



DEPARTMENT OF
ECOLOGY
State of Washington

**Addendum 3 to
Quality Assurance Project Plan**

**Freshwater Fish Contaminant
Monitoring Program**

September 2015
Publication No. 15-03-121

Publication Information

Addendum

This addendum is on the Department of Ecology's website at <https://fortress.wa.gov/ecy/publications/SummaryPages/1503121.html>

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

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search Study ID FFCMP14

Activity Tracker code

Ecology's Activity Tracker code for this addendum is 02-500.

Original Publications

Quality Assurance Project Plan: Freshwater Fish Contaminant Monitoring Program
Publication No. <https://fortress.wa.gov/ecy/publications/SummaryPages/1303111.html>

Addendum 2 focused on the 2014 fish sampling effort in the Yakima River basin:
<https://fortress.wa.gov/ecy/publications/summarypages/1403122.html>

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Signatures are not available on the Internet version.

EAP: Environmental Assessment Program

TSU: Toxics Studies Unit

WQP: Water Quality Program

3.0 Background

This document describes the supplemental analysis of select samples for chlorinated pesticides by high resolution gas chromatography with high resolution mass spectrometry (HRGC/HRMS). The samples were collected during the 2014 sampling effort by Ecology's Freshwater Fish Contaminant Monitoring Program (FFCMP).

One of the goals of the FFCMP is to compare sampling results to water quality criteria. Subsequent to Addendum 2 of the Quality Assurance Project Plan (Seiders and Deligeannis, 2014), Washington's governor and Ecology proposed changes to the state's water quality criteria for toxic substances. Staff from the Water Quality Program at Ecology's Central Regional Office in Yakima expressed renewed interest in obtaining results for Yakima River fish that would be adequate to compare to the proposed standards.

The use of Environmental Protection Agency (EPA) method 8081 often yields reporting limits that are higher than current or proposed water quality standards for six chlorinated pesticides in fish tissue. These pesticides are aldrin, alpha-BHC, dieldrin, heptachlor, heptachlor epoxide, and toxaphene. Of particular concern are dieldrin and toxaphene, because they are the pollutant responsible for about a dozen 303(d) listings in the Yakima River Basin. These six pesticides were identified in Table D-1 of the original QAPP as possibly needing extra effort by Ecology's Manchester Environmental Laboratory (MEL) or other labs to achieve desired reporting limits (Seiders, 2013).

Preliminary results from MEL's analyses of the 2014 samples indicates that desired reporting limits for the six pesticides above were not met due to interferences or other limitations with analytical method EPA 8081. Options and funding for supplemental analyses of about 12 samples using a method to meet the goals were identified. This addendum describes the plan for supplemental analysis. This addendum was originally drafted in April 2015 and approval was obtained in May 2015 to perform the supplemental laboratory analyses.

9.0 Measurement Methods

An HRGC/HRMS method for chlorinated pesticides, such as method EPA 1699 or equivalent, will be used to meet the needs for these supplemental analyses. A qualified laboratory will be selected through the Department of Enterprise bid solicitation process. About 12 samples of archived fish tissue will be sent to a contract lab in May 2015 so that results can be received before the end of the current biennium. These samples were collected between September and November of 2014 and will be analyzed within the one-year holding time for the analytical method. The sample number of 12 may be adjusted depending on the cost per sample.

Table 1 shows the parameters to be analyzed with detection limits, quantitation limits, and the proposed and current water quality criteria; all are expressed as ug/kg wet weight. Pesticides other than the six mentioned above are also being analyzed to help inform MEL about issues related to interferences and interpretations of their analysis using EPA 8081.

Table 1. Analytes, detection limits, quantitation limits, and water quality criteria for supplemental analysis of fish tissue samples, FFCMP 2014 (ug/kg wet weight).

Analyte	CAS #	Required SDL	Desired QL	Proposed WQ FTEC	Current WQ FTEC	Expected Range of Results
Aldrin	309-00-2	0.13	0.27	0.268	0.654	ND - 1.0
alpha-BHC (alpha-HCH)	319-84-6	0.25	0.51	0.507	1.69	ND - 1.0
Dieldrin	60-57-1	0.14	0.29	0.285	0.654	ND - 5.0
Heptachlor	76-44-8	0.51	1.01	1.01	2.35	ND - 1.0
Heptachlor Epoxide	1024-57-3	0.25	0.50	0.502	1.23	ND - 2.0
Toxaphene	8001-35-2	2.08	4.15	4.15	9.56	ND - 50
beta-BHC (beta-HCH)	319-85-7	0.91	1.82	1.82	5.98	ND - 1.0
Endosulfan I	959-98-8	126	251	251	540	ND - 2.0
Endosulfan II	33213-65-9	126	251	251	540	ND - 2.0
Endosulfan Sulfate	1031-07-8	126	251	251	540	ND - 2.0
Hexachlorobenzene	118-74-1	1.43	2.85	2.85	6.69	ND - 2.0
Lindane (gamma-BHC, -HCH)	58-89-9	1.24	2.47	2.47	8.19	ND - 1.0

CAS: Chemical Abstract Service.
 FTEC: Fish Tissue Equivalent Criterion.
 ND: Non detect
 QL: Quantitation Limit
 SDL: Sample Detection Limit.

10.0 Quality Control

Table 2 shows laboratory quality control procedures.

Table 2. Laboratory quality control sample types and frequencies, FFCMP 2014.

Parameter	Analytical Method	Lab Duplicates	Lab Control Standards	Surrogates	MS/MSD	Method Blanks
Chlorinated pesticides	HiRes GC/MS (EPA 1699 or equivalent)	1/ batch ^a	each sample & 1/batch ^b	NA	NA	1/batch

^a “Batch” is defined as up to 20 samples analyzed together.

^b Labeled compounds in each sample and Ongoing Precision and Recovery standards in each batch.

15.0 References

Seiders, K, 2013. Quality Assurance Project Plan: Freshwater Fish Contaminant Monitoring Program. Washington State Department of Ecology, Olympia, WA. Publication No. 13-03-111. <https://fortress.wa.gov/ecy/publications/summarypages/1303111.html>

Seiders, K. and C. Deligeannis, 2013. Addendum 2 to Quality Assurance Project Plan: Freshwater Fish Contaminant Monitoring Program. Washington State Department of Ecology, Olympia, WA. Publication No. 14-03-122. <https://fortress.wa.gov/ecy/publications/summarypages/1403122.html>