Washington State Department of Agriculture

Addendum 7 to Quality Assurance Project Plan

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

AGR Publication 103-512 (N/3/16)
October 2015

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Prepared for:
Natural Resources Assessment Section Ambient Surface Water Monitoring Program: 2014 and 2015 field seasons

Publication Information

Addendum

The purpose of this addendum is to document changes to the Washington State Department of Agriculture's ongoing monitoring of surface water quality. This addendum details changes to the program that affect the 2014 and 2015 monitoring seasons; it is an addition to an original Quality Assurance Project Plan and does not contain corrections or errata to the original Quality Assurance Project Plan.

This addendum and additional project documentation are available on WSDA's website at http://agr.wa.gov/FP/Pubs/NaturalResourcesAssessmentPubs.aspx

Washington Water Resource Inventory Areas (WRIAs) and associated waterbodies:
WRIA 1 – Nooksack: Bertrand Creek
WRIA 3 – Lower Skagit-Samish: Big Ditch Slough, Browns Slough, Indian Slough, Samish River
WRIA 8 – Cedar-Sammamish: Thornton Creek
WRIA 9 – Green-Duwamish: Longfellow Creek
WRIA 37 – Lower Yakima: Marion Drain, Sulphur Creek, Spring Creek
WRIA 40 – Alkali-Squilchuck: Stemilt Creek
WRIA 45 – Wenatchee: Peshastin Creek, Mission Creek, Brender Creek, Wenatchee River

Original Publication and Previous Addenda

Quality Assurance Project Plan: Washington State Surface Water Monitoring program for Pesticides in Salmonid Habitat for Two Index Watersheds
Ecology Publication No. 03-03-104, May 2003

Addendum to QA Project Plan for Surface Water Monitoring Program for Pesticides in Salmonid Bearing Streams: Addition of Skagit-Samish Watersheds, and Extension of Program through June 2009
Ecology Publication No. 03-03-104ADD, February 2006

Addendum to Quality Assurance Project Plan for Surface Water Monitoring Program for Pesticides in Salmonid Bearing Streams: Addition of Wenatchee and Entiat Watersheds in the Upper Columbia Basin
Ecology Publication No. 03-03-104ADD#2, February 2007

Addendum 3 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds
Ecology Publication No. 03-03-104ADD3, April 2009

Addendum 4 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds
Ecology Publication No. 03-03-104-Addendum 4, April 2011

Addendum 5 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds
Ecology Publication No. 03-03-104-Addendum 5, February 2012

Addendum 6 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds
Ecology Publication No. 13-03-106, February 2013

Quality Assurance Project Plan: Marion Drain Intensive Surface Water Sampling for Pesticides in Salmonid-Bearing Streams
Ecology Publication No. 07-03-105, June 2007

Quality Assurance Project Plan: Skagit-Samish Watershed Intensive Surface Water Sampling for Pesticides in Salmonid-Bearing Streams
Ecology Publication No. 09-03-120, August 2009

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2.0 Abstract

The purpose of this addendum is to document changes to the Pesticides in Salmon-Bearing Streams Monitoring Program for the 2014 and 2015 monitoring seasons. Two pilot projects were trialed during the 2015 monitoring season: sediment sampling and glyphosate analysis. Five of the current monitoring sites were chosen for sediment analysis. These sites were close to urban or agricultural uses, had previous pesticide detections, and had available bed sediment for sampling; 122 pesticides and pesticide degradates were sampled at these sites. A glyphosate method was developed based on the USGS method that detects the presence of glyphosate, glufosinate (another herbicide structurally related to glyphosate), and aminomethylphosphonic acid (AMPA) (which is a degradate of glyphosate). In addition to these new sampling and analysis methods, 3 monitoring sites were discontinued (2 in 2014 and 1 in 2015), analytes were both added to and removed from existing analytical methods, and new equipment for monitoring and data collection was tested and adopted.

3.0 Background

3.1 Discontinued Monitoring Locations

The monitoring locations on the Lower Samish River (WRIA 3) in Skagit County and on the Wenatchee River (WRIA 45) in Chelan County were discontinued before the 2014 monitoring season. Flow at the Lower Samish River is high, which reduces the likelihood of pesticide detections even when pesticides are used in the watershed. At this site, none of the pesticide detections measured between 2006 (when the site was established) and 2013 were found at levels that approached any scientific or regulatory criteria. The Wenatchee River monitoring location had detections above criteria each year that sampling was conducted; however in 2014 the main chemical detected (endosulfan) was phased out of use. As a result, testing at these sites does not convey much information about agricultural pesticide use in these watersheds and WSDA has elected to discontinue these sites.

Before the 2015 monitoring season WSDA discontinued monitoring at Longfellow Creek in WRIA 9, the Green/Duwamish watershed. This site in urban King County was originally added to the monitoring program in 2009 due to pre-spawn mortality incidents with juvenile salmonids. Since 2009 WSDA has monitored this watershed for 27 weeks each year. In 2014 there were 3 other local, state, and federal agencies also monitoring this site, allowing WSDA to discontinue the site and reallocate resources to other pesticide and water quality projects.

3.2 Glyphosate Monitoring in Surface Water

Glyphosate is the most commonly used conventional pesticide active ingredient in the US agricultural sector (Grube et al. 2011). WSDA has never monitored for this herbicide or its primary degradate AMPA, due to the previously prohibitive cost of laboratory analysis by the EPA method (Winfield et al. 1990). The purpose of this glyphosate monitoring trial was to determine whether glyphosate monitoring should be added to the regular monitoring program during peak use periods (spring and fall). Samples were collected and analyzed at all 14 monitoring sites for 5 weeks in the spring of 2015.

WSDA collected samples to analyze for the presence of glyphosate, glufosinate, and AMPA. The samples were analyzed by the Washington State Department of Ecology's Manchester Environmental Laboratory (MEL) using a modified version of the methods developed by Hanke et al. (2008) and USGS (Meyer et al. 2009). This method relies on derivatization with 9-fluorenylmethylchloroformate followed by solid-phase extraction and quantification through liquid chromatography with tandem mass spectrometry and offers a cost effective alternative to other traditional analytical methods used to test for glyphosate (Winfield et al. 1990). The reporting limit for all three chemicals following this method was 0.008 µg/L.

Table 1. Analytes and method for glyphosate monitoring trial, 2015

CAS #	Analyte	Class	Method
1071-83-6	Glyphosate	Herbicide	Hanke et al., 2008 Meyer et al., 2009
1066-51-9	Aminomethylphosphonic acid (AMPA)	Herbicide	Hanke et al., 2008 Meyer et al., 2009
77182-82-2	Glufosinate	Herbicide	Hanke et al., 2008 Meyer et al., 2009

3.3 Sediment Sampling

Five sites were chosen for sediment collection; the downstream sampling site on Bertrand Creek (Nooksack – WRIA 1), the upstream sampling site on Big Ditch Slough (Lower Skagit-Samish – WRIA 3), Thornton Creek (Cedar-Sammamish – WRIA 8), Marion Drain (Lower Yakima – WRIA 37), and Brender Creek (Wenatchee – WRIA 45). These sites were chosen based on their proximity to urban or agricultural areas, previous pesticide detections in the water, and availability of bed sediment. This pilot tested for 122 pesticides and pesticide degradates at each of the sites.

Pesticides commonly detected in sediment tend to be persistent and bind well to the organic carbon fraction of sediment. Many of the analytes in this study have been detected in sediment during previous studies (Miles and Pfeuffer 1997; Hladik and Orlando 2008; Anderson 2011a; Kuivila et al. 2012; Moran et al. 2012; Weston et al. 2013). Of the compounds selected as analytes for this study 22 have been previously detected in stream bed sediment through the National Water Quality Assessment Program (NAWQA) (Norman et al. 2012).

Pyrethroid insecticides are of special interest due to their tendency to concentrate in sediment and because they have been shown to be a major contributor to sediment toxicity when detected (Weston et al. 2013). Pyrethroids are a class of insecticides that have become increasingly popular, in both agricultural and urban areas, as organophosphate insecticides have been phased out (Amweg et al. 2005; Ding et al. 2010). Previous studies in California and Illinois have detected pyrethroids in urban and agricultural waterways at toxic levels (Weston et al. 2004; Ding et al. 2010). This class of insecticides is known to be strongly hydrophobic with log K_{ow} values ranging between 5 and 7 (Laskowski 2002). Specifically, pyrethroids have a strong affinity for the organic carbon fraction of sediment as opposed to the water column. Currently there are no regulatory criteria for pyrethroids in sediment.

Of the selected sites, Thornton Creek is the only site that has been previously sampled for pyrethroids in sediment. Anderson (2011a) detected 6.1 µg/kg dry weight of bifenthrin at Thornton Creek in a study aimed at determining pyrethroid sediment concentrations due to storm water runoff in an urban setting. The analytes for WSDA's surface water monitoring program currently include several pyrethroids. Sampling and testing for these compounds has taken place at all of WSDA's current monitoring sites, including those selected for this study. All surface water detections, except 3, were below the minimum reporting limit. There has been little evidence that pyrethroid detections in water correlate with sediment concentrations. The compound cis-permethrin was detected in Thornton Creek in surface water during 2007 at 0.11 µg/L (Anderson and Duggar 2008). Bifenthrin was detected in surface water at Upper Big Ditch in 2011 at 0.11 µg/L (Sargeant et al. 2013), and in 2013 at 0.059 µg/L (Tuttle 2014).

To assess toxicity of individual compounds, results for each detected compound will be compared to available data in the following order of priority: 1) sediment benchmark screening level values compiled by Norman et al. (2012), and 2) sediment toxicity values gathered from literature. To assess overall toxicity of the sediment due to compound mixtures the toxic unit approach will be taken, as described in You et al. (2008), for all compounds with available invertebrate chronic toxicity data.

All samples were extracted using AOAC 2007.011 (Lehotay 2007) and analyzed by EPA method 8270d (US Environmental Protection Agency 2014). A list of sediment analytes is presented in Appendix A.

3.4 Analyte Changes

New analytes were added to the surface water analysis methods for both the 2014 and 2015 monitoring seasons (Table 2 and Table 3). These analytes were added to existing methods in order to capture both changes in pesticide use practices and current pesticide occurrence data. Five analytes were removed from existing methods between the 2013 and 2014 monitoring seasons: 2,4,5-TP (Silvex), sulprofos (Bolstar), fenithrothion, fensulfothion, and fenthion. Two analytes were removed from existing methods between the 2014 and 2015 monitoring seasons because of changing use practices; phorate O.A. and diazoxon.

Table 2. New analytes added for 2014 monitoring season

CAS #	Analyte	Class	Extraction method	Analysis method	Instrument
135410-20-7	Acetamiprid	Neonicotinoid insecticide	n/a	8321B[2]	LC/MS/MS[4]
149877-41-8	Bifenazate	Unknown mode of action, acaricide	3535A[1]	8270D[3]	GC/MS[5]
210880-92-5	Clothianidin	Neonicotinoid insecticide	n/a	8321B[2]	LC/MS/MS
165252-70-0	Dinotefuran	Neonicotinoid insecticide	n/a	8321B[2]	LC/MS/MS
153233-91-1	Etoxazole	Etoxazole acaricide	3535A[1]	8270D[3]	GC/MS
104098-48-8	Imazapic	Herbicide	n/a	8321B[2]	LC/MS/MS
81334-34-1	Imazapyr	Herbicide	n/a	8321B[2]	LC/MS/MS
161050-58-4	Methoxyfenozide	Diacylhydrazine insecticide	n/a	8321B[2]	LC/MS/MS
946578-00-3	Sulfoxaflor	Sulfoxaflor insecticide	n/a	8321B[2]	LC/MS/MS
153719-23-4	Thiamethoxam	Neonicotinoid insecticide	n/a	8321B[2]	LC/MS/MS
111988-49-9	Thiacloprid	Neonicotinoid insecticide	n/a	8321B[2]	LC/MS/MS

[1](US Environmental Protection Agency 2007a)
[2](US Environmental Protection Agency 2007b)
[3](US Environmental Protection Agency 2014)
[4]Liquid chromatography/triple quadrupole mass spectrometry
[5]Gas chromatography/mass spectrometry

Table 3. New analytes added for 2015 monitoring season

CAS #	Analyte	Class	Extraction method	Analysis method	Instrument
131860-33-8	Azoxystrobin	Fungicide	n/a	8321B[2]	LC/MS/MS
64902-72-3	Chlorsulfuron	Herbicide	n/a	8321B[2]	LC/MS/MS
68359-37-5	Cyfluthrin	Pyrethroid/pyrethrin insecticide	3535A[1]	8270D[3]	GC/MS
134-62-3	Diethyl toluamide (DEET)	Insect repellent	3535A[1]	8270D[3]	GC/MS
119446-68-3	Difenoconazole	Fungicide	n/a	8321B[2]	LC/MS/MS
35367-38-5	Diflubenzuron	Benzoylurea insecticide	n/a	8321B[2]	LC/MS/MS
2593-15-9	Etridiazole	Fungicide	3535A[1]	8270D[3]	GC/MS
114369-43-6	Fenbuconazole	Fungicide	n/a	8321B[2]	LC/MS/MS
131341-86-1	Fludioxonil	Fungicide	3535A[1]	8270D[3]	GC/MS
103361-09-7	Flumioxazin	Herbicide	3535A[1]	8270D[3]	GC/MS
81406-37-3	Fluroxypyr 1-methylheptyl ester	Herbicide	3535A[1]	8270D[3]	GC/MS
69409-94-5	Fluvalinate (tau-fluvalinate)	Pyrethroid/pyrethrin acaricide/insecticide	3535A[1]	8270D[3]	GC/MS
82558-50-7	Isoxaben	Herbicide	n/a	8321B[2]	LC/MS/MS
74223-64-6	Metsulfuron	Herbicide	n/a	8321B[2]	LC/MS/MS
88671-89-0	Myclobutanil	Fungicide	n/a	8321B[2]	LC/MS/MS
19666-30-9	Oxadiazon	Herbicide	3535A[1]	8270D[3]	GC/MS
82-68-8	Pentachloronitro-benzene (PCNB)	Fungicide	3535A[1]	8270D[3]	GC/MS
60207-90-1	Propiconazole	Fungicide	n/a	8321B[2]	LC/MS/MS
175013-18-0	Pyraclostrobin	Fungicide	n/a	8321B[2]	LC/MS/MS
129630-19-9	Pyraflufen-ethyl	Herbicide	3535A[1]	8270D[3]	GC/MS
96489-71-3	Pyridaben	METI acaricide/insecticide	3535A[1]	8270D[3]	GC/MS
53112-28-0	Pyrimethanil	Fungicide	n/a	8321B[2]	LC/MS/MS
122836-35-5	Sulfentrazone	Herbicide	3535A[1]	8270D[3]	GC/MS
74222-97-2	Sulfometuron	Herbicide	n/a	8321B[2]	LC/MS/MS
64700-56-7	Triclopyr, butoxyethyl ester (BEE)	Herbicide	3535A[1]	8270D[3]	GC/MS
141517-21-7	Trifloxystrobin	Fungicide	n/a	8321B[2]	LC/MS/MS
156052-68-5	Zoxamide	Fungicide	n/a	8321B[2]	LC/MS/MS

[1](US Environmental Protection Agency 2007a)
[2](US Environmental Protection Agency 2007b)
[3](US Environmental Protection Agency 2014)

3.5 New Equipment

In 2015, the MobileDemand xTablet T1600 was tested as a replacement for the Trimble Yuma 2 rugged tablet. The larger screen of the xTablet T1600 is more user friendly, and reduces data entry errors. Testing was successful and the MobileDemand xTablet T1600 will be the primary device used for field data collection, with the Trimble Yuma 2 being used as a backup.

Beginning in 2014, Marsh-McBirney Flo-Mate meters were replaced with OTT MF pro meters for flow measurements at sites without gauging stations. In addition, flow standard operating procedures were updated to use the more recent version of the Washington State Department of Ecology's Standard Operating Procedure for Measuring and Calculating Stream Discharge (Shedd 2014).

4.0 Project Description

The goals of the pesticide sediment sampling pilot study were as follows:

1) Determine if pesticides exist in the sediment at the selected sites,
2) Assess if measured pesticide concentrations have the potential to be toxic towards benthic invertebrates,
3) Determine if pesticide monitoring in sediment should be added to routine monitoring.

Sediment samples were collected from the designated locations 3 times during the monitoring season, in April, July, and September. The purpose of this schedule was to collect samples that were representative of sediment deposition prior to, during, and after the growing season. If pesticide detections occur in any of the samples, detected concentrations will be compared to the respective toxicity endpoints. Comparing pesticide sediment concentrations to measured toxicological endpoints will allow an evaluation of whether or not exposure presents a risk to benthic invertebrates. Detections of multiple pesticides in sediment samples will be evaluated using a toxic unit model to assess overall toxicity with the assumption that the effects are additive. Based on the results a recommendation will be given on whether or not sediment sampling for pesticides should be added to the established water quality monitoring program.

The goals of the glyphosate pilot study were as follows:

1) Develop and test an economical method for analysis of glyphosate and glyphosate degradates,
2) Determine if glyphosate is present in water samples at monitored sites,

3) Assess if detected glyphosate concentrations have the potential to be harmful to aquatic life,
4) Determine if glyphosate monitoring should be added to routine monitoring.

Water samples were collected and analyzed for glyphosate and glyphosate degradates at each of WSDA's 14 monitored sites from the second week in April to the second week in May, 2015. This sampling period is representative of the peak spring glyphosate use pattern seen in both urban and agricultural areas. WSDA will compare these data to known toxicological endpoints and use them to determine whether there is value in including glyphosate in the routine surface water monitoring program.

5.0 Project Schedule and Budget

5.1 Schedule

To determine whether sampling could proceed at the Western Washington sampling sites (Bertrand Creek, Big Ditch Slough, and Thornton Creek), an assessment of flow occurred prior to the initial sampling event. One goal of this assessment was to determine if stream conditions allowed for safe sampling during the relatively high flow conditions found in those watersheds. An additional goal of this assessment was to determine whether stream conditions allowed for sampling meeting the guidelines outlined in the standard operating procedure (SOP) for collecting stream bed sediment for pesticide analysis (Curtin and McLain 2014). Based on this assessment, sediment sampling was conducted at the Western Washington sampling sites as planned. The schedule for sampling events, laboratory analysis, data analysis, and report writing for both the sediment sampling and glyphosate analysis is described in Table 4 and Table 5.

Table 4. Proposed schedule of sampling, analysis, and report for the sediment pilot study

Activity	Timeline
1st sampling event	April 2015
2nd sampling event	July 2015
3rd sampling event	September 2015
Laboratory analysis completed	November 2015
Data analysis	June 2016
Report-first draft	June 2016
Report-final	August 2016

Table 5. Schedule of sampling, analysis, and report for glyphosate analysis

Activity	Timeline
Weekly sampling for 5 weeks	April 13 – May 11
Laboratory analysis completed	November 2015
Data analysis	August 2016
Quality assurance report	August 2016
Fact sheet and technical bulletin	October 2016

5.2 Budget and funding

Table 6. Estimated laboratory costs, sediment sampling

Analysis	Field sample #	Field replicate count	Total sample #	Price per sample	Total
Pesticide extraction and analysis	15	3	24	$530	$12,720.00
TOC[1]	15	3	18	$50	$900.00
					Total cost $13,620.00

[1]Total organic carbon

Table 7. Estimated laboratory costs, glyphosate sampling

Analysis	Field sample #	QA[1] sample count	Total sample #	Price per sample	Total
Glyphosate	70	12	82	$150	$12,300.00
					Total cost $12,300.00

[1]Quality assurance

6.0 Quality objectives

The quality objectives for sediment sampling are to obtain data sufficient in both quality and quantity to determine if pesticides exist at the selected sites and if detected concentrations have the potential to negatively affect benthic invertebrates. The quality objectives for glyphosate sampling are to obtain data sufficient in both quality and quantity to determine if glyphosate, its degradate AMPA, and glufosinate are present at monitored sites and if detected concentrations exceed water quality criteria and have the potential to negatively affect aquatic species.

Ecology's Manchester Environmental Laboratory will be conducting the laboratory analysis of all sediment and glyphosate samples. MEL is expected to meet all of the quality control requirements of the analytical methods being used for this study. The recovery and precision objectives for this study are the analytical method's recovery limit and relative percent difference (RPD) values.

7.0 Sampling Design

Sediment samples were taken from 5 sites that span the majority of Washington State. Four of the sites are in agricultural areas (Brender Creek, Lower Bertrand Creek, Upper Big Ditch, and Marion Drain). Thornton Creek is in a primarily urban area. Samples were collected three times from all sites during the monitoring season. Each sediment sample was analyzed for the designated pesticides and total organic carbon. Determining TOC allows for data comparability to other studies and toxicity assessments. Sorption of highly hydrophobic contaminants is directly related to the organic carbon content of the sediment, which in turn influences exposure to the biota (Di Toro et al. 1991). Sediment quality criteria are commonly normalized to 1% organic carbon.

Water samples for glyphosate were taken for 5 weeks in the spring use period at all 14 monitoring sites in the state. A separate 100-mL container of water was collected and analyzed for glyphosate, glufosinate, and AMPA. Detections will be compared against known toxicological endpoints and reported.

8.0 Sampling Procedures

Sediment samples were collected in accordance with the procedures described in Standard Operating Procedure: Collecting and Processing of Stream Bed Sediment for Pesticide Analysis, developed by WSDA (Curtin and McLain 2014).

All sediment samples were collected in glass wide mouth jars with Teflon-lined lids. After collection samples were placed on ice for transport to the laboratory. Temperatures of 6° C or less for no more than four days are allowable, at which point the sample can be held at -18 °C or less, for up to 1 year (Manchester Environmental Laboratory, 2008). Chain of custody documentation was maintained from sample collection through transport to the laboratory.

Glyphosate samples were collected, stored, and transported in accordance with the Ecology's Environmental Assessment Program SOP, Standard Operating Procedures for Sampling of Pesticides in Surface Waters, Version 2.1, developed by the Washington State Department of Ecology (Anderson 2012). Departures from the SOP include: samples were collected in 100-mL brown polyethylene bottles, samples were collected midstream rather than on quarter point transects of the stream.

Decontamination procedures as described by Parsons et al. (2012) will be followed in order to prohibit invasive species from spreading via equipment.

9.0 Laboratory Procedures

Sediment samples were analyzed at Manchester Environmental Laboratory in Port Orchard, WA. Laboratory reporting limits and analytical methods are given in Table 8 and Table 9.

Table 8. Sediment sampling methods and reporting limits

Analysis	Reporting limit	Preparation method	Analytical method	Instrument
Pesticides	Analyte specific	AOAC 2007.01[1]	EPA 8270d[2]	GC/MS
TOC	0.1 % mg/kg	n/a	PSEP 1986[3]	TOC analyzer
Percent solids	0.001 %	n/a	Standard Methods 2540G[4]	n/a

[1](Lehotay 2007)
[2](US Environmental Protection Agency 2014)
[3](Puget Sound Estuary Program (PSEP) 1986)
[4](American Public Health Association (APHA) et al. 2012)

Table 9. Glyphosate sampling methods and reporting limits

Analysis	Reporting limit	Preparation method	Analytical method
Glyphosate, glufosinate, and AMPA	0.008 µg/L	Hanke al., 2008	Hanke et al., 2008 Meyer et al., 2009

10.0 Quality Control Procedures

To assure quality sample collection, drafts of this QAPP, including all relevant SOPs, were available during the study's activities. Strict adherence to the QAPP was used to avoid contamination and invalidation of samples. Chain of custody was recorded throughout collection and transport via MEL's Laboratory Analysis Required form (Manchester Environmental Laboratory 2008).

10.1 Field

Field quality control (QC) samples consisted of field replicates for the sediment sampling study. Field replicates for sediment samples and TOC samples were used to assess overall variability in sampling methods and analytical procedures. Replicates were prepared by collecting twice the normal amount of sample, homogenizing, and then splitting the sample between 2 sample containers. Field blanks were not prepared for the sediment sampling study.

Field replicates were collected once per sampling event for both TOC and pesticide analysis and represented 20% of the total samples. All field replicate samples were submitted blind to the laboratory.

Field replicates and field blanks were collected for glyphosate analysis. Field replicates and field blanks represented 9.8% of the total samples collected for glyphosate analysis. Field replicates and field blanks were collected in the same fashion as regular samples but were submitted blind to the laboratory.

Table 10. Data quality objectives for field QC samples for sediment study

Parameter	Number of field replicates	Number of field blanks	Data quality objective (RPD)
Pesticides in sediment	3	0	±40[1]
TOC	3	0	±20[1]

[1](Anderson 2011b)

Table 11. Data quality objectives for field QC samples for glyphosate analysis

Parameter	Number of field replicates	Number of field blanks	Data quality objective (RPD)
Glyphosate, glufosinate, and AMPA	4	4	±40

Any QC results exceeding the data quality objectives listed in Table 10 and Table 11 for field QC samples, will be qualified or rejected.

10.2 Laboratory

Routine laboratory procedures followed by MEL staff fulfill the quality control requirements of this project. MEL's QC procedures are described in the Manchester Environmental Laboratory User's Manual (Manchester Environmental Laboratory 2008).

Laboratory QC measures consisted of laboratory control standards, duplicates, matrix spikes and method blanks.

Table 12. Laboratory QC samples for sediment

Parameter	Lab control samples	Lab control sample duplicates	Matrix spike	Matrix spike duplicate	Method blank	Duplicate
Pesticides	1/batch	1/batch	1/batch	1/batch	1/batch	n/a
TOC	1/batch	0	n/a	n/a	1/batch	2/batch
Percent solids	n/a	n/a	n/a	n/a	1/batch	2/batch

Table 13. Laboratory QC samples for glyphosate, glufosinate, and AMPA

Parameter	Lab control samples	Lab control sample duplicates	Matrix spike	Matrix spike duplicate	Method blank	Duplicate
Glyphosate, glufosinate, and AMPA	1/batch	1/batch	4	4	1/batch	n/a

Any QC results not meeting criteria established by MEL for laboratory QC samples were qualified or rejected. Results qualified as "J" indicate that the analyte was positively identified and that the associated numerical value is the approximate concentration of the analyte in the sample; "J" qualified results are seen as acceptable to use per EPA's *Guidance for Data Usability in Risk Assessment* (1991). Results that met the stated data quality objectives had no data qualifier associated with them or were qualified as "D", indicating that the analyte was positively identified and was detected at the reported concentration and therefore that result has the highest degree of confidence (Anderson 2011a).

11.0 Data Management Procedures

Site visit data for the sediment study was recorded as per the established water quality monitoring program, with the exception of an additional parameter, a sediment particle size description. All records were directly entered into the surface water monitoring program database at the time of sampling using a Trimble YUMA 2 handheld rugged computer or a MobileDemand xTablet T1600.

MEL provided results as a text file along with a case narrative following the completion of the laboratory work. The case narrative was used to assess if all QC requirements were met. The results text file was used to input data into the surface water monitoring program's database and then used for all data analysis and verification.

Data quality will be assessed using best professional judgment and take into consideration all field and laboratory QC results. Data that meet the data quality objectives will be accepted. Data that does not meet the data quality objectives will be either rejected or accepted with qualifications.

12.0 Data Analysis and Report

Data gathered from sampling activities will be used to meet the project's goals, described in Section 4.0 of this document. Results that indicate detections will determine if pesticides do or do not exist in the sediment at selected sites. The potential for harmful effects to benthic

organisms will be determined using “J” and “D” qualified (or unqualified) results and comparing them to the appropriate toxicological endpoints listed in the final report. In order to effectively compare concentrations across studies and to toxicological endpoints, pesticide sediment concentration results will be normalized to 1% TOC and reported on a dry weight basis. Further monitoring of pesticides in sediment will be decided based on the quantity and level of concentrations found.

Data gathered from surface water glyphosate sampling activities will be used to compare detection information with known toxicological endpoints for glyphosate, glufosinate, and AMPA.

Detailed reports containing a quality assurance section will be written for both the sediment monitoring and the glyphosate, glufosinate, and AMPA analysis. Reports will contain a rationale for whether or not the analysis will be added to the regular surface water monitoring program. In addition, short fact sheets will be produced detailing both the sediment monitoring results and the glyphosate, glufosinate, and AMPA analysis results.

References

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Appendix A: Pesticides and degradation products to be analyzed in sediment samples

Table 14. Pesticides and degradation products analyzed for in sediment samples. All samples were extracted using AOAC 2007.011 (Lehotay 2007) and analyzed by EPA method 8270d (US Environmental Protection Agency 2014)

CAS #	Name	Class
53-19-0	2,4'-DDD	Degradate / organochlorine
3424-82-6	2,4'-DDE	Degradate / organochlorine
789-02-6	2,4'-DDT	Insecticide / organochlorine
72-54-8	4,4'-DDD	Degradate / organochlorine
72-55-9	4,4'-DDE	Degradate / organochlorine
50-29-3	4,4'-DDT	Insecticide / organochlorine
90-98-2	4,4'-Dichlorobenzophenone	Degradate
34256-82-1	Acetochlor	Herbicide
15972-60-8	Alachlor	Herbicide
309-00-2	Aldrin	Insecticide / organochlorine
319-84-6	Alpha-BHC	Insecticide / organochlorine
1912-24-9	Atrazine	Herbicide
2642-71-9	Azinphos-ethyl	Insecticide / organophosphate
86-50-0	Azinphos-methyl	Insecticide / organophosphate
1861-40-1	Benfluralin	Herbicide
28249-77-6	Thiobencarb	Herbicide / carbamate
319-85-7	Beta-BHC	Insecticide / organochlorine
82657-04-3	Bifenthrin	Insecticide / pyrethroid
188425-85-6	Boscalid	Fungicide
314-40-9	Bromacil	Herbicide
23184-66-9	Butachlor	Herbicide
2008-41-5	Butylate	Herbicide
133-06-2	Captan	Fungicide
1897-45-6	Chlorothalonil	Fungicide
101-21-3	Chlorpropham	Herbicide
5598-15-2	Chlorpyrifos O.A.	Degradate / organophosphate
5598-13-0	Chlorpyrifos-methyl	Insecticide / organophosphate
5103-71-9	cis-Chlordane	Insecticide / organochlorine
5103-73-1	cis-Nonachlor	Insecticide / organochlorine
54774-45-7	cis-Permethrin	Insecticide / pyrethroid
56-72-4	Coumaphos	Insecticide / organophosphate
21725-46-2	Cyanazine	Herbicide
1134-23-2	Cycloate	Herbicide

52315-07-8	Cypermethrin	Insecticide / pyrethroid
319-86-8	Delta-BHC	Insecticide / organochlorine
52918-63-5	Deltamethrin	Insecticide / pyrethroid
2303-16-4	Di-allate	Herbicide
333-41-5	Diazinon	Insecticide / organophosphate
962-58-3	Diazinon oxon	Degradate / organophosphate
1194-65-6	Dichlobenil	Herbicide
60-57-1	Dieldrin	Insecticide / organochlorine
60-51-5	Dimethoate	Insecticide / organophosphate
957-51-7	Diphenamid	Herbicide
6/5/2497	Disulfoton sulfone	Insecticide / organophosphate
959-98-8	Endosulfan I	Insecticide / organochlorine
33213-65-9	Endosulfan II	Insecticide / organochlorine
1031-07-8	Endosulfan sulfate	Degradate / organochlorine
72-20-8	Endrin	Insecticide / organochlorine
53494-70-5	Endrin ketone	Degradate / organochlorine
2104-64-5	EPN	Insecticide / organophosphate
759-94-4	Eptam	Herbicide
55283-68-6	Ethalfluralin	Herbicide
563-12-2	Ethion	Insecticide / organophosphate
13194-48-4	Ethoprop	Insecticide / organophosphate
153233-91-1	Etoxazole	Insecticide / etoxazole
22224-92-6	Fenamiphos	Insecticide / organophosphate
31972-44-8	Fenamiphos sulfone	Degradate / organophosphate
60168-88-9	Fenarimol	Fungicide
51630-58-1	Fenvalerate	Insecticide / pyrethroid
120068-37-3	Fipronil	Insecticide / pyrazole
205650-65-3	Fipronil desulfinyl	Degradate / insecticide
120067-83-6	Fipronil sulfide	Degradate / insecticide
120068-36-2	Fipronil sulfone	Degradate / insecticide
59756-60-4	Fluridone	Herbicide
944-22-9	Fonofos	Insecticide / organophosphate
58-89-9	Gamma-BHC	Insecticide / organochlorine
76-44-8	Heptachlor	Insecticide / organochlorine
1024-57-3	Heptachlor epoxide	Degradate / organochlorine
118-74-1	Hexachlorobenzene	Fungicide
51235-04-2	Hexazinone	Herbicide
732-11-6	Phosmet	Insecticide / organophosphate
115-32-2	Dicofol	Insecticide / organochlorine
121-75-5	Malathion	Insecticide / organophosphate

57837-19-1	Metalaxyl	Fungicide
950-37-8	Methidathion	Insecticide / organophosphate
72-43-5	Methoxychlor	Insecticide / organochlorine
2821-88-2	Chlorpyrifos	Insecticide / organophosphate
950-35-6	Methyl paraoxon	Degradate / organophosphate
298-00-0	Methyl parathion	Insecticide / organophosphate
51218-45-2	Metolachlor	Herbicide
21087-64-9	Metribuzin	Herbicide
7786-34-7	Mevinphos	Insecticide / organophosphate
113-48-4	MGK264	Synergist / insecticide
2385-85-5	Mirex	Insecticide / organochlorine
2212-67-1	Molinate	Herbicide
6923-22-4	Monocrotophos	Insecticide / organophosphate
15299-99-7	Napropamide	Herbicide
27314-13-2	Norflurazon	Herbicide
19044-88-3	Oryzalin	Herbicide
27304-13-8	Oxychlordane	Degradate / organochlorine
42874-03-3	Oxyfluorfen	Herbicide
56-38-2	Parathion	Insecticide / organophosphate
1114-71-2	Pebulate	Herbicide
40487-42-1	Pendimethalin	Herbicide
26002-80-2	Phenothrin	Insecticide / pyrethroid
298-02-2	Phorate	Insecticide / organophosphate
2600-69-3	Phorate O.A.	Insecticide / organophosphate
51-03-6	Piperonyl butoxide (PBO)	Synergist
1610-18-0	Prometon	Herbicide
7287-19-6	Prometryn	Herbicide
23950-58-5	Pronamide	Herbicide
1918-16-7	Propachlor	Herbicide
2312-35-8	Propargite	Insecticide / sulfite ester
139-40-2	Propazine	Herbicide
10453-86-8	Resmethrin	Insecticide / pyrethroid
122-34-9	Simazine	Herbicide
1014-70-6	Simetryn	Herbicide
3689-24-5	Sulfotepp	Insecticide / organophosphate
5902-51-2	Terbacil	Herbicide
961-11-5	Tetrachlorvinphos	Insecticide / organophosphate
27813-21-4	Tetrahydrophthalimide	Degradate / fungicide
153719-23-4	Thiamethoxam	Insecticice / neonicotinoid
34643-46-4	Tokuthion	Insecticide / organophosphate

66841-25-6	Tralomethrin	Insecticide / pyrethroid
5103-74-2	trans-Chlordane	Insecticide / organophosphate
39765-80-5	trans-Nonachlor	Insecticide / organochlorine
61949-77-7	trans-Permethrin	Insecticide / pyrethroid
43121-43-3	Triadimefon	Fungicide
2303-17-5	Triallate	Herbicide
327-98-0	Trichloronate	Insecticide / organophosphate
41814-78-2	Tricyclazole	Fungicide
1582-09-8	Trifluralin	Herbicide