11 U		0.1 U	U 1.1 U		1 U	U	0.11 U	U		1.1
Cusimano	Snohomish R	EBE23-388089	14-Sep-93	14.0	7.4	160			8.0	1.3	U 0.11 U		0.1 U	U 1.1 U		1 U	U	0.11 U	U		1
Cusimano	Snohomish R	SNO16-388090	24-May-94	14.0	7.4	120			12.0	1.3	P 0.12 P		0.1	P 2.1		1.4 P	P	0.11 P			4.9
Cusimano	Snohomish R	SNO16-388091	24-May-94	13.5	7.4	850			7.0	1.3	U 0.11 U		0.1 U	U 1.1 U		1 U	U	0.11 U	U		1.8
Cusimano	Snohomish R	STM31-218108	24-May-94	13.5	7.4	30			5.0	1.1	U 0.11 U		0.1 U	U 1 U		1 U	U	0.11 U	U		1 U
Cusimano	Snohomish R	STM31-218110	24-May-94			30			6.0	1.1	P 0.1 P		0.1	P 1.5 P		1.9 P	P	0.21 P			
Cusimano	Snohomish R	EBE23-218112	24-May-94	14.5	7.8	90	13		6.0	1.2	U 0.1 U		0.1 U	U 1 U		1 U	U	0.1 U	U		1.1
Cusimano	Snohomish R	EBE23-218113	24-May-94	13.0	7.5	28	13		5.0	1.3	U 0.1 U		0.1 U	U 1 U		1 U	U	0.1 U	U		1.1
Cusimano	Snohomish R	SNO16-218114	24-May-94	14.0	7.7	40	13		4.0	1.2	U 0.1 U		0.1 U	U 1 U		1 U	U	0.1 U	U		1 U
Cusimano	Snohomish R	SNO14-218115	24-May-94	14.0	7.5	25	13		4.0	1.1	U 0.1 U		0.1 U	U 1 U		1 U	U	0.1 U	U		1
Cusimano	Snohomish R	SNO14-218116	24-May-94	13.0	7.5	45	12		5.0	1.1	U 0.1 U		0.1 U	U 1 U		1 U	U	0.1 U	U		1 U
Cusimano	Snohomish R	SNO14-218117	24-May-94	14.0	7.5	40			4.0	1.1	U 0.1 U		0.1 U	U 1 U		1 U	U	0.1 U	U		1 U
Cusimano	Snohomish R	SNO14-218118	24-May-94								U 0.1 U		0.1 U	U 1 U		1 U	U	0.1 U	U		

Metals data qualifiers: U=not detected at or above reported result; P=detected but below quantitation limit; J=estimated value; B=possible blank contamination; UJ=not detected at or above reported estimate

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