DEPARTMENT OF
ECOLOGY
State of Washington

# Addendum 5 to
# Quality Assurance Project Plan

# Washington State
# Surface Water Monitoring Program
# for Pesticides in Salmonid Habitat
# for Two Index Watersheds

February 2012

Publication No. 03-03-104-Addendum 5

# Publication Information

**Addendum**

This addendum is an addition to an original Quality Assurance Project Plan. The addendum is not a correction (errata) to the original plan.

This addendum is available on the Department of Ecology's website at
www.ecy.wa.gov/biblio/0303104Addendum5.html

Ecology's Activity Tracker Code for this study is 03-501.

**Original Publication**

Quality Assurance Project Plan: Washington State Surface Water Monitoring program for Pesticides in Salmonid Habitat for Two Index Watersheds

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The Quality Assurance Project Plan is available on the Department of Ecology's website at
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# DEPARTMENT OF ECOLOGY

Environmental Assessment Program

February 24, 2012

**TO:** Jim Cowles, Washington State Department of Agriculture

**THROUGH:** Dale Norton, Unit Supervisor, Environmental Assessment Program
Will Kendra, Section Manager, Environmental Assessment Program

**FROM:** Paul D. Anderson, Environmental Assessment Program

**SUBJECT**: Addendum to Quality Assurance Project Plan for Washington State Surface Water Monitoring program for Pesticides in Salmonid Habitat for Two Index Watersheds
Activity Tracker Code: 03-501
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This addendum documents several changes planned for the Pesticides in Salmonid Habitat Monitoring program 2012 sampling season. These changes include:

- Changing laboratory methods for analysis of carbamates
- Using an electronic device to record field notes
- Discontinuing use of the DH-81 depth integrating sampler at select sites
- Dropping one of two monitoring sites on Spring Creek
- Adding copper monitoring

A more detailed discussion of the planned changes follows.

In an effort to save time and money Manchester Environmental Laboratory (MEL) decided to move to direct injection of carbamate samples. Using the direct injection method reduces the sample volume needed for analysis and removes the need for extraction while still maintaining current detection limits and data quality.

In 2011, a Trimble Yuma rugged mobile tablet was tested for field data collection. This rugged tablet is a fully functional computer. An Access form was created for the sampling teams to use for data collection. Use of the Trimble Yuma reduces paper use, streamlines workflow from the field to the office, and minimizes transcription errors. The project has successfully tested and migrated to using a rugged mobile tablet for field data collection.

During the 2011 sampling season a study was conducted comparing DH-81 and grab-collected samples (Anderson, 2011). The purpose of this study was to determine if there was a difference in pesticide results between the two sampling methods. The results of the study showed that there was not a statistically significant difference in pesticide results. At the sites tested, water is well mixed and there are no significant water inputs upstream of the sampling sites (Sargeant, 2011). Based on the results of the study, the project will discontinue use of the DH-81 at the Indian Slough, Marion Drain, and downstream Big Ditch sites.

In addition to procedural changes, sampling at the upstream Spring Creek site will be discontinued as of 2012. Currently, two sites on Spring Creek (an upstream and downstream site) have similar land use and pesticide results. The upstream site will be discontinued to free up laboratory funds that will be used to add additional sampling parameters for 2012.

For the 2012 sampling season copper (total recoverable and dissolved), hardness, dissolved organic carbon (DOC), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), sulfate, chloride, and alkalinity will be added to the current suite of parameters. These parameters will be used to assess copper concentrations in the creeks and rivers that are a part of the original project. Hardness-based water quality standards will be calculated at each site. At a subset of sampling sites, the hardness-based water quality standards and Biotic Ligand Model (BLM) water quality standards will be compared. Additionally, the data collected for this study will help to inform data gaps in the Puget Sound toxics loading analysis.

The copper sampling is described in detail below.

cc: Kirk Cook, Washington State Department of Agriculture
Debby Sargeant, Project Manager, Environmental Assessment Program
Evan Newell, Eastern Washington Field Lead, Environmental Assessment Program
Bill Kammin, Ecology Quality Assurance Officer
Dean Momohara, Interim Director, Manchester Environmental Laboratory

# Background and Project Description

A recently completed report by Ecology, *Control of Toxic Chemicals in Puget Sound: Assessment of Selected Toxic Chemicals in the Puget Sound Basin, 2007-2011* (Norton et al., 2011) identified urban lawn and garden use of copper as the potentially largest source of copper in the Puget Sound basin. To determine if elevated concentrations of copper are present in urban and agricultural settings, we will add copper to the pesticide monitoring program for the 2012 sampling season.

Currently, the State of Washington uses a hardness-based calculation to determine acute and chronic water quality criteria. In addition to sampling for total and dissolved copper, we will collect data to support use of the Biotic Ligand Model (BLM). The BLM is used to evaluate the availability and toxicity of metals like copper. It uses a number of different water quality variables to calculate the availability and toxicity of metals. The BLM results will be compared to the hardness-based criteria to determine if there is a difference in the watersheds tested. The overall goals of the copper sampling portion of this project will be to:

1. Assess whether elevated copper concentrations are present in urban and agricultural watersheds in the pesticide monitoring program.
2. Determine if measurable concentrations of copper exceed water quality standards.
3. Evaluate differences between hardness-based and BLM-derived water quality criteria.

Sampling of copper will occur during the 2012 monitoring season (March through September). Results from the copper sampling and the BLM will be presented in a report separate from the annual pesticide data summary report. Based on the 2012 monitoring results, we will evaluate the need to continue copper monitoring.

# Schedule and Deliverables

Table 1. Proposed schedule for completing field and laboratory work, data entry into EIM, and a final report for copper study.

| Field and laboratory work | Due date | Lead staff |
|---|---|---|
| Field work completed | September 2012 | Paul D. Anderson |
| Laboratory analyses completed | December 2012 | |
| Environmental Information System (EIM) database | | |
| EIM user study ID | DSAR0010 | |
| Product | Due date | Lead staff |
| EIM data loaded | July 2013 | Paul D. Anderson |
| EIM quality assurance | August 2013 | Amy Cook |
| EIM complete | September 2013 | Paul D. Anderson |
| Final report | | |
| Author lead / support staff | Paul D. Anderson/ Amy Cook | |
| Schedule | | |
| Draft due to supervisor | April 2013 | |
| Draft due to client/peer reviewer | May 2013 | |
| Final (all reviews done) due to publications coordinator | June 2013 | |
| Final report due on web | July 2013 | |

# Budget

The total laboratory cost for the project is estimated at $29, 819.69. A breakdown of the projected cost is detailed in Table 2. Cost estimate includes a 50% discount for MEL.

Table 2. Estimated laboratory costs*.

| | Analysis | Sample | Blank | Total | Price per Sample | Total |
|---|---|---|---|---|---|---|
| | Copper, Total Recoverable LL analysis | 65 | 6 | 71 | $ 39.45 | $ 2,800.95 |
| | Clean room prep per sample | 65 | 6 | 71 | $ 31.15 | $ 2,211.65 |
| | | | | Total | $ 70.60 | $ 5,012.60 |
| | Copper, dissolved LL analysis | 169 | 6 | 175 | $ 39.45 | $ 6,903.75 |
| | Filter | 169 | 6 | 175 | $ 28.03 | $ 4,095.25 |
| | Clean room prep per sample | 169 | 6 | 175 | $ 31.15 | $ 5,451.25 |
| | | | | Total | $ 98.63 | $17,260.25 |
| | Hardness | 169 | - | 169 | $ 22.84 | $ 3,859.96 |
| BLM Parameters | DOC | 28 | - | 24 | $ 37.34 | $ 896.16 |
| | Ca, Mg, Na, K[1] | 28 | - | 24 | $ 71.63 | $ 1,719.12 |
| | Sulfate | 28 | - | 24 | $ 13.50 | $ 324.00 |
| | Chloride | 28 | - | 24 | $ 13.50 | $ 324.00 |
| | Alkalinity | 28 | - | 24 | $ 17.65 | $ 423.60 |
| | pH[2] | 28 | - | 24 | $ - | $ - |
| | Temperature[2] | 28 | - | 24 | $ - | $ - |
| | | | | | **Total Cost** | **$29,819.69** |

*Costs include 50% discount for MEL

LL: low level

[1] Will be included in the total recoverable copper analysis

[2] Hydrolab measurement – no cost

# Quality Objectives

Quality objectives for this study are to obtain data of sufficient quality and quantity so that the data can be used to evaluate the stated objective of the study. These objectives will be achieved through careful planning, sampling, and adherence to the procedures described in the Quality Assurance Project Plan and all associated addendums.

## Laboratory

Ecology's MEL will perform the chemical analysis for this study. MEL is expected to meet all the quality control requirements of the analytical methods being used for this project.

Measurement quality objectives (MQOs) for this study are shown in Table 3. The recovery and precision objectives are the acceptance limits of the analytical methods. The lowest concentrations of interest are MEL's reporting limits.

Table 3. Measurement quality objectives.

| Analysis | LCS (% recovery) | Duplicate Samples (RPD) | Matrix Spike (% recovery) | Matrix Spike Duplicates (RPD) | Lowest Concentration of Interest |
|---|---|---|---|---|---|
| Copper | 75-125 | ±20 | 75-125 | ±20 | 0.1 ug/L |
| Hardness | 85-115 | ±20 | 75-125 | ±20 | 1 mg/L |
| Ca, Mg, Na, K | 85-115 | ±20 | 75-125 | ±20 | 0.1 ug/L |
| DOC | 80-120 | ±20 | 75-125 | ±20 | 1 mg/L |
| Sulfate | 90-110 | ±20 | 75-125 | ±20 | 0.5 mg/L |
| Chloride | 90-110 | ±20 | 75-125 | ±20 | 0.1 mg/L |
| Alkalinity | 80-120 | ±20 | n/a | n/a | 5 mg/L |

n/a: not applicable
RPD: relative percent difference

# Sampling Design

## Copper

Thirteen sites will be sampled for dissolved copper and hardness. Eight of the 13 sampling sites are in Eastern Washington: Marion Drain, Sulphur Creek Wasteway, downstream Spring Creek, Mission Creek, Peshastin Creek, Entiat River, Wenatchee River, and Brender Creek. The remaining five sites are in Western Washington and discharge directly to Puget Sound: Longfellow Creek, Samish River, Brown Slough, downstream Big Ditch, and Indian Slough. In addition to dissolved copper, total recoverable copper will be included at the five Western Washington sites. Copper samples will be obtained every other week during the sample season beginning the second week of March. There will be a total of 13 sample events.

## Biotic Ligand Model

Parameters associated with the BLM (dissolved organic carbon, calcium, sodium, magnesium, potassium, sulfate, chloride, and alkalinity) will be sampled once a month during the project sampling season. Four sites, one per watershed, will be sampled for the BLM parameters: Wenatchee River, Marion Drain, Longfellow Creek, and Samish River. Sites were chosen based on documented presence of salmonids or because the sites drain directly to a waterbody supporting species of endangered salmonids. Water quality standards calculated by the BLM will be compared to those generated by the hardness-based water quality standards.

# Sampling Procedures

Collection of water samples for metals will follow Ecology Standard Operating Procedure (SOP) EAP029 *Collection and Field Processing of Metals Samples* (Ward, 2010).

Non-metal water samples will be collected by hand as simple grabs from mid-channel following the Ecology SOP EAP015 *Manually Obtaining Surface Water Samples* (Joy, 2006). Both total and dissolved metals will be collected. Samples for dissolved metals will be field filtered within 15 minutes of collection.

Water samples will be collected in appropriate sample containers (Table 4).

Table 4. Sample containers, preservation, and holding times.

| Analysis | Minimum Sample Size | Container | Preservation | Holding Time |
|---|---|---|---|---|
| Total Rec. Copper | 350 mL | 500 mL HDPE bottle | $HNO_3$ to pH<2; Cool to ≤6°C | 6 months |
| Dissolved Copper | 350 mL | 500 mL HDPE bottle | Filter within 15 minutes of collection; then add $HNO_3$ to pH<2; Cool to ≤6°C | 6 months |
| Ca, Mg, Na, K | 350 mL | 500 mL HDPE bottle (combined in Total Rec. Copper bottle) | $HNO_3$ to pH<2; Cool to ≤6°C | 6 months |
| Hardness | 100 mL | 125 mL poly bottle | $H_2SO_4$ to pH<2; Cool to ≤6°C | 6 months |
| DOC | 50 mL | 60 mL poly bottle; 0.45 um pore size filter | Filter in field with 0.45 um pore size filter; 1:1 HCl to pH<2; Cool to ≤6°C | 28 days |
| Sulfate | 100 mL | 500 mL poly bottle (combined in same bottle) | Refrigerate, 0-6°C | 28 days |
| Chloride | | | | 28 days |
| Alkalinity | | | | 14 days |

HDPE: High density polyethylene

# Laboratory Procedures

Project samples will be analyzed at MEL. Laboratory reporting limits and analytical methods are given in Table 5.

Table 5. Laboratory reporting limits and analytical methods.

| Analysis | Reporting Limit | Analytical Method |
|---|---|---|
| Copper | 0.1 ug/L | ICP/MS EPA 200.8 |
| Ca, Mg, Na | 50 ug/L | ICP/MS EPA 200.8 |
| K | 500 ug/L | ICP/MS EPA 200.8 |
| Hardness | 0.3 mg/L | SM2340B |
| DOC | 1 mg/L | SM5310B |
| Sulfate | 0.5 mg/L | EAP 300.0; SM4110C |
| Chloride | 0.1 mg/L | EPA 300.0; SM4110C |
| Alkalinity | 5 mg/L | EPA 310.2; SM2320B |

ICP/MS: Inductively coupled plasma/mass spectrometry
SM: Standard Methods

# Quality Control Procedures

## Field

Transfer blanks and filter blanks will be analyzed for copper to assess potential for contamination arising from sample containers or handling. The transfer blank will be prepared by pouring MEL blank water into sample bottles in the field. MEL blank water will be filtered in the field to prepare the filter blanks. Blanks will be collected and analyzed once per quarter at selected sites.

Laboratory duplicates will be used in place of replicates to assess overall variability.

## Laboratory

The laboratory quality control procedures routinely followed by MEL will be satisfactory for the purposes of this project. MEL will follow SOPs as described in the Manchester Environmental Laboratory Quality Assurance Manual (MEL, 2006).

The laboratory quality control samples that will be used for this project are listed in Table 6.

Table 6. Laboratory quality control samples.

| Analysis | LCS | Method Blank | Analytical Duplicate | MS/MSD |
|---|---|---|---|---|
| Total Rec. Copper | 1/batch | 1/batch | 1/batch | 1/batch |
| Dissolved Copper | 1/batch | 1/batch | 1/batch | 1/batch |
| Hardness | 1/batch | 1/batch | 1/batch | 1/batch |
| Ca, Mg, Na, K | 1/batch | 1/batch | 1/batch | 1/batch |
| DOC | 1/batch | 1/batch | 1/batch | n/a |
| Sulfate | 1/batch | 1/batch | 1/batch | n/a |
| Chloride | 1/batch | 1/batch | 1/batch | n/a |
| Alkalinity | 1/batch | 1/batch | 1/batch | n/a |

LCS: Laboratory control sample
MS/MSD: Matrix Spike/Matrix Spike Duplicate

In Table 6, analytical duplicates are samples split at the laboratory as opposed to replicate samples collected separately in the field. The field samplers will identify the samples that are to be analyzed in duplicate (split) by the laboratory.

# Data Analysis and Report

The data collected for this study will be used in several different ways. The total recoverable copper data from the Western Washington sites will be used to assess whether elevated copper concentrations are present in urban and agricultural watersheds in the pesticide monitoring program. The dissolved copper data coupled with hardness data for both Eastern and Western Washington will be used to assess potential toxicity to salmonids and their prey base.

As a comparison to the hardness-based water quality standards the BLM will be used to calculate water quality standards. The BLM takes into account many mitigating parameters (hardness, calcium, magnesium, sodium, potassium, DOC, sulfate, chloride, and alkalinity) when calculating the water quality standard instead of relying solely on hardness.

A paired t-test will be used to determine if there is a statistically significant difference between the hardness-based and the BLM-based water quality standards. The power of this comparison is estimated as follows: assuming that 28 sample pairs are tested for a two-sided difference at the 95% confidence level, this study can reasonably expect (at 80% power) to detect a difference in mean water quality standards which exceeds 0.55 standard deviations of the differences between pairs. This calculation was derived using R v.2.14.1 ©2011 The R Foundation for Statistical Computing.

A report will be written detailing the information discussed in the preceding paragraphs.

# References

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