## **Quality Assurance Project Plan**

## Receiving Water Study for Puget Sound Boatyards: Metals Translators and Hardness

by Art Johnson

Environmental Assessment Program Washington State Department of Ecology Olympia, Washington 98504-7710

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Waterbody Numbers:

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- o Fidalgo Bay/Guemes Channel WA-03-0020
- o Lake Union/Seattle Ship Canal WA-08-9340
- o Commencement Bay (Outer) WA-10-0010

For more information contact: Carol Norsen Environmental Assessment Program P.O. Box 47600 Olympia, WA 98504-7600 E-mail: CNOR461@ecy.wa.gov Phone: 360-407-7486

Washington State Department of Ecology - www.ecy.wa.gov/

- o Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Yakima 509-575-2490
   Eastern Regional Office, Snakana 500-220-2400
- oEastern Regional Office, Spokane509-329-3400

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#### **Quality Assurance Project Plan**

#### Receiving Water Study for Puget Sound Boatyards: Metals Translators and Hardness

September 2008

#### Approved by:

Signature:	Date: August 2008
Gary Bailey, Client, Water Quality Program	
Signature:	Date: August 2008
Bill Moore, Section Manager, Water Quality Program	
Signature:	Date: August 2008
Art Johnson, Principal Investigator, EAP	
Signature:	Date: August 2008
Michael Friese, EIM Data Engineer, EAP	
Signature:	Date: August 2008
Dale Norton, Supervisor, Toxics Studies Unit, EAP	
Signature:	Date: August 2008
Will Kendra, Manager, Statewide Coordination Section, EAP	
Signature:	Date: August 2008
Bob Cusimano, Manager, Western Operations Section, EAP	
Signature:	Date: August 2008
Stuart Magoon, Director, Manchester Environmental Laboratory, EAP	
Signature:	Date: September 2008
Bill Kammin, Ecology Quality Assurance Officer	

Signatures are not available on the Internet version EAP - Environmental Assessment Program EIM - Environmental Information Management system

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#### Abstract

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After study completion, a final report describing the results will be posted to the Internet.

A Boatyard Receiving Water Study is being conducted to verify assumptions on metals translators and hardness used in the Boatyard General Permit issue by Ecology in November 2005. The study is required by decision of the Pollution Control Hearing Board.

The Boatyard General Permit includes numeric benchmarks for copper that apply to stormwater runoff from boatyards. The permit used several assumptions in setting water quality criteria for freshwater (hardness assumption), estimating the fraction of dissolved metals in the receiving water (metals translators), and accounting for potential effects the receiving water may have on metals toxicity (water effects ratio). The permit used copper as an indicator parameter for lead and zinc, also associated with boatyard runoff.

The Boatyard Receiving Water Study will collect samples in three marine and two freshwater areas of Puget Sound in September 2008, January 2009, and May 2009. The samples will be analyzed for total recoverable and dissolved copper, lead, and zinc; and hardness (freshwater). Because the permit to be reissued in August of 2008 will not use water effects ratios, these will not be determined in the study.

## Background

The Washington State Department of Ecology (Ecology) reissued the third Boatyard General Permit on November 2, 2005 (<u>www.ecy.wa.gov/programs/wq/permits/boatyard/index.html</u>). The permit includes numeric benchmarks for copper that apply to stormwater runoff. The primary source of copper from boatyards is antifouling paints which discourage marine growth on boat hulls. The permit uses copper as an indicator parameter for lead and zinc, also associated with boatyard runoff.

The Northwest Marine Trade Association (NMTA) and the Puget Soundkeeper Alliance (PSA) appealed the permit. While under appeal, the permit was modified (May 2006) to correct a mistake in the lake discharge benchmark. The Pollution Control Hearings Board (PCHB) heard the appeal in July 2006 and issued a decision on January 26, 2007. The PCHB concluded that some of the assumptions used in the permit calculations were potentially flawed (www.ecy.wa.gov/programs/wq/permits/boatyard/index.html). The assumptions in question were for dissolved metals translators, hardness, and water effects ratios:

- **Metals Translators**: The aquatic life criteria for metals in freshwater and saltwater apply to the dissolved fraction. However, by federal regulation, effluent limits must be expressed as total recoverable. A "translator" therefore must be used to convert dissolved metals criteria into an effluent limitation (EPA, 1996a). Because Ecology had no boatyard data, a copper translator of 30% was used in the Boatyard General Permit, derived from data on shipyard discharges.
- **Hardness**: The aquatic life criteria for copper, lead, and zinc in freshwater vary with hardness. The permit assumed a hardness of 25 mg/L. Ecology considered this value typical of western Washington waterbodies where boatyards are located on freshwater.
- Water Effects Ratios: The aquatic life criteria for copper, lead, and zinc are based on bioassays (standard biological tests) using laboratory water. The difference between a metal's bioavailability and effective toxicity in laboratory water compared to a receiving water can be accounted for using a Water Effects Ratio (WER; EPA, 1992). The WER is the LC-50 (lethal concentration for 50% of test organisms) in the receiving water compared to the LC-50 in laboratory water. The Boatyard General Permit used a copper WER of 1.43 for marine waters and 2.5 for freshwater, based on studies not specific to Puget Sound boatyards.

The NMTA and the PSA appealed the decision of the PCHB to the Washington State Superior Court in February 2007. The NMTA, PSA, and Ecology reached a settlement in the appeal in July 2007 (www.ecy.wa.gov/programs/wq/permits/boatyard/settlement.pdf).

The PCHB decision on the Boatyard General Permit appeal required Ecology or the boatyards to collect receiving water data to verify the assumptions used in formulating the copper benchmark. The receiving water data were to be used for reissuance of the permit.

The permit used literature values for copper water effect ratios to derive benchmarks for copper. However, the permit to be reissued in August of 2008 will contain technology-based benchmarks and limits for copper and zinc. Lead concentrations in boatyard stormwater are being monitored and have been shown to be at or near detection levels when copper and zinc benchmarks/limits are being met.

The proposed technology-based limits for metals will be compared to area-wide receiving water parameters of hardness (freshwater), ratios of dissolved/total recoverable, and background concentrations to determine if the limits comply with Washington State water quality standards. Water effects ratios will not be utilized in this comparison.

## **Project Description**

The objective of the Boatyard Receiving Water Study will be to obtain data to verify or modify the metals translator and hardness assumptions used to develop the benchmarks in the current Boatyard General Permit (2006).

The study will be conducted at five locations in the vicinity of Puget Sound boatyards. Three marine and two freshwater areas will be sampled (Figure 1). These locations were proposed by the Northwest Marine Trade Association and the Puget Soundkeeper Alliance and agreed to by Ecology. Specific sampling sites have been selected based on their distance from local sources of contamination and should be representative of the receiving water as a whole.

Water samples will be obtained at each location and analyzed for total recoverable copper, lead, and zinc; dissolved copper, lead, and zinc; and hardness (freshwater). Salinity (marine waters) and total suspended solids will also be analyzed. The samples will be collected in September 2008, January 2009, and May 2009.

The study will be conducted by the Ecology Environmental Assessment Program. Samples will be analyzed by the Ecology Manchester Environmental Laboratory and Frontier GeoSciences, Seattle, a contract laboratory. A draft report on the results for stakeholder review is anticipated in November 2009.



Figure 1. Sampling Sites for Ecology's 2008-09 Boatyard Receiving Water Study

## **Organization and Schedule**

The following people have a major role in this project. All are employees of the Washington State Department of Ecology, except as noted.

Staff (EAP unless noted otherwise)	Title	Responsibilities
Art Johnson Toxics Studies Unit, SCS (360) 407-6766	Principal Investigator	Prepares the QAPP, oversees field sampling and transportation of samples to the laboratory, conducts QA review of data, analyzes and interprets data, and prepares the project report.
Randy Coots Toxics Studies Unit, SCS (360) 407-6690	Boat Master	Research vessel skipper.
Casey Deligeannis Toxics Studies Unit, SCS (360) 407-7395	Field Assistant	Assists with field sampling.
Michael Friese Toxics Studies Unit, SCS (360) 407-6737	Data Engineer	Enters project data in EIM.
Dale Norton Toxics Studies Unit, SCS (369) 407-6765	Unit Supervisor	Provides internal review and approval of the QAPP, budget, and project report.
Will Kendra SCS (360) 407-6698	Section Manager	Reviews the project scope and budget, tracks progress, reviews and approves the QAPP.
Gary Bailey Water Quality Program (360) 407-6433	Client	Defines scope of the project, provides reviews, and approves the QAPP and project report.
Stuart Magoon MEL (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin (360) 407-6964	Ecology Quality Assurance Officer	Reviews and approves the QAPP.
Dean Momohara MEL (360) 871-8808	Inorganics Unit Supervisor	Oversees chemical analysis of project samples.
Cindy Moulder Frontier GeoSciences Seattle, WA (206) 957-1407	Project Manager	Project manager for seawater metals analyses.
Karin Feddersen MEL (360) 871-8801	Chemist	Contracts for sample analysis by Frontier GeoSciences and provides QA review of their data.

Table 1. Organization and Responsibilities of Project Staff.

EAP – Environmental Assessment Program SCS – Statewide Coordination Section QAPP – Quality Assurance Project Plan MEL – Manchester Environmental Laboratory

EIM – Environmental Information Management system

Table 2. Proposed Schedule for Field Work, Laboratory Analysis, EIM Data Entry, and Reports.

Field and laboratory work				
Field work completed	September 2008, January 2009, May 2009			
Laboratory analyses completed	July 2009			
Environmental Information System (EIM) system				
EIM data engineer	Michael Friese			
EIM user study ID	AJOH0057			
EIM study name	Puget Sound Boatyard Receiving Water			
Data due in EIM	December 2009			
Final report				
Author lead	Art Johnson			
Schedule				
Draft due to supervisor	September 2009			
Draft due to client/peer review	October 2009			
Draft due for stakeholder review	November 2009			
Final report due on web	December 2009			

## **Quality Objectives**

Quality objectives for this project are to obtain data of sufficient quality so that uncertainties are minimized and accurate and representative results are obtained for the parameters of interest. These objectives will be achieved through careful attention to the sampling, measurement, and quality control (QC) procedures described in this plan.

#### **Measurement Quality Objectives**

Manchester Laboratory and Frontier GeoSciences are expected to meet all QC requirements of the analytical methods being used for this project.

Measurement quality objectives (MQOs) for the analyses being conducted are shown in Table 3. The recovery and relative percent difference (RPD) objectives are the acceptance limits of the analytical methods. The lowest concentrations of interest indicated for copper, lead, and zinc are the background levels anticipated for seawater and freshwater in the areas being sampled (Crecelius, 1998; Johnson, 1994).

Analysis	Check Stds./ LCS/ CRM (% recov.)	Duplicate Samples (RPD)	Matrix Spikes (% recov.)	Matrix Spike Duplicates (RPD)	Lowest Concentration of Interest
Seawater					
Copper	75-125%	20%	70-130%	20%	0.4 ug/L
Lead	80-120%	20%	75-125%	20%	0.01 ug/L
Zinc	75-125%	20%	65-135%	20%	0.3 ug/L
Freshwater					
Copper	85-115%	20%	75-125%	20%	0.3 ug/L
Lead	85-115%	20%	75-125%	20%	0.04 ug/L
Zinc	85-115%	20%	75-125%	20%	1.0 ug/L
Hardness	80-120%	20%	75-125%	20%	1 mg/L
Salinity	80-120%	20%	NA	NA	0.1 g/Kg
TSS	80-120%	20%	NA	NA	1 mg/L

Table 3. Measurement Quality Objectives for Boatyard Receiving Water Study: Chemistry.

LCS = laboratory control sample

CRM = certified reference material RPD = relative percent difference NA = not applicable

TSS = total suspended solids

ug/L = parts per billion

mg/L = parts per million

g/Kg = parts per thousand

#### **Representativeness, Comparability, and Completeness**

The intent of the sampling design for this project is to obtain representative data on metals concentrations and hardness in the waterbodies of interest. Steps being taken to ensure representativeness include sampling at three different time periods, use of appropriate sampling and sample handling procedures, and use of replicate samples.

The field and laboratory methods being used are standardized and comparable to similar studies in Puget Sound and elsewhere. Accredited laboratories will analyze the samples.

The completeness goal for this project is to have valid, defensible data for 100% of the samples collected.

## Sampling Design

Table 4 has descriptions of the five sampling sites for the Boatyard Receiving Water Study. Their locations are shown in Figures 2-5. As previously mentioned, these waterbodies were agreed to by the Northwest Marine Trade Association, the Puget Soundkeeper Alliance, and Ecology. Specific sampling sites within these waterbodies were selected so as to be away from local sources of contamination and representative of the receiving water as a whole.

Waterbody	Location of Sampling Site	Approx. Depth (ft.)	Figure No.	Comment
Strait of Juan de Fuca	Five miles north of Dungeness Spit light	380	2	True marine water
Guemes Channel/ Fidalgo Bay	1/2 mile east of Cap Sante	90	3	Sheltered marine water without river influence
Seattle Ship Canal	East entrance to Salmon Bay	30	4	Freshwater
Lake Union	Center of south basin	60	4	Freshwater
Commencement Bay	1.5 miles south of Browns Point light	390	5	Sheltered marine water with river influence

Table 4. Description of Sampling Sites for Boatyard Receiving Water Study (surface water samples).

Surface water samples will be collected at each site once each month during September 2008, January 2009, and May 2009. These dates span the period when stormwater runoff primarily occurs and include active times for the boatyards. The sampling periods have been agreed to by the parties to the Pollution Control Hearings Board settlement.

Two samples will be collected each month at each location and analyzed for dissolved copper, lead, and zinc; total recoverable copper, lead, and zinc; hardness (freshwater); salinity (marine water); and total suspended solids. The samples are being collected in replicate to enhance the representativeness of the data. The replicates will be collected approximately 30 minutes apart.

Clean sampling techniques will be used. The dissolved metals samples will be filtered (0.4 micron) in the field immediately on collection and acidified at the analyzing laboratory. Low-level analytical methods will be used to ensure that copper, lead, and zinc concentrations are consistently quantified in both the total and dissolved samples.

All samples will be taken at a depth of approximately one meter. Surface samples are appropriate for boatyards as they discharge at or near the surface. The samples will be collected with a pumping system to avoid including the surface microlayer, where toxic contaminants can concentrate. An aluminum hull boat, not painted with antifouling, will be used as the sampling platform. The marine samples will be collected during an incoming tide.

Table 5 summarizes the sampling design. If results show a low station-to-station variation, the number of samples being collected may be reduced as the study progresses, as a cost saving measure.

Analysis	No. of Sites	Sampling Dates	Samples per Site Each Month	Sample Subtotals	Field Blanks	Lab Splits	Total Samples
Seawater							
Diss. Cu, Pb, Zn	3	Sept Jan May	2	18	3	3	24
Tot. Rec. Cu, Pb, Zn	3	Sept Jan May	2	18	3	3	24
Freshwater							
Diss. Cu, Zn, Pb	2	Sept Jan May	2	12	0	3	15
Tot. Rec. Cu, Zn, Pb	2	Sept Jan May	2	12	3	3	18
Hardness (freshwater sites)	2	Sept Jan May	2	12	NA	3	15
Total Suspended Solids	5	Sept Jan May	2	30	NA	3	33
Salinity (marine sites)	3	Sept Jan May	2	18	NA	3	21

Table 5. Summary of Sampling Design for Boatyard Receiving Water Study

Diss. = Dissolved Tot. Rec. = Total recoverable NA = Not analyzed



Figure 2. Sampling Site in Strait of Juan de Fuca off Port Angeles.



Figure 3. Sampling Site in Guemes Channel/Fidalgo Bay, Anacortes.



Figure 4. Sampling Sites in Seattle Ship Canal and Lake Union, Seattle.



Figure 5. Sampling Site in Commencement Bay, Tacoma.

## **Sampling Procedures**

Sample containers, preservation, and handling for this project are shown in Table 6.

Parameter	Minimum Sample Size	Container	Preservation	Holding Time
Total Recov. Cu, Pb, Zn	200 mL	250/500 mL HPDE or Teflon	HNO <sub>3</sub> to pH<2, $4^{\circ}C^{*}$	6 months
Dissolved Cu, Pb, Zn	200 mL	250/500 mL HPDE or Teflon	Filter, HNO <sub>3</sub> to pH<2, 4°C*	6 months
Hardness	100 mL	125 mL poly bottle	HNO <sub>3</sub> to pH<2, $4^{\circ}C$	6 months
Salinity	300 mL	500 mL poly bottle	Cool to 4°C	28 days
Total Suspended Solids	1000 mL	1000 mL poly bottle	Cool to 4°C	7 days

 Table 6. Field Procedures for Boatyard Receiving Water Study

\*Filtered within 15 minutes of collection (Federal Register / Vol. 72, No. 57 / March 26, 2007)

Sample collection and handling will follow EPA Method 1669 *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (EPA, 1996b). The water column samples will be collected with a pumping system employing a Masterflex variable speed peristaltic pump head and drive. A short length of C-Flex tubing will be used in the pump head; the remainder of the tubing will be Teflon. Filters for dissolved metals will be in-line, Gelman Aqua Prep 250 Capsule, 0.4 micron, or equivalent. The first few mils of filtrate will be discarded. The metals samples will be acidified at the analyzing laboratory to avoid introducing contamination in the field and for reasons of health and safety.

The tubing, filters, and seawater metals bottles will be acid-cleaned at Frontier GeoSciences and sealed in plastic bags. Frontier will be analyzing the seawater samples for this project. Sample bottles for freshwater metals (acid-cleaned) and other parameters will be obtained through Manchester Laboratory where these samples are being analyzed.

New filters will be used for each dissolved metals sample. A separate length of tubing will be used for seawater sites and freshwater sites. To reduce the potential for cross-contamination, the sites known or assumed to be the cleanest will be sampled first (e.g., Strait of Juan de Fuca sampled before Commencement Bay). The tubing will be cleaned between sites by pumping one liter of deionized water acidified with high-purity nitric acid, followed by deionized water. This water will be provided by Frontier GeoSciences. The metals bottles will be filled inside a glove box made of PVC tubing and polyethylene sheeting. Non-talc gloves will be worn by sampling personnel.

All containers will be rinsed with a small amount of sample water before filling, except for hardness bottles which contain acid preservative.

Field data and observations will be recorded in a bound notebook of waterproof paper. Sampling stations will be located by a Global Positioning System and visual fixes. An aluminum hull sampling vessel will be used; the hull does not have antifouling paint.

All samples will be labeled with the site name, date, and a unique sample number, placed in plastic bags, and stored on ice for transport. The field team will transport the seawater metals samples to Frontier GeoSciences at the end of each of the three sampling periods. The remaining samples will be returned to Ecology headquarters and transported by courier to Manchester Laboratory. Chain-of-custody will be maintained throughout.

### **Measurement Procedures**

The analytical methods to be used for this project are shown in Table 7.

Analysis	Number of Samples	Expected Range of Results	Reporting Limit	Sample Preparation Method	Analytical Method	Lab
Seawater						
Diss. Cu	21	0.1 - 2 ug/L	0.05 ug/L	RP	ICP/MS FGS-109/054	FGS
Diss. Pb	21	0.01 - 0.1 ug/L	0.01 ug/L	APDC/RP	ICP/MS FGS-032/054	"
Diss. Zn	21	0.2 - 5 ug/L	0.08 ug/L	RP	ICP/MS FGS-109/054	"
Tot. Rec. Cu	21	0.2 - 5 ug/L	0.05 ug/L	RP	ICP/MS FGS-109/054	"
Tot. Rec. Pb	21	0.02 - 0.2 ug/L	0.01 ug/L	APDC/RP	ICP/MS FGS-032/054	"
Tot. Rec. Zn	21	0.4 - 10 ug/L	0.08 ug/L	RP	ICP/MS FGS-109/054	"
Freshwater						
Diss. Cu	12	0.3 - 2 ug/L	0.1 ug/L	none	ICP/MS EPA 200.8	MEL
Diss. Pb	12	0.02 - 0.3 ug/L	0.02 ug/L	none	"	-
Diss. Zn	12	0.4 - 5 ug/L	1 ug/L	none	"	-
Tot. Rec. Cu	15	0.5 - 5 ug/L	0.1 ug/L	acid digest	"	=
Tot. Rec. Pb	15	0.04 - 0.5 ug/L	0.1 ug/L	acid digest	"	-
Tot. Rec. Zn	15	5 - 10 ug/L	5 ug/L	acid digest	"	
Hardness	12	10- 50 mg/L	1 mg/L		ICP EPA 200.7	=
Salinity	18	10-32 g/Kg	0.1 g/Kg		SM 2520	"
TSS	30	1 - 100 mg/L	1 mg/L		EPA 160.2	"

 Table 7. Laboratory Procedures for Boatyard Receiving Water Study

APDC = ammonium pyrrolidine dithiocarbamate

RP = reductive precipitation

ICP/MS = Inductively Coupled Plasma / Mass Spectrometry

FGS = Frontier GeoSciences

MEL = Ecology Manchester Environmental Laboratory

TSS = total suspended solids

The analytical methods selected for metals provide the lowest reporting limits currently available. These should be adequate to quantify copper, lead, and zinc concentrations in all field samples.

The seawater metals analyses will be conducted through a Manchester Laboratory contract with Frontier GeoSciences. Frontier is accredited by Ecology to conduct these analyses (<a href="http://www.ecy.wa.gov/programs/eap/lab-accreditation.html">www.ecy.wa.gov/programs/eap/lab-accreditation.html</a>) and is on the General Administration master contract.

The laboratory cost estimate for this project is as follows:

Frontier GeoSciences* =	\$22,586
Manchester <sup><math>\dagger</math></sup> =	\$4,188
Total Lab =	\$26,774

\*includes 25% Manchester surcharge for contracting and data review

<sup>†</sup> includes 50% discount for Manchester Laboratory

## **Quality Control Procedures**

#### Field

Field blanks will be analyzed for copper, lead, and zinc. These quality control samples will be used to assess contamination arising from sample preparation, containers, and handling.

Blank water will be obtained from Frontier GeoSciences. Filter blanks will be prepared by filtering blank water through the pumping system. Transfer blanks will be prepared by pumping blank water from its original container into a sample container. One filter and two transport blanks will be analyzed each month, separate transport blanks being prepared for Frontier and Manchester sample containers. The filter blank will be analyzed at Frontier.

#### Laboratory

Laboratory quality control for samples being analyzed for this project is shown in Table 8.

Analysis	Check Standards/ LCS	Certified Reference Material	Method Blanks	Analytical Duplicates	MS/MSD
Seawater metals	1/batch	1/batch	3/batch	1/batch	1/batch
Freshwater metals	1/batch	1/batch	1/batch	1/batch	1/batch
Hardness	1/batch	NA	1/batch	1/batch	NA
Salinity	1/batch	NA	1/batch	1/batch	NA
Total Suspended Solids	1/batch	NA	1/batch	1/batch	NA

 Table 8. Laboratory Quality Control Samples for Boatyard Receiving Water Study

LCS = laboratory control sample

MS/MSD = matrix spike and matrix spike duplicate

NA = Not analyzed

The certified reference materials (CRMs) for the metals analyses will be CASS-4 (seawater) and SLRS-4 (freshwater), National Research Council of Canada. Certified values are given in Table 9.

Table 9. Certified Reference Material Values (ug/L)

Metals	CASS-4	SLRS-4
Copper	$0.592\pm0.055$	$1.81\pm0.08$
Lead	$0.0098 \pm 0.0036$	$0.086\pm0.007$
Zinc	$0.381 \pm 0.057$	$0.93 \pm 0.10$

CASS-4 = Nearshore Seawater Reference Material for Trace Metals SLRS-4 = Riverine Water Reference Material for Trace Metals

#### **Data Management Procedures**

Field data and observations will be recorded in a bound notebook of waterproof paper. Field data will be transferred to Excel spreadsheets and verified for accuracy by another individual on the project team.

Manchester's data will be downloaded from their Laboratory Information Management System (LIMS) into Excel spreadsheets. The Frontier GeoSciences data will be provided to Ecology in Excel spreadsheet format.

#### **Data Verification**

Manchester Laboratory will conduct a review of all chemistry data and associated case narratives. Manchester will verify that (1) methods and protocols specified in this Quality Assurance Project Plan were followed; (2) all calibrations, checks on quality control, and intermediate calculations were performed for all samples; and (3) the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, laboratory control sample and CRM analyses, and appropriateness of data qualifiers assigned. Manchester Laboratory will prepare written data verification reports based on the results of their data review. A case summary will meet the requirements for a data verification report.

The project lead will review the laboratory data packages and data verification reports. To determine if project MQOs have been met for the chemical analyses, results for check standards/LCS, CRMs, duplicate samples, and matrix spikes will be compared to QC limits. Method and field blank results will be examined to verify there was no significant contamination of the samples. To evaluate whether the targets for reporting limits have been met, the results will be examined for non-detects and to determine if any values exceed the lowest concentration of interest.

Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis or re-sampling considered.

## **Data Quality (Usability) Assessment**

Once the data have been verified, the project lead will determine if they can be used to make the calculations, determinations, and decisions for which the project was conducted. If the MQOs have been met, the quality of the data should be useable for meeting project objectives, and report preparation will proceed.

The client has ultimate responsibility for establishing Ecology's position on the validity of the metals translators and hardness values used in the Boatyard General Permit. Therefore, data analysis for this project will be limited.

The project report will assess the quality of the data and identify any shortcomings in its usefulness. Summary statistics will be provided for the metals and hardness data. Dissolved:total recoverable ratios will be calculated for copper, lead, and zinc. The data will be compared to results of similar studies in Puget Sound and comparable waterbodies, as available.

### **Audits and Reports**

#### **Audits**

Manchester Laboratory participates in performance and system audits of their routine procedures. Results of these audits are available on request.

The seawater metals analyses are being contracted out to a laboratory accredited by Ecology. The Ecology Laboratory Accreditation Unit (LAU) evaluates a laboratory's quality system, staff, facilities and equipment, test methods, records, and reports. LAU establishes that the laboratory has the capability to provide accurate, defensible data. Results of on-site assessments and proficiency tests are available from LAU on request.

#### Reports

On or before October 2009, a draft report will be prepared for peer and client review. The draft report will include:

- Maps of the study area showing monitoring stations
- Coordinates and detailed descriptions of each station
- Descriptions of field and laboratory methods
- Discussion of data quality and the significance of any problems encountered in the analyses
- Summary tables of the chemical data
- Metals translators and hardness values determined in the study
- Comparisons with results of similar studies, as available

Based on review comments, the draft will be revised and sent out for stakeholder review. The anticipated date for the stakeholder draft is November 2009.

A final project report is anticipated in December 2009. The responsible staff member for the report is Art Johnson.

All project data will be entered into Ecology's Environmental Information Management (EIM) system on or before December 2009. The responsible staff member is Michael Friese.

#### References

Crecelius, E.A., 1998. Background Metals Concentrations in Selected Puget Sound Marine Receiving Waters. Prepared for Western States Petroleum Association by Battelle Marine Sciences Laboratory, Sequim, Washington.

EPA, 1992. Interim Guidance on Interpretation and Implementation of Aquatic Life Criteria for Metals. Office of Science and Technology, U.S. Environmental Protection Agency.

EPA, 1996a. The Metals Translator: Guidance For Calculating A Total Recoverable Permit Limit From A Dissolved Criterion. Office of Water, U.S. Environmental Protection Agency. EPA 823-B-96-007.

EPA, 1996b. Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. Office of Water, U.S. Environmental Protection Agency.

Johnson, A., 1994. Zinc, Copper, Lead, and Cadmium Concentrations in Four Washington Rivers. Washington State Department of Ecology, Olympia, WA. Publication No. 94-58. www.ecy.wa.gov/biblio/9458.html

# List of Acronyms and Abbreviations

Following is a list of acronyms and abbreviations used frequently in this report.

CRM	Certified reference material
Cu	Copper
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
LCS	Laboratory control sample
MQO	Measurement quality objectives
NMTA	Northwest Marine Trade Association
Pb	Lead
PCHB	Pollution Control Hearings Board
PSA	Puget Soundkeeper Alliance
QC	Quality control
Zn	Zinc